

Claudia Ertl BSc

**Carbon dioxide hydrogenation to methanol:  
an overview on copper-based catalysts**

**MASTER'S THESIS**

to achieve the university degree of  
Diplom-Ingenieurin

Master's degree program:  
Chemical and Pharmaceutical Engineering

submitted to  
**Graz University of Technology**

**Supervisor**

Ass.Prof. Dipl.-Ing. Dr.techn. Susanne Lux  
Dipl.-Ing. Sascha Kleiber BSc  
Institute of Chemical Engineering and Environmental Technology

## AFFIDAVIT

I declare that I have authored this thesis independently, that I have not used other than the declared sources/resources, and that I have explicitly indicated all material which has been quoted either literally or by content from the sources used. The text document uploaded to TUGRAZonline is identical to the present master's thesis.

08.01.2021

ErH Claudia

---

Date, Signature

# Acknowledgements

Firstly, I would like to thank my supervisors, Ass.Prof. Dipl.-Ing. Dr.techn. Susanne Lux and Dipl.-Ing. Sascha Kleiber BSc, for their guidance and advice during my research and writing.

I owe thanks to my fellow students and friends for being a major source of support through this stage of my life.

Special thanks are due to my family for providing me with reliable support and continuous encouragement throughout my study.

## Abstract

Since several years the hydrogenation of carbon dioxide to methanol has raised much awareness among scientists. It presents an effective method to transform the greenhouse gas carbon dioxide into methanol which is a promising way to decrease carbon dioxide emissions to stem global warming. Methanol is a very attractive product as it is a versatile substance and can be utilized as chemical feedstock, solvent or fuel. To enable the reaction to proceed at an adequate reaction rate a catalyst is necessary.

The purpose of this work is to give an overview on the current state of research concerning heterogenous, copper-based catalysts for the hydrogenation of carbon dioxide to methanol. A variety of copper-based catalysts was prepared by several methods and tested in different compositions with various supporting materials and promoters to get a highly active, selective and stable catalyst for the wanted reaction.

To facilitate the development of the most suitable catalyst with all desired properties knowledge of the reaction mechanism is essential. By now the main reaction route is not entirely known. In literature a formate pathway, a hydrocarboxyl pathway and a reverse water-gas shift reaction and carbon monoxide hydrogenation pathway can be found.

Prospective it is fundamental to put more emphasis on the reaction mechanism to gain a deeper understanding of the reaction and on treatment of the spent catalysts.

# Kurzfassung

Seit einigen Jahren ist die Hydrierung von Kohlenstoffdioxid zu Methanol ein aktuelles Thema in der Forschung. Sie stellt eine wirkungsvolle Methode zur Umwandlung des Treibhausgases Kohlenstoffdioxid zu Methanol dar, mit dem Ziel die Kohlenstoffdioxidemissionen zu senken und damit die globale Erwärmung einzudämmen. Die Produktion von Methanol ist vorteilhaft, da Methanol eine vielseitige Chemikalie ist, die als Ausgangsprodukt für andere Substanzen, als Lösungsmittel oder als Treibstoff eingesetzt werden kann. Um das Abfließen der Reaktion mit einer ausreichend hohen Geschwindigkeit möglich zu machen, ist ein Katalysator notwendig.

Ziel dieser Arbeit ist es, einen Überblick über den aktuellen Stand der Forschung zur Hydrierung von Kohlenstoffdioxid zu Methanol mithilfe von heterogenen, kupferbasierten Katalysatoren zu geben. Kupfer-basierte Katalysatoren werden mit verschiedenen Herstellungsmethoden und in unterschiedlichen Zusammensetzungen erzeugt, um einen möglichst aktiven, selektiven und stabilen Katalysator für die gewünschte Reaktion zu erhalten. In der Zusammensetzung werden die Menge von Supportmaterialien, Promotoren und Kupfer variiert, als auch verschiedene Materialien als Supportmaterial und Promotor eingesetzt.

Wissen über den Reaktionsmechanismus ist hilfreich, um einen Katalysator mit allen gewünschten Eigenschaften entwickeln zu können. Derzeit ist der Reaktionsmechanismus noch nicht gänzlich geklärt. In der Literatur werden drei Reaktionswege diskutiert: die Formate-Route, die Carboxy-Route und die umgekehrte Wassergas-Shift-Reaktion und Kohlenstoffmonoxid Hydrierungs-Route.

In Zukunft ist es wichtig, sich in der Forschung vermehrt auf den Reaktionsmechanismus zu konzentrieren, um die Reaktion besser verstehen zu können. Aber auch der Entsorgung der Katalysatoren muss Aufmerksamkeit geschenkt werden.

# Table of contents

1. Introduction .....	1
2. Catalysts for CO <sub>2</sub> hydrogenation.....	6
2.1. Copper-based catalysts .....	6
2.1.1. Catalyst activity .....	7
2.1.2. Deactivation.....	8
2.1.3. Preparation methods .....	8
2.1.4. Comparison and discussion of ongoing research.....	10
2.1.5. Summary .....	45
3. Reaction mechanism of Cu-based catalysts .....	49
3.1. Formate pathway .....	49
3.2. RWGS reaction and CO hydrogenation pathway.....	54
3.3. Hydrocarboxyl pathway .....	56
3.4. Summary .....	57
4. Conclusion and outlook.....	59
5. References.....	61
6. List of abbreviations .....	72
7. List of figures.....	73

# 1. Introduction

Catalysis means increasing the reaction rate of a chemical reaction without changing the chemical equilibrium by adding a catalyst.[1] Catalysts can support reactions to proceed at milder conditions without being consumed. Further, the introduction of catalysts to chemical reactions can modify the selectivity of the resulting products.[2] In over 90 % of the production of chemical substances at least one catalytic step is involved.[3] In the past decades the production of methanol by catalysis using CO<sub>2</sub> (carbon dioxide) and H<sub>2</sub> (hydrogen) as starting materials has become of high interest.[4]

Catalysis can be divided into homogeneous and heterogeneous catalysis. Homogeneous catalysis describes reactions where the reactants and the catalyst are present in the same phase. Whereas in the case of heterogeneous catalysis the reactants and the catalyst are not present in the same phase which involves advantages like higher stability, easier handling, easier separation of the catalyst and the reaction mixture and the possibility to reuse and recycle the catalyst.[5][6] Often the catalyst is a solid material while the reactants are liquids or gases.[7] Heterogeneous catalysis is based on the coordination of reactant molecules on the active sites of the catalyst. The catalyst surface has active sites, meaning free coordination sites where reactant molecules can adsorb. Regarding Sabatier's principle intermediate states between the catalyst surface and the reactants are built during the reaction. After the reaction the product desorbs and the procedure is repeated. Thus, the catalyst is active for many reaction cycles.[1]

In times of climate change the awareness for worldwide carbon dioxide emissions rises. As CO<sub>2</sub> is a greenhouse gas it contributes to global warming.[8] In the last 800 000 years the CO<sub>2</sub> concentration was always below 300 ppm. This changed with the industrial revolution where people started to burn fossil fuels. Comparing global carbon dioxide emissions in 1950 with those from 2017 the annual emissions increased from about  $5 \cdot 10^9$  tons up to over  $36 \cdot 10^9$  tons as shown in Figure 1.[9] The concentration of CO<sub>2</sub> in the atmosphere increased about 20 % in the last forty years and reached 410.88 ppm (state: November 2019) which is the highest value in the last 3 million years.[9][10] The global CO<sub>2</sub> emissions are distributed as follows:

40 % account for energy and heat generation as coal is an important, carbon-rich energy source, 20 % account for manufacturing and industrial processes, as well as transportation of goods and people account for another 20 %.[8] To keep the global mean temperature increase at 2–2.4 °C above the pre-industrial temperature the CO<sub>2</sub> emissions have to decrease by 50 % relative to the level in 2007 by 2050.[11] For that reason, CO<sub>2</sub> capture, storage and utilization have been considered as important issues over the past decades in order to recycle carbon and lower CO<sub>2</sub> emissions.[12][13] Carbon dioxide capture could lower CO<sub>2</sub> emissions by 60 %.[8]

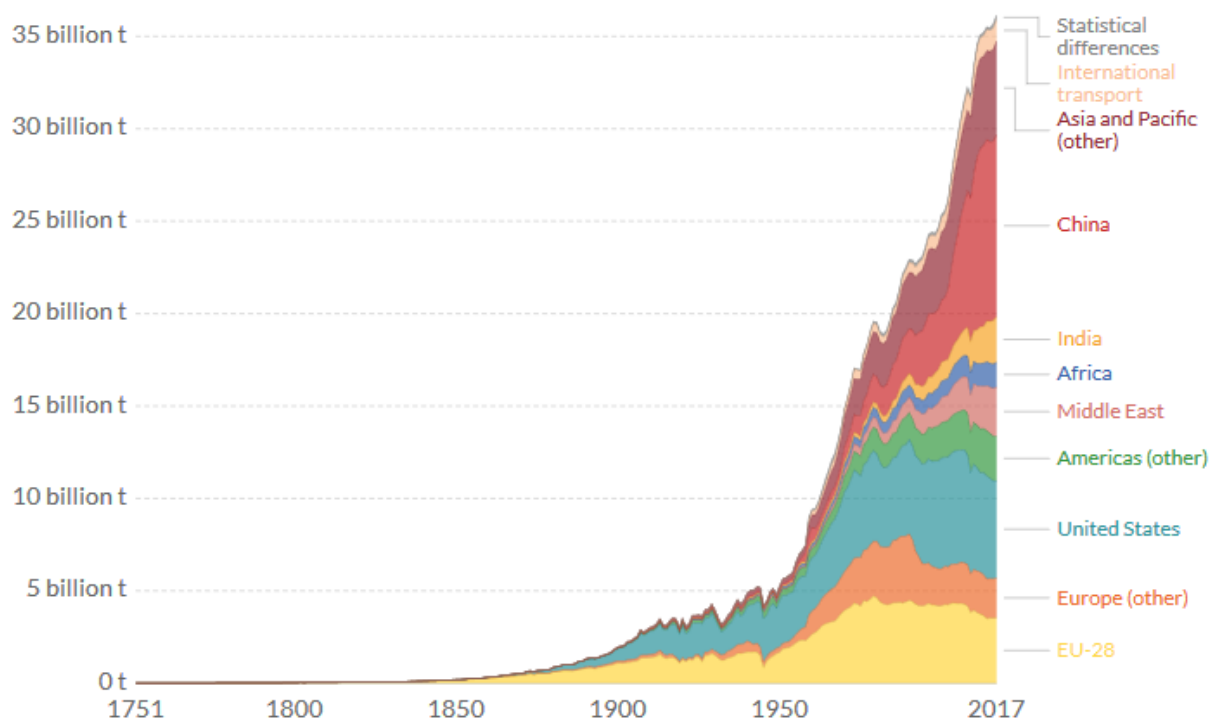


Figure 1: Annual CO<sub>2</sub> emissions from 1751-2017. Statistical differences means the difference between global estimate and the sum of the world regions.[9]

Carbon dioxide is an essential starting material, for example in the production of urea, methanol, formaldehyde and formic acid.[14] The normal boiling point of carbon dioxide is -78.5 °C and the molecular weight is 44.01 g/mol.[15] Its chemical structure is shown in Figure 2.

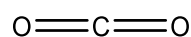


Figure 2: Chemical structure of carbon dioxide



Methanol (CH<sub>3</sub>OH) is of high interest as it is utilized as solvent and alternative fuel.[12][16][17] In comparison to gasoline methanol shows higher performance, lower emissions and lower flammability.[17] Moreover, it is converted to hydrocarbons as in the methanol-to-gasoline, methanol-to-propene and methanol-to-olefins processes to generate for example propene, ethylene and propylene.[13][18][19] Methanol is the basis for production of paints, plastics and adhesives.[8] Additionally, it can be used as an energy carrier to store excess energy that is produced from wind generators or photovoltaic plants at peak production times. For that, the excess energy is converted into chemical energy in the form of hydrogen and further transformed into methanol in order to store the energy in an energy dense liquid form which is safe in comparison to hydrogen.[18][20] The sustainable production and utilization of methanol and its derivatives is called methanol economy.[18] Methanol is a clear liquid with a normal boiling point of 64.7 °C and a molar mass of 32.042 g/mol.[21][22] The chemical structure of methanol is pictured in Figure 3.

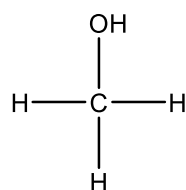


Figure 3: Chemical structure of methanol (MeOH)

Methanol is produced commercially using syngas, a mixture consisting of CO (carbon monoxide), CO<sub>2</sub> and H<sub>2</sub>, *via* heterogeneous catalysis according to reaction 1. For that purpose, syngas is manufactured by steam methane reforming (reaction 2 and 3).[16]



Reaction 1 is carried out over a co-precipitated Cu/Zn/Al<sub>2</sub>O<sub>3</sub> catalyst at 200-300 °C and 5-10 MPa.[23] Currently, 2.3 billion liters of methanol are produced per year in this

way.[24] By-products that can occur are higher alcohols, ethers, esters, hydrocarbons and ketones.[25]

In order to leave fossil fuels behind many researchers focus on green methanol synthesis. Here, carbon dioxide and hydrogen are converted to methanol and water (reaction 4) over a catalyst as a method for CO<sub>2</sub> utilization. Additionally, there are two reactions that also occur: the reverse water-gas shift (RWGS) reaction (reaction 5) and the hydrogenation of carbon monoxide (reaction 1).[26]



Besides the wanted reaction, namely CO<sub>2</sub> hydrogenation, there is CO produced *via* the reverse water-gas shift reaction which is also converted to methanol by hydrogenation. Side products that can form are methane and dimethyl ether due to methanation of CO or CO<sub>2</sub> (back reaction of reaction 2 and 3, respectively)[27] and dehydration of methanol (reaction 6)[8], respectively.[26] In contrast to conventional methanol production water is a by-product of reaction 4 and 5. This can lead to catalyst deactivation and inhibits the reaction due to crystallization and sintering of the active sites of the catalyst.[13][19][28] In order to avoid catalyst deactivation and formation of side products an appropriate and selective catalyst has to be found.

Since the hydrogenation of CO<sub>2</sub> is an exothermic reaction and the number of molecules decreases during the reaction course low temperatures and high pressure are favorable for shifting the equilibrium to the product side according to Le Châtelier's principle. In contrast to that the stability and inertness of CO<sub>2</sub> ( $\Delta G_f^0 = -394.38$  kJ/mol)[29] requires high energy substances like hydrogen and a high temperature for activation which favors the endothermic reverse water-gas shift reaction.[17][30] Therefore, a suitable catalyst is needed to enable activation of CO<sub>2</sub> at lower temperatures.

The CO<sub>2</sub> for the reaction can be captured from combustion processes. There are three possibilities for capturing CO<sub>2</sub> in combustion plants. These are postcombustion

capture, where the formed gases after fuel combustion are captured, precombustion capture, where the carbon is removed from the fuel before the combustion by partial oxidation or gasification, as well as oxyfuel combustion, meaning combustion with pure oxygen giving water vapor and carbon dioxide.[8][31] Further, carbon dioxide can be taken directly from the air, for example with a membrane separation technology as described in the book “Industrial Membrane Separation Technology” by K. Scott and R. Hughes.[18][20][32] Its properties make CO<sub>2</sub> an appealing raw material, as it is non-toxic, non-flammable as well as inert but it is also thermodynamically stable and needs high energy substances for activation.[16][29][33] Carbon dioxide is also directly used in refrigeration systems, as dry ice, in waste water treatment, just to mention a few applications.[31]

In order to make the hydrogenation of CO<sub>2</sub> an environmentally friendly process, the generation of hydrogen also needs to be reconsidered, since it currently is produced from fossil fuels *via* steam methane reforming, partial oxidation of light oil residues or coal gasification.[8][16] This can be realized through the production of hydrogen by the electrolysis of water into hydrogen and oxygen with the help of renewable energy, like wind power.[13][20] How electrolysis of water works was described, for instance, by K. G. dos Santos *et al.*[34] Another possibility for H<sub>2</sub> production is the high-temperature electrolysis of steam instead of water.[35]

Despite all this knowledge, there are many open questions about reduction of CO<sub>2</sub> using H<sub>2</sub> like the choice of a suitable catalyst, the reaction mechanism and the carbon-source, respectively. Due to this many scientists do research on this challenging topic. The current knowledge about catalysts, in particular copper-based ones, and the reaction mechanism is collected in the following chapters.

## 2. Catalysts for CO<sub>2</sub> hydrogenation

The reduction of carbon dioxide to methanol can proceed *via* heterogeneous catalysis, homogeneous catalysis, photocatalysis or electrochemical.[29] Advantages of homogeneous catalysis are the good selectivity and activity but the recovery and the regeneration are difficult.[30] Li *et al.* did some research on this topic.[36] Unfortunately, both photo- and electrocatalysis show insufficient efficiency and selectivity. The fundamentals of these can be taken from Wu *et al.*[37]

This thesis focuses on heterogeneous catalysis of CO<sub>2</sub> reduction. Heterogeneous catalysts are composed of an active phase, a support material and a promoter.[17] In the catalyst an interaction is formed between the active phase and the support. This affects not only the formation and stabilization of the active phase but also the catalytic properties of the active phase.[1][38] Further, the supporting material influences the basicity of the catalyst and the interaction between promoter and active phase.[4][38] A promoter is an additive which increases the catalytic activity, stability and selectivity.[1]

The catalytic activity of the hydrogenation of CO<sub>2</sub> to methanol is influenced by many factors, like the structures of metal and catalyst, the particle size and surface area of the metal, the metal distribution on the supporting material, the kind of promoters and supports and the active sites on the catalyst.[39]

In the last years many different types of catalysts for the reduction of carbon dioxide yielding methanol were tested, such as copper-based catalysts, using copper as active component with different support materials, and noble metal catalysts, for example with palladium, platinum, gallium, gold and silver as active phase combined with supports like ZnO, Ga<sub>2</sub>O<sub>3</sub>, In<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, Si<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub> as well as other catalysts like NiGa, CoGa, Mo<sub>2</sub>C, Fe<sub>3</sub>C, LaCr<sub>0.5</sub>Cu<sub>0.5</sub>O<sub>3</sub>, Co supported on Mo<sub>2</sub>C, Fe supported on Mo<sub>2</sub>O and catalysts using In<sub>2</sub>O<sub>3</sub> or ZnO as active phase, just to name a few of them.[7][13][16][17][19][20][29]

### 2.1. Copper-based catalysts

Many researchers pay high attention to copper-based catalysts, as they are very active and selective.[17] Various supporting materials were tested in combination with

different promoters. Al<sub>2</sub>O<sub>3</sub>-supports[40] were examined with Zn-[26][41], Zr-[41][42], Mg-[41], Ba-[43], K-[43], Ti-[44], V-[45], Ce-[46] and Y-promotion.[46] The influence of Zr[47][48][49], Ga[50][51][52][49], Ti[48][53], In[54], Al[49] and Cr[49] on ZnO-supported catalysts[55][56] was investigated and SiO<sub>2</sub>-supporting materials were doped with Zn[23][50][51][57][58][59][60][61], Cr[23], Mn[23][59][58], Fe[23], Co[23], Ni[23], Pd[60], Ga[50][51], Ti[62] and Zr[57][62]. Further, ZrO<sub>2</sub>-carriers[63][64][65] were combined with promoters like Zn[26][66][67], Ga[68], B[68], Ag[69] and La.[70] There are studies concerning graphene-oxide supported catalysts containing Zn[71][72][73], Zr[71][73] and Al.[73] TiO<sub>2</sub>-supports were combined with Mg[74], Zn[75] and Ce.[75] Some research was done with respect to CeO<sub>2</sub>[76] as a supporting material with Zn-[66], Pd-[77] and Ni-promotion.[78] Another often used supporting material is a combination of ZnO and ZrO<sub>2</sub>. [57][79][80][81][82][83][84][85] Promoters which were taken along with this support are Si[86], La[87], Ce[87], Nd[87], Pr[87], W[88][89], Cr[89], Mo[89], Ga[90], Mn[90][91], B[90], In[90], Gd[90], Y[90] and Mg[90]. A further support-combination is ZnO with Al<sub>2</sub>O<sub>3</sub>[60][66][85][92][93][94] promoted by In[54], Si[95], Ti[95], Mn[96], La[96], Ce[96], Zr[96], Y[96], Pd[97] and F.[98] The frequently tested multicomponent support consisting of ZnO, Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>[73][85][94][99][100][101] was tested with F-promotion.[102] Another multicomponent support contains ZnO, TiO<sub>2</sub> and ZrO<sub>2</sub>. [103] Additional, Ga<sub>2</sub>O<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> were studied as supporting material.[63] Carbon nanotubes with different functional groups were also tried as supporting material for the hydrogenation of CO<sub>2</sub>. [104]

### **2.1.1. Catalyst activity**

The activity of a catalyst depends on its characteristics such as the distribution of the active sites, the distribution of promotor and active phase, the basicity of the catalyst, the particle size of the catalyst which is related to the porosity and surface area and the particle size of the active phase. These factors can greatly be influenced by the kind of support and promotor.[4][23][33] A small particle size results in a lower diffusion resistance of the reactant molecules in the pore of the catalyst which leads to an increased activity. Additionally, the larger surface area enhances the active metal dispersion which counteracts sintering.[4][38] A high copper surface area can adsorb and split more hydrogen which can further hydrogenate more carbon dioxide. Another

influencing factor are the basic sites. Strong basic sites favor the production of methanol.[74] A high surface basicity favors the adsorption of CO<sub>2</sub> as it is an acidic substance.[55][105]

### 2.1.2. Deactivation

Deactivation of the catalyst by sintering, agglomeration, ageing or poisoning is an issue during the reaction course. High temperatures lead to sintering and agglomeration of the catalyst. This problem can be avoided by using a fitting promoter which increases the thermal stability. It is also important to ensure a sulfur and chlorine free reaction since these substances are catalyst poisons.[4] As mentioned before, the resulting water formation of the reaction acts inhibiting and deactivates the catalyst. Water oxidizes the metallic copper according to reaction 7 resulting in deactivation of active sites. In order to solve this problem one could remove water from the reaction mixture. The oxidized copper can be activated again through reaction with CO where also CO<sub>2</sub> is produced as stated in reaction 8.[17]



### 2.1.3. Preparation methods

In the following chapter some important preparation methods for copper-based catalysts are described. Prior to the usage of the catalysts, most preparation methods require a reduction step with hydrogen to reduce the copper species to metallic copper in order to activate them.

#### Precipitation method

The precipitation method is commonly used for catalyst preparation. To start, a homogeneous solution of the precursors of the active components in form of their salts, for example nitrates or chlorides, is formed by dissolving them in a suitable liquid, like water. The solution is precipitated through change in pH by adding a precipitation agent, often a carbonate, to reach a supersaturated state, where nucleation starts, which is followed by growth and agglomeration. In order to gain the solid, the

precipitate is filtered and dried. The resulting product is grinded to a powder to get rid of the irregular shape. At last, the powder is calcinated to form oxides. This can happen through reaction with air at elevated temperature. The properties of the catalyst are determined by the chosen preparation parameters. The precipitation method leads to a homogeneous component distribution and a small, uniform particle size but a wide particle size distribution. Advantageous are the low costs of this method.[106][107] Deposition precipitation means a connection of precipitation and deposition where the precipitated particles interact with the support.[108] Reverse co-precipitation means that the support is suspended with the precipitation agent, before the solution of precursors is slowly added under ultrasound irradiation.[71][86]

### **Impregnation method**

For the impregnation method a solution containing precursors of the active phase is encountered with the solid support or another active solid phase. The components in the solution are deposited on the surface of the solid material. For incipient wetness impregnation the volume of the solution is the same as the pore volume of the support or another active material, whereas for wet impregnation the solution volume is much higher than the pore volume. The catalyst is then dried and calcinated. Co-impregnation means that several active components are added in one step. Compared to the precipitation method, the impregnation method is faster and cheaper, but it is difficult to produce catalysts with a high concentration.[106][107]

### **Sol-gel method**

In the sol-gel method the metal precursors are dissolved in a suitable liquid and mixed with a metalorganic precursor. Afterwards, the metalorganic precursor is hydrolyzed. A sol is produced by polymerization which is converted to a gel by drying. Catalysts prepared with the sol-gel method have a high surface area and a high dispersion of the active species. Further, the catalysts are thermally stable. [103][103][109] In this preparation method the type of precursor, the precursor concentration, the type of solvent, the temperature and the drying process highly influence the gel structure and hence, the properties of the catalyst.[110]

### **Combustion synthesis**

A solution containing the dissolved precursors is prepared. Afterwards a fuel is added to the solution. The obtained mixture is sonicated until a sol is formed and then dried

to a gel which is ignited. The resulting product is a fine powder.[57][79][80][103] Combustion synthesis is considered as a simple, fast and cheap method to gain catalysts in any size and shape with a high homogeneity.[80][111][112]

### Solid-state reaction method

The precursors are mixed before citric acid is added to them. Then the mixture is ground, dried and calcinated. This method provides a solvent-free, fast and cheap method for catalyst preparation. The calcination temperature has a great impact on the properties of the catalyst.[81][103]

### Ion-exchange method

This preparation method is based on the applying of dissolved precursors on the support mostly using an ammonium hydroxide solution. A direct treatment with hydrochloric acid is also possible. After that, the catalysts are dried and calcinated. Influencing factors in the ion-exchange method are the calcination conditions, the degree of ion-exchange and exchange treatment.[113]

## 2.1.4. Comparison and discussion of ongoing research

The recent state of research on copper-based catalysts are summed up in Table 1 to Table 12 and the results are discussed afterwards.

### 2.1.4.1. Unsupported catalysts

Copper alone was found to be inactive for CO<sub>2</sub> hydrogenation to methanol. (Table 1) Neither CO<sub>2</sub> conversion nor methanol production could be observed.[55]

Table 1: Unsupported copper-based catalysts for the hydrogenation of CO<sub>2</sub> to methanol with composition, preparation method (unless otherwise stated the used precursors were nitrates), reaction conditions (temperature [°C] and pressure [MPa]), feed composition, CO<sub>2</sub> conversion  $X_{CO_2}$  [%], methanol selectivity  $S_{MeOH}$  [%], methanol activity (=space-time-yield STY) [ $mol_{MeOH}/kg_{cat}/h$ ] and reference.

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	$X_{CO_2}$	$S_{MeOH}$	STY	Ref
	molar ratio	weight percent							
Cu			commercial powder	250 °C 3 MPa	1:3	0	0	0	[55]
CuZn		28 Zn 72 Cu	commercial powder	250 °C 3 MPa	1:3	0	0	0	[55]



### 2.1.4.2. Al<sub>2</sub>O<sub>3</sub>-supported catalysts

Table 2 gives an overview of Al<sub>2</sub>O<sub>3</sub> (alumina)-supported catalysts.

Table 2: Al<sub>2</sub>O<sub>3</sub>-supported catalysts for the hydrogenation of CO<sub>2</sub> to methanol with composition, preparation method (unless otherwise stated the used precursors were nitrates), reaction conditions (temperature [°C] and pressure [MPa]), feed composition, CO<sub>2</sub> conversion X<sub>CO<sub>2</sub></sub> [%], methanol selectivity S<sub>MeOH</sub> [%], methanol activity (=space-time-yield STY) [mol<sub>MeOH</sub>/kg<sub>cat</sub>/h] and reference.

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO<sub>2</sub></sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Zn-Cu/Al <sub>2</sub> O <sub>3</sub>		30 Cu 41 ZnO	co-precipitation	210 °C 5 MPa	1:6	9.9	48	-	[26]
Zn-Cu/Al <sub>2</sub> O <sub>3</sub>		30 Cu 41 ZnO	co-precipitation	220 °C 5 MPa	1:3.9	11.1	43	-	[26]
Cu/HAl		10 Cu	incipient wetness impregnation	260 °C 3 MPa	1:3	10.5	30.3	-	[40]
Cu/UAl		10 Cu	incipient wetness impregnation	260 °C 3 MPa	1:3	13.5	23.1	-	[40]
Cu/ γ-Al <sub>2</sub> O <sub>3</sub>			impregnation	250 °C 2 MPa	1:3	8.98	13.44	0.25	[41]
Zn-Cu/ γ-Al <sub>2</sub> O <sub>3</sub>	2 Cu 1 Zn		impregnation	250 °C 2 MPa	1:3	9.34	17.37	0.34	[41]
ZrO <sub>2</sub> -Cu/γ-Al <sub>2</sub> O <sub>3</sub>	2 Cu 1 Zr		impregnation	250 °C 2 MPa	1:3	8.85	13.75	0.27	[41]
Zn-Zr-Cu/ γ-Al <sub>2</sub> O <sub>3</sub>	2 Cu 1 Zn 1 Zr		impregnation	250 °C 2 MPa	1:3	10.8 7	22.44	0.62	[41]
Mg-Zn-Zr-Cu/ γ-Al <sub>2</sub> O <sub>3</sub>	2 Cu 1 Zn 0.9 Zr 0.1 Mg		impregnation	250 °C 2 MPa	1:3	12.1 2	35.98	0.97	[41]
Cu/γ-Al <sub>2</sub> O <sub>3</sub>		12 Cu	impregnation	260 °C 3 MPa	1:3	15.6	10.7	-	[42]
Zr-Cu/γ-Al <sub>2</sub> O <sub>3</sub>		12 Cu 10 Zr 90 Al <sub>2</sub> O <sub>3</sub>	impregnation	260 °C 3 MPa	1:3	16.5	14.6	-	[42]
Cu/Al <sub>2</sub> O <sub>3</sub>		18 Cu 82 Al <sub>2</sub> O <sub>3</sub>	incipient wetness impregnation	200 °C 3 MPa	1:3.8	1.2	42.6	0.47	[43]
Cu/Al <sub>2</sub> O <sub>3</sub>		18 Cu 82 Al <sub>2</sub> O <sub>3</sub>	incipient wetness impregnation	200 °C 36 MPa	1:3.8	8.4	37.3	3.23	[43]
Ba-Cu/Al <sub>2</sub> O <sub>3</sub>		5 Ba 17.1 Cu 77.9 Al <sub>2</sub> O <sub>3</sub>	incipient wetness impregnation	200 °C 3 MPa	1:3.8	1.6	62.8	0.94	[43]
Ba-Cu/Al <sub>2</sub> O <sub>3</sub>		5 Ba 17.1 Cu 77.9 Al <sub>2</sub> O <sub>3</sub>	incipient wetness impregnation	200 °C 36 MPa	1:3.8	4.3	57.2	2.31	[43]
K-Cu/Al <sub>2</sub> O <sub>3</sub>		5 K 17.1 Cu 77.9 Al <sub>2</sub> O <sub>3</sub>	incipient wetness impregnation	200 °C 3 MPa	1:3.8	2.2	10.8	0.23	[43]
K-Cu/Al <sub>2</sub> O <sub>3</sub>		5 K 17.1 Cu 77.9 Al <sub>2</sub> O <sub>3</sub>	incipient wetness impregnation	200 °C 36 MPa	1:3.8	8.9	4.1	0.34	[43]
Ti-Cu/γ-Al <sub>2</sub> O <sub>3</sub>	9 Ti 1 Al	12 Cu	impregnation	240 °C 3 MPa	1:3	23	61	-	[44]

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO2</sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Cu/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>		12 Cu	impregnation	240 °C 3 MPa	1:3	10	16	-	[45]
V-Cu/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>		12 Cu 6 V	impregnation	240 °C 3 MPa	1:3	14	24	-	[45]
Cu/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>		5 Cu	co-impregnation	250 °C 2.9 MPa	1:5	-	54.91	3.24	[46]
Ce-Cu/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>		5 Cu 50 CeO <sub>2</sub>	co-impregnation	250 °C 2.9 MPa	1:5	-	75.98	4.10	[46]
Y-Ce-Cu/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	10 Y	5 Cu 50 Y-CeO <sub>2</sub>	co-impregnation	250 °C 2.9 MPa	1:5	-	86.29	6.88	[46]

A comparison of hierarchical meso-macroporous alumina (HAI) and unimodal mesoporous alumina (UAI) was done, exposing that the HAI-supported catalyst showed a 3 % lower CO<sub>2</sub> conversion explainable by the lower exposed Cu area but it had a higher stability and a 7.2 % higher methanol selectivity.[40]

Ren *et al.* found that ZnO and ZrO<sub>2</sub> as well as MgO raise the dispersion of copper, the copper metal surface area and the formation of small Cu<sup>0</sup> particles on Al<sub>2</sub>O<sub>3</sub>-supported catalysts. It was stated that the Cu<sup>0</sup> particles are the active sites of the catalyst. The size of them is also depending on the activation temperature. Tests with a Cu-ZnO-ZrO<sub>2</sub>-MgO/Al<sub>2</sub>O<sub>3</sub> catalyst showed that an elevated reaction temperature influences the hydrogenation in a negative way and favors the reverse water-gas shift reaction and methanation.[41]

Zr-Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was proven to have a higher activity and methanol selectivity than Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>. Doping  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with zirconium led to a higher CuO dispersion with ZrO<sub>2</sub> dispersed on the support indicating strong interaction between CuO and ZrO<sub>2</sub>. Catalytic tests showed that Zr-promotion could increase the CO<sub>2</sub> conversion and methanol selectivity by 0.9 and 3.9 %, respectively.[42]

Bansode *et al.* investigated the impact of K and Ba on Cu/Al<sub>2</sub>O<sub>3</sub> catalysts, respectively. K acted positive on the reverse water-gas shift reaction or rather CO formation and negative on methanol synthesis. Oppositely, Ba promoted methanol formation, especially at low temperatures. Both promoters suppressed dimethyl ether (DME) formation which was formed by the unpromoted catalyst. XRD experiments showed that potassium covers parts of the copper and aluminum surface leading to less

reduction of the copper and further lower activity. While Ba-promotion increased the metallic copper surface area and prevented sintering without covering the active surface.[43]

Ti-promotion on  $\gamma$ - $\text{Al}_2\text{O}_3$ -supported catalysts decreased the catalyst's crystallite size, increased the copper dispersion and promoted the CuO reduction leading to a good catalytic performance.[44]

V-promotion led to a volcano-shaped curve of  $\text{CO}_2$  conversion and an increasing curve of methanol selectivity as a function of V content, respectively. V was stated to cause a better dispersion of CuO.[45]

Adding  $\text{CeO}_2$  to alumina-supports led to a better copper oxide dispersion. Y-promotion led to larger crystals of ceria.  $\text{CeO}_2$ -doping was examined to enhance the catalytic performance of alumina-supported catalysts due to an interaction between copper and ceria leading to an increase of  $\text{CH}_3\text{OH}$  selectivity and space-time-yield of about 21 % and 0.86 %, respectively. Yttria-promotion into ceria did elevate the results even more resulting in 86.29 % selectivity and a space-time yield of 6.88  $\text{mol}_{\text{MeOH}}/\text{kg}_{\text{cat}}/\text{h}$ .[46]

The main products of  $\text{CO}_2$  hydrogenation on  $\text{Cu}/\text{Al}_2\text{O}_3$  catalysts were  $\text{CH}_3\text{OH}$ , CO and DME, which is formed by dehydration of methanol on alumina. A reason for that is that Lewis acidic supports favor the formation of methanol, but strong Lewis acids also lead to dehydration of methanol. The formation of CO can happen through many pathways conveyed by  $\text{Al}_2\text{O}_3$ .[114] Since the unpromoted  $\text{Cu}/\text{Al}_2\text{O}_3$  catalysts needs improvement regarding the methanol selectivity, ZnO-,  $\text{ZrO}_2$ -, MgO-, K-, Ba-, Ti- and V-promotion on these catalysts was tested. ZnO- and  $\text{ZrO}_2$ -addition only had a small impact on  $\text{CO}_2$  conversion but ZnO had a noticeable effect on the STY and the selectivity of methanol. The introduction of both, ZnO and  $\text{ZrO}_2$ , led to an even higher performance. If also MgO was added, the results were remarkably improved.[41][42] K-doping promoted the unwanted reverse water-gas shift reaction. Therefore, K is not a suitable promoter for  $\text{Cu}/\text{Al}_2\text{O}_3$  catalysts although it inhibited DME formation. Reduced DME formation was also noticed on a Ba-promoted catalyst. Ba and V did promote methanol formation.[43][45] Remarkably, Ti-promotion led to the best results compared to all promoters discussed before.[44] It was found that the pore structure of the catalyst has influence on the catalytic performance. As hierarchical meso-macroporous alumina led to a shorter mesopore diffusion path length it exhibited a better performance than

unimodal mesoporous alumina.[40] Additional supporting of alumina with yttria-doped ceria did also increase the catalytic performance.[46]

### 2.1.4.3. ZnO-supported catalysts

Table 3 sums up the research work on ZnO-supported catalysts.

Table 3: ZnO-supported catalysts for the hydrogenation of CO<sub>2</sub> to methanol with composition, preparation method (unless otherwise stated the used precursors were nitrates), reaction conditions (temperature [°C] and pressure [MPa]), feed composition, CO<sub>2</sub> conversion X<sub>CO<sub>2</sub></sub> [%], methanol selectivity S<sub>MeOH</sub> [%], methanol activity (=space-time-yield STY) [mol<sub>MeOH</sub>/kg<sub>cat</sub>/h] and reference.

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO<sub>2</sub></sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Zr-Cu/ZnO		34.1 Cu 31.6 Zn 6.9 Zr	co-precipitation	250 °C 3 MPa	1:3	19.4	29.3	-	[47]
Zr-Cu/ZnO	40 Cu 40 Zn 20 ZrO <sub>2</sub>		oxalate co-precipitation	240 °C 3 MPa	22:66 (:12 N <sub>2</sub> )	17.0	41.5	-	[48]
Ti-Cu/ZnO	40 Cu 40 Zn 20 TiO <sub>2</sub>		oxalate co-precipitation	240 °C 3 MPa	22:66 (:12 N <sub>2</sub> )	16.4	38.8	-	[48]
Ti-Zr-Cu/ZnO	40 Cu 40 Zn 10 TiO <sub>2</sub> 10 ZrO <sub>2</sub>		oxalate co-precipitation	240 °C 3 MPa	22:66 (:12 N <sub>2</sub> )	17.4	43.8	-	[48]
Cu/ZnO		50 Cu 50 ZnO	co-precipitation	250 °C 5 MPa	1:3	-	-	16.1 0	[49]
Ga-Cu/ZnO		50 Cu 25 ZnO 25 Ga <sub>2</sub> O <sub>3</sub>	co-precipitation	250 °C 5 MPa	1:3	-	-	23.0 3	[49]
Al-Cu/ZnO		50 Cu 45 ZnO 5 Al <sub>2</sub> O <sub>3</sub>	co-precipitation	250 °C 5 MPa	1:3	-	-	22.5 0	[49]
Zr-Cu/ZnO		50 Cu 40 ZnO 10 ZrO <sub>2</sub>	co-precipitation	250 °C 5 MPa	1:3	-	-	20.7 6	[49]
Cr-Cu/ZnO		50 Cu 45 ZnO 5 Cr <sub>2</sub> O <sub>3</sub>	co-precipitation	250 °C 5 MPa	1:3	-	-	18.7 9	[49]
Ga-Cu/ZnO (LS)		6.0 Cu 1.9 Ga <sub>2</sub> O <sub>3</sub>	incipient wetness impregnation	270 °C 2 MPa	1:3	2.0	51.0	2.02	[50]
Ga-Cu/ZnO (HS)		6.8 Cu 2.5 Ga <sub>2</sub> O <sub>3</sub>	incipient wetness impregnation	270 °C 2 MPa	1:3	2.0	55.5	1.88	[50]
Cu/ZnO (HS)		5.6 Cu 94.4 ZnO	impregnation (precursor: methoxide-acetylacetonone)	270 °C 2 MPa	1:3	2.2	100	4.54	[51]
Ga-Cu/ZnO (LS)		5.4 Cu 92.1 ZnO 2.5 Ga <sub>2</sub> O <sub>3</sub>	impregnation (precursor: methoxide-acetylacetonone)	270 °C 2 MPa	1:3	4.6	83.5	8.11	[51]
Ga-Cu/ZnO (HS)		5.6 Cu 91.7 ZnO 2.7 Ga <sub>2</sub> O <sub>3</sub>	impregnation (precursor: methoxide-acetylacetonone)	270 °C 2 MPa	1:3	6.0	88	11.8 1	[51]
Cu/ZnO	43 Cu 57 Zn		co-precipitation	240 °C 4.5 MPa	1:2.8	20	44	-	[52]

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO<sub>2</sub></sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Ga-Cu/ZnO	43 Cu 56.5 Zn 0.5 Ga		co-precipitation	240 °C 4.5 MPa	1:2.8	21	46	-	[52]
Ga-Cu/ZnO	43 Cu 52 Zn 5 Ga		co-precipitation	240 °C 4.5 MPa	1:2.8	27	50	-	[52]
Cu/ZnO	1 Cu 1 Zn		co-precipitation	220 °C 3 MPa	1:3 (: 0.5 N <sub>2</sub> )	13.1	44.2	1.25	[53]
Ti-Cu/ZnO	1 Cu 1 Zn 0.2 Ti		co-precipitation	220 °C 3 MPa	1:3 (: 0.5 N <sub>2</sub> )	14.8	50.2	1.6	[53]
In-Cu/ZnO		67.5 CuO 25 ZnO 7.5 In <sub>2</sub> O <sub>3</sub>	co-precipitation	250 °C 5 MPa	1:8 (:1 CO)	13.9 9	99.75	6.03	[54]
Cu/ZnO		0.70 Zn 0.30 Cu	co-precipitation	250 °C 3 MPa	1:3	10.7	-	1.6	[55]
Cu + ZnO		0.7 Zn 0.3 Cu	mechanical mixture	250 °C 3 MPa	1:3	0.7	100	1.4	[55]
CuZn@ZnO <sub>x</sub>		0.48 Zn 0.52 Cu	surface modification precipitation (core-shell catalyst)	250 °C 3 MPa	1:3	0.3	100	0.6	[55]
Cu@ZnO <sub>x</sub>		0.09 Zn 0.91 Cu	surface modification precipitation (core-shell catalyst)	250 °C 3 MPa	1:3	2.3	100	4.6	[55]
Cu/ZnO	1 Cu 1 Zn		co-precipitation	220 °C 2 MPa	1:3	5.5	55	1.56	[56]
Cu/ZnO	1 Cu 1 Zn		chitosan-assisted co-precipitation (0.0015 g/mL chitosan)	220 °C 2 MPa	1:3	10.0	65	3.59	[56]
Cu/ZnO	1 Cu 1 Zn		chitosan-assisted co-precipitation (0.0030 g/mL chitosan)	220 °C 2 MPa	1:3	9.0	60	2.97	[56]
Cu/ZnO	1 Cu 1 Zn		chitosan-assisted co-precipitation (0.0045 g/mL chitosan)	220 °C 2 MPa	1:3	7.9	60	2.50	[56]
Cu/ZnO	6 Cu 1.5 Zn		citric acid impregnation	180 °C 4 MPa	1:3	5.7	93.9	37.7	[59]

Raudaskoski *et al.* did investigations on the suspension ageing times during the catalyst preparation in the co-precipitation method. The results indicated that longer ageing times (12 or 24 h) result in a higher methanol selectivity and CO<sub>2</sub> conversion. Whereas low ageing times caused a higher sodium content and therefore, lower surface area, bigger particles or too strong CO<sub>2</sub> adsorption on the catalyst.[47]

A comparison of CuO/ZnO catalysts modified with TiO<sub>2</sub> and ZrO<sub>2</sub> was done by Xiao *et al.* An increase in catalytic performance when adding TiO<sub>2</sub> or ZrO<sub>2</sub> and both, TiO<sub>2</sub> as well as ZrO<sub>2</sub>, was described. Best results were gained by adding both promoters resulting in a CO<sub>2</sub> conversion of 17.4 % and a methanol selectivity of 43.8 %. It was explained that two sites are responsible for the activity of copper catalyst, namely the support, where CO<sub>2</sub> is adsorbed, and copper, where H<sub>2</sub> is adsorbed and dissociated. The atomic hydrogen is transported to the support by spillover.[48]

Saito *et al.* investigated various metal oxides on Cu/ZnO catalysts. The activity of the catalysts can be ranged as follows: Ga<sub>2</sub>O<sub>3</sub>-Cu/ZnO > Al<sub>2</sub>O<sub>3</sub>-Cu/ZnO > ZrO<sub>2</sub>-Cu/ZnO > Cr<sub>2</sub>O<sub>3</sub>-Cu/ZnO > Cu/ZnO. The scientists discovered a linear relationship between space-time-yield (STY) and copper surface area. The STY was elevated for all promoters, but the specific activity in mg/m<sup>2</sup>/h was only increased for Ga<sub>2</sub>O<sub>3</sub>- and Cr<sub>2</sub>O<sub>3</sub>-promotion by 40 % and 30 %, respectively. It was suggested that Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub> lead to a higher copper dispersion whilst Ga<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> do not increase the copper dispersion but increase the specific activity due to an enhanced Cu<sup>+</sup>/Cu<sup>0</sup> ratio at the surface.[49]

Toyir *et al.* investigated the influence of Ga<sub>2</sub>O<sub>3</sub> on different supports of copper-based catalysts prepared by incipient wetness impregnation using nitrate precursors. The kind of support had a great impact on the physical properties of gallium-promoted catalysts, for example SiO<sub>2</sub>-supported catalysts had higher surface areas than ZnO-supported catalysts. Catalytic experiments showed that SiO<sub>2</sub>-supported catalysts perform better regarding methanol selectivity and yield than ZnO-supported. Without Ga-promotion the Cu-Zn/SiO<sub>2</sub> catalyst was measured to have a lower methanol activity and selectivity which demonstrated that gallium is an advantageous promoter. The methanol selectivity could be increased to nearly 100 % by addition of Ga to the Cu-Zn/SiO<sub>2</sub> catalyst. Ga<sub>2</sub>O<sub>3</sub> was found to be dispersed in small particles on the surface.[50]

Later, the same authors did a comparison of ZnO-supported catalysts with SiO<sub>2</sub>-supported ones prepared by impregnation with methoxide-acetylacetonate precursors. Surprisingly, the study showed that ZnO-supported catalysts have a higher methanol selectivity and methanol formation rate which is contradictory to the prior study. The impregnation with methoxide-acetylacetonate precursors did form catalysts which showed a highly increased catalytic activity and stability, especially when promoted

with Ga. A higher copper dispersion and lower gallium dispersion was observed when using methoxide-acetylacetonate precursors.[51]

Li *et al.* investigated the influence of Ga on Cu/ZnO catalysts. Addition of 5 mol% Ga led to the best results in terms of catalytic performance due to the highest Zn<sup>0</sup> content. CO<sub>2</sub> conversion, CH<sub>3</sub>OH selectivity and yield showed a volcano-shaped profile with increasing Ga content in the catalyst. Ga-promotion was stated to enhance the Cu dispersion.[52]

TiO<sub>2</sub>-doping on Cu/ZnO catalysts increased the dispersion of CuO and ZnO and the interaction between those oxides. A Ti loading of 10 % in the catalyst gave the best results for the catalytic performance. The CO<sub>2</sub> conversion showed a maximum with increasing TiO<sub>2</sub> content whereas the methanol selectivity increased continuously.[53]

Le Valant *et al.* discussed a Cu-ZnO synergy which makes CO<sub>2</sub> hydrogenation selective for methanol whereas Cu and ZnO alone showed only little to no conversion to methanol. Under influence of H<sub>2</sub> the CuO in the catalyst got reduced to metallic Cu while ZnO stayed the same. They stated that Cu cannot be the only active site since the turn-over frequency increased when the metallic surface area of copper decreased but the activity comes from the interaction between Cu and ZnO. Catalysts based on core-shell structure with a ZnO<sub>x</sub> shell showed methanol activity and 100 % selectivity. These catalysts were prepared by a surface modification precipitation method where citric acid and distilled water were mixed with a Cu powder and a CuZn brass powder, respectively, before zinc nitrate was added and the standard procedure for the precipitation method was followed. Mechanical mixtures of Cu and ZnO were also 100 % selective for methanol and displayed a volcano-shaped profile in catalytic activity with varying Zn content. CO was produced through the reverse water-gas shift reaction while usage of a co-precipitated Cu/ZnO catalyst which decreased the selectivity.[55]

The influence of reaction temperature on Cu/ZnO catalysts prepared with chitosan was investigated. Best results were reached when using a small amount of chitosan (0.0015 g/mL). With increasing temperature in a range from 180 to 260 °C the CO<sub>2</sub> conversion rose from 4 to 17 %, the methanol selectivity decreased from 98 to 39 %, whereas the space-time-yield showed a maximum of 140 g<sub>MeOH</sub>/kg<sub>cat</sub>/h at 240 °C. At 260 °C the CO<sub>2</sub> conversion was still increasing but starting deactivation was observed

at high chitosan concentrations. Chitosan-assisted co-precipitation was proven to increase the copper surface area due to a better dispersion.[56]

ZnO-supports are often used in catalysts for CO<sub>2</sub> hydrogenation to methanol. For unpromoted Cu/ZnO catalysts the methanol selectivity is an issue because much CO is produced *via* the reverse water-gas shift reaction as by-product.[55] Whereas, using high-surface ZnO the selectivity for methanol was stated to be 100 %. Further, a high-surface ZnO-support led to a significantly better catalytic performance than a low surface ZnO-support. The precursor used in the catalyst preparation was found to have a great impact on catalytic performance. Promotion with Ga<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> or Cr<sub>2</sub>O<sub>3</sub> improves the catalytic performance.[50][51][49] There exists a maximum for a certain Ga content (5 mol%) where the performance parameters are the highest.[52] Using a small amount of chitosan (0.0015 g/mL) in the co-precipitation method was found to deliver an enhanced catalytic performance by changed physiochemical properties of the catalyst.[56] ZrO<sub>2</sub>, TiO<sub>2</sub> and a combination of both were proven to increase the catalytic performance of ZnO-supported catalysts.[48][53] A study on the ageing time during catalyst preparation showed that longer ageing times lead to a higher activity of the catalyst because the ageing time strongly influences the catalyst properties. A longer ageing time results in a lower sodium content and finer crystallites of the catalyst which has an impact on the pore volume in small pores, the particle size, the reduction of copper and the dispersion.[47]

#### 2.1.4.4. SiO<sub>2</sub>-supported catalysts

Table 4 lists SiO<sub>2</sub>-supported catalysts that were experimentally tested.

Table 4: SiO<sub>2</sub>-supported catalysts for the hydrogenation of CO<sub>2</sub> to methanol with composition, preparation method (unless otherwise stated the used precursors were nitrates), reaction conditions (temperature [°C] and pressure [MPa]), feed composition, CO<sub>2</sub> conversion  $X_{CO_2}$  [%], methanol selectivity  $S_{MeOH}$  [%], methanol activity (=space-time-yield STY) [mol<sub>MeOH</sub>/kg<sub>cat</sub>/h] and reference.

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	$X_{CO_2}$	$S_{MeOH}$	STY	Ref
	molar ratio	weight percent							
Zn-Cu/SBA-15	0.6 Cu 0.15 Zn 1 SBA-15		citric acid impregnation	180 °C 4 MPa	1:3	7.7	97.3	-	[23]
Cr-Zn-Cu/SBA-15	0.6 Cu 0.15 Zn 0.05 Cr 1 SBA-15		citric acid impregnation	180 °C 4 MPa	1:3	8.7	97.1	-	[23]



Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO2</sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Mn-Zn-Cu/SBA-15	0.6 Cu 0.15 Zn 0.05 Mn 1 SBA-15		citric acid impregnation	180 °C 4 MPa	1:3	10.5	98.6	-	[23]
Fe-Zn-Cu/SBA-15	0.6 Cu 0.15 Zn 0.05 Fe 1 SBA-15		citric acid impregnation	180 °C 4 MPa	1:3	5.7	96.9	-	[23]
Co-Zn-Cu/SBA-15	0.6 Cu 0.15 Zn 0.05 Co 1 SBA-15		citric acid impregnation	180 °C 4 MPa	1:3	6.6	90.8	-	[23]
Ni-Zn-Cu/SBA-15	0.6 Cu 0.15 Zn 0.05 Ni 1 SBA-15		citric acid impregnation	180 °C 4 MPa	1:3	6.3	72.4	-	[23]
Ga-Zn-Cu/SiO <sub>2</sub>		4.7 Cu 2.6 ZnO 1.7 Ga <sub>2</sub> O <sub>3</sub>	incipient wetness impregnation	270 °C 2 MPa	1:3	2.0	99.8	4.15	[50]
Ga-Zn-Cu/SiO <sub>2</sub> (HD)		4.7 Cu 2.3 ZnO 1.5 Ga <sub>2</sub> O <sub>3</sub>	incipient wetness impregnation	270 °C 2 MPa	1:3	5.6	99.5	10.9 1	[50]
Zn-Cu/SiO <sub>2</sub>		5.0 Cu 5.0 ZnO	incipient wetness impregnation	270 °C 2 MPa	1:3	2.0	47.2	2.04	[50]
Zn-Cu/SiO <sub>2</sub>		4.4 Cu 2.5 ZnO	impregnation (precursor: methoxide-acetylacetone)	270 °C 2 MPa	1:3	1.8	99.5	3.16	[51]
Ga-Zn-Cu/SiO <sub>2</sub>		4.5 Cu 2.0 ZnO 1.6 Ga <sub>2</sub> O <sub>3</sub>	impregnation (precursor: methoxide-acetylacetone)	270 °C 2 MPa	1:3	3.4	76	5.17	[51]
Ga-Zn-Cu/SiO <sub>2</sub> (HD)		4.3 Cu 2.4 ZnO 2.0 Ga <sub>2</sub> O <sub>3</sub>	impregnation (precursor: methoxide-acetylacetone)	270 °C 2 MPa	1:3	2.5	82.5	4.04	[51]
Zn-Cu/SBA-15	1 Cu 1 Zn		impregnation-sol-gel auto-combustion	250 °C 3 MPa	1:3 (: 0.4 N <sub>2</sub> )	8.9	27.74	4.94	[57]
Zn-Zr-Cu/SBA-15	1 Cu 1 Zn	6.31 CuO 5.89 ZnO 7.74 ZrO <sub>2</sub>	impregnation-sol-gel auto-combustion	250 °C 3 MPa	1:3 (: 0.4 N <sub>2</sub> )	19.2	30.60	11.7 4	[57]
Mn-Zn-Cu/MCF	6 Cu 1.5 Zn 0.5 Mn 10 MCF		citric acid impregnation	180 °C 4 MPa	1:3	3.9	>99	47.9	[58]
Mn-Zn-Cu/KIT-6	6 Cu 1.5 Zn 0.5 Mn 10 KIT-6		citric acid impregnation	180 °C 4 MPa	1:3	8.2	>99	105. 3	[58]
Mn-Cu/SBA-15	6 Cu 1.5 Mn 10 SBA-15		citric acid impregnation	180 °C 4 MPa	1:3	7.9	87.0	45.8	[59]
Mn-Zn-Cu/SBA-15	6 C 1.5 Zn 0.5 Mn 10 SBA-15		citric acid impregnation	180 °C 4 MPa	1:3	10.7	98.0	69.5	[59]
Cu/SiO <sub>2</sub>		10 Cu	co-impregnation	250 °C 4.1 MPa	24:72 (:4 Ar)	2.8	15	0.18	[60]
Pd-Cu/SiO <sub>2</sub>	1 Cu 0.33 Pd	10 Cu	co-impregnation	250 °C 4.1 MPa	24:72 (:4 Ar)	6.7	30	1.01	[60]

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO2</sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Pd-Cu/SiO <sub>2</sub>	1 Cu 0.52 Pd	10 Cu	co-impregnation	250 °C 4.1 MPa	24:72 (:4 Ar)	6.6	34	1.12	[60]
Pd-Cu/SiO <sub>2</sub>	1 Cu 0.52 Pd	10 Cu	sequential impregnation	250 °C 4.1 MPa	24:72 (:4 Ar)	5.0	23	0.58	[60]
Pd-Cu/SiO <sub>2</sub>	1 Cu 0.52 Pd	10 Cu	sequential impregnation	250 °C 4.1 MPa	24:72 (:4 Ar)	4.9	24	0.54	[60]
Cu/ MCM-41		10 Cu	co-impregnation	250 °C 4.1 MPa	24:72 (:4 Ar)	<1	40	0.07	[60]
Pd-Cu/ MCM-41	1 Cu 0.33 Pd	10 Cu	co-impregnation	250 °C 4.1 MPa	24:72 (:4 Ar)	6.2	23	0.65	[60]
Cu/SBA-15		10 Cu	co-impregnation	250 °C 4.1 MPa	24:72 (:4 Ar)	1.5	12	0.11	[60]
Pd-Cu/ SBA-15	1 Cu 0.33 Pd	10 Cu	co-impregnation	250 °C 4.1 MPa	24:72 (:4 Ar)	6.5	23	0.72	[60]
Cu/MSU-F		10 Cu	co-impregnation	250 °C 4.1 MPa	24:72 (:4 Ar)	<1	18	0.11	[60]
Pd-Cu/ MSU-F	1 Cu 0.33 Pd	10 Cu	co-impregnation	250 °C 4.1 MPa	24:72 (:4 Ar)	5.3	18	0.40	[60]
Zn-Cu/SiO <sub>2</sub>	1 Cu 2.03 Zn	10 Cu	co-impregnation	250 °C 4.1 MPa	24:72 (:4 Ar)	2.2	50	0.43	[60]
Cu@m-SiO <sub>2</sub>		12 Cu	mesoporous silica shell (precursor: acetate)	260 °C 5 MPa	1:3 (:0.1 N <sub>2</sub> )	11.5	21.2	1.59	[61]
Zn-Cu@m-SiO <sub>2</sub>	7 Cu 3 Zn	12 Cu	mesoporous silica shell (precursor: acetate)	260 °C 5 MPa	1:3 (:0.1 N <sub>2</sub> )	11.0	63.5	4.56	[61]
Cu/m-SiO <sub>2</sub>		12 Cu	incipient wetness impregnation (precursor: acetate)	260 °C 5 MPa	1:3 (:0.1 N <sub>2</sub> )	3.4	18.2	0.41	[61]
Cu/SiO <sub>2</sub>		5.2 Cu	decomposition	250 °C 0.65 MPa	1:3	< 1	42	0.36	[62]
Zr-Cu/SiO <sub>2</sub>		5.2 Cu 5.0 ZrO <sub>2</sub>	decomposition	250 °C 0.65 MPa	1:3	< 1	82	0.54	[62]
Ti-Cu/SiO <sub>2</sub>		5.2 Cu 5.0 ZrO <sub>2</sub> 5.0 TiO <sub>2</sub>	decomposition	250 °C 0.65 MPa	1:3	< 1	68	0.65	[62]
Ti-Zr-Cu/SiO <sub>2</sub>		5.2 Cu 5.0 TiO <sub>2</sub>	decomposition	250 °C 0.65 MPa	1:3	< 1	93	1.62	[62]

A study on the impact of transition metal promoters (Cr, Mn, Fe, Co, Ni) on silica-supported Cu-ZnO-based catalysts was done by Koh *et al.* The copper crystal size was smaller for all promoted catalysts, especially for Cr- and Mn-promotion, compared to an unpromoted Cu-ZnO-based catalyst. Experiments for catalytic hydrogenation of CO<sub>2</sub> showed that Cr and Mn increased the performance of the catalyst, while

application of Fe, Co and Ni as promoters resulted in a reduction of the catalyst performance even though they decreased the copper particle size. Therefore, the authors concluded that the performance does not only depend on the copper crystal size, but also on the interaction of CuO with other oxide species. It is noteworthy, that the Co-promoted catalyst was the only one which produced methane as a side product.[23]

Toyir *et al.* proposed that SiO<sub>2</sub> effects a higher surface area and pore volume of the catalyst compared to ZnO. ZnO-supported catalysts showed a higher activity and selectivity than SiO<sub>2</sub>-supported ones. Further, high-surface ZnO increased the activity more than low-surface ZnO. Gallium turned out to enhance the catalytic activity and stability in CO<sub>2</sub> hydrogenation. In comparison to nitrate precursors, methoxide-acetylacetone precursors delivered a higher methanol yield.[51]

An unsupported Cu-ZnO-ZrO<sub>2</sub> catalyst was found to have a 37.9-fold lower methanol yield than an SBA-15-supported one which supplied a high surface area. Oppositely, the unsupported catalysts yielded in a 2.71 % higher methanol selectivity. A higher loading of Cu-ZnO-ZrO<sub>2</sub> was determined to decrease the catalytic performance due to bigger active-phase particles. Zirconium-promotion was seen to elevate the space-time-yield, as well as methanol selectivity substantially.[57]

The impact of different morphological distinct siliceous porous supports on Cu-ZnO-MnO catalysts were determined. SBA-15 is a two-dimensional mesoporous silica, whereas MCF and KIT-6 are three-dimensional mesoporous silica. SBA-15 consists of long parallel pore channels which are in a hexagonal order. MCF is built of large uniform spherical cells and KIT-6 has a gyroid cubic structure. KIT-6 performed best by providing the smallest copper particle size, the best CuO dispersion, the largest exposed copper area and efficient diffusion of reactants to the active sites leading to a higher CO<sub>2</sub> conversion than MCF or SBA-15 and also to a remarkably high methanol space-time-yield of 105.3 mol<sub>MeOH</sub>/kg<sub>cat</sub>/h.[58]

It was seen by Koh *et al.* that using SBA-15 supports led to a higher surface area of the catalyst and an improved metal dispersion. SBA-15 along with MnO increased the CO<sub>2</sub> adsorption capacity probably due to formation of smaller copper particles. Concerning the catalytic performance, SBA-15 supported catalysts had a higher CO<sub>2</sub> conversion than Cu/ZnO and Cu/MnO explainable by the reducibility of the catalysts

due to smaller copper crystallites and adsorption behaviors as the researchers found that CO<sub>2</sub> molecules form a weaker bonding on the surface of the catalyst. The methanol selectivity could be increased significantly by addition of metal-oxides like ZnO and MnO by reason of interactions between copper and the metal-oxide.[59]

Jiang *et al.* stated that the hydrogenation of CO<sub>2</sub> works much faster on bimetallic Cu/Pd catalysts than on monometallic catalysts. Co-impregnation was found to deliver better results compared to sequential impregnation. The formed Cu/Pd alloy is responsible for the enhanced catalytic activity. Pd-Cu/SiO<sub>2</sub> catalysts were stated to be long-term stable.[60]

A mesoporous silica support was compared to mesoporous silica shell supports. The results indicated that core-shell catalysts have a higher stability, copper dispersion and prevent from sintering. Notable, the CO<sub>2</sub> conversion of the core-shell catalysts was much higher than of the Cu/m-SiO<sub>2</sub> catalyst because of the smaller copper particles and the consistent dispersion. The methanol selectivity was distributed as follows: CuO-ZnO@m-SiO<sub>2</sub> > CuO@m-SiO<sub>2</sub> > CuO/m-SiO<sub>2</sub> since the addition of ZnO resulted in more strongly basic sites.[61]

Schilke *et al.* investigated the impact of Zr- and Ti-promotion on SiO<sub>2</sub>-supported catalysts. Both dopants increased the CH<sub>3</sub>OH selectivity and formation. ZrO<sub>2</sub> was stated to have a better influence on the selectivity, whereas TiO<sub>2</sub> leads to a higher improvement of the methanol formation rate. Best results were obtained by usage of a combination of both leading to a selectivity of 93 % and a methanol formation rate of 1.62 mol<sub>MeOH</sub>/kg<sub>cat</sub>/h. With increasing ZrO<sub>2</sub> content the methanol yield rose because copper and zirconia participate on the methanol formation. Oppositely, increasing TiO<sub>2</sub> content did not yield in a higher formation rate. Therefore, methanol formation was stated to happen solely on copper. Further, TiO<sub>2</sub> does not enhance copper dispersion. Hence, it was concluded that TiO<sub>2</sub> promotes the activity of the copper surface area.[62]

Extensive studies have been made related to silica-supported copper-catalysts. A promoting effect could be determined for Cr and Mn, while Fe, Co and Ni suppressed the methanol formation by carbon dioxide hydrogenation on Cu-ZnO/SBA-15.[23] Cu/m-SiO<sub>2</sub> catalysts exhibit a rather low CO<sub>2</sub> conversion (3.4%) and methanol selectivity (18.2 %). Usage of core-shell structured catalysts could improve the catalytic activity significantly to a CO<sub>2</sub> conversion of 11.5 % and a methanol selectivity of

21.2 % for a Cu@m-SiO<sub>2</sub> catalyst.[61] The influence of the SiO<sub>2</sub> morphology was determined to be great on Cu-ZnO-ZrO<sub>2</sub> containing catalysts. The catalytic performance was the following: KIT-6 > SBA-15 > MCF.[58] As mentioned for ZnO-supported catalysts, also for SiO<sub>2</sub>-supported catalysts Ga-promotion improved the catalytic performance.[50][51] Zn- or Pd-doping of a Cu/SiO<sub>2</sub> catalyst yielded in a highly increased methanol selectivity and yield.[60] Addition of ZrO<sub>2</sub> to Cu-ZnO/SBA-15 strongly improved the catalytic performance. SBA-15-support of a Cu-ZnO-ZrO<sub>2</sub> catalyst led to a remarkably high STY of 11.71 mol<sub>MeOH</sub>/kg<sub>cat</sub>/h and CO<sub>2</sub> conversion of 19.2 % but to a slightly lower methanol selectivity of 30.60 % compared to an unsupported catalyst whose methanol selectivity was 33.31 %.[57] ZrO<sub>2</sub>-doping had a better effect on methanol selectivity, while TiO<sub>2</sub>-doping had a more significant effect on the methanol activity. A combination of both yielded in even better results.[62] MnO-promotion was found to favor the formation of small copper particles and produced 4.5 mol<sub>MeOH</sub>/kg<sub>cat</sub>/h more methanol, while ZnO-doping yielded in a 10.3 % higher methanol selectivity.[59] The results obtained by Koh *et al.*[59] were notably higher than the results from Jiang *et al.*[60], which may be caused by the temperature and pressure difference and the different preparation procedure.

#### 2.1.4.5. ZrO<sub>2</sub>-supported catalysts

Table 5 shows the research that has been done on ZrO<sub>2</sub>-supported catalysts.

Table 5: ZrO<sub>2</sub>-supported catalysts for the hydrogenation of CO<sub>2</sub> to methanol with composition, preparation method (unless otherwise stated the used precursors were nitrates), reaction conditions (temperature [°C] and pressure [MPa]), feed composition, CO<sub>2</sub> conversion X<sub>CO2</sub> [%], methanol selectivity S<sub>MeOH</sub> [%], methanol activity (=space-time-yield STY) [mol<sub>MeOH</sub>/kg<sub>cat</sub>/h] and reference.

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO2</sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Zn-Cu/ZrO <sub>2</sub>		30 Cu 41 ZnO	co-precipitation	220 °C 5 MPa	1:3.9	8.7	56	-	[26]
Zn-Cu/ZrO <sub>2</sub>		30 Cu 41 ZnO	co-precipitation	220 °C 5 MPa	1:6	10.0	55	-	[26]
Cu/ZrO <sub>2</sub>		2 Cu	impregnation	250 °C 3 MPa	22:75 (:3 He)	0.99	69	3.6	[63]
Cu/ZrO <sub>2</sub>		40 CuO 60 ZrO <sub>2</sub>	deposition precipitation	240 °C 2 MPa	1:3	7.2	49.3	-	[64]
Cu/ZrO <sub>2</sub>		30 CuO 70 ZrO <sub>2</sub>	deposition precipitation	240 °C 2 MPa	1:3	6.3	48.8	11.2 4	[64]

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO2</sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Cu/a-ZrO <sub>2</sub>		10 Cu	incipient wetness impregnation	260 °C 3 MPa	1:3	7.9	42	2.56	[65]
Cu/m-ZrO <sub>2</sub>		10 Cu	Incipient wetness impregnation	260 °C 3 MPa	1:3	4.9	48	0.47	[65]
Cu/t-ZrO <sub>2</sub>		10 Cu	incipient wetness impregnation	260 °C 3 MPa	1:3	5	51	1.90	[65]
Zn-Cu/ZrO <sub>2</sub>		43 CuO 15 ZnO 42 ZrO <sub>2</sub>	reverse co-precipitation	240 °C 5 MPa	1:3 (:0.3 N <sub>2</sub> )	22.4	64	-	[66]
Cu/ZrO <sub>2</sub>		58.6 CuO 41.4 ZrO <sub>2</sub>	reverse co-precipitation	200 °C 3 MPa	1:3 (:0.3 N <sub>2</sub> )	7.2	70.2	-	[67]
Zn-Cu/ZrO <sub>2</sub>		15.1 CuO 41.8 ZnO 43.1 ZrO <sub>2</sub>	reverse co-precipitation	200 °C 3 MPa	1:3 (:0.3 N <sub>2</sub> )	6.5	70.9	-	[67]
Ga-Cu/ZrO <sub>2</sub>		27 Cu 3 Ga <sub>2</sub> O <sub>3</sub> 70 ZrO <sub>2</sub>	co-precipitation	250 °C 2 MPa	1:3	-	-	0.14	[68]
Ga-Cu/ZrO <sub>2</sub>		27 Cu 3 Ga <sub>2</sub> O <sub>3</sub> 70 ZrO <sub>2</sub>	deposition co-precipitation	250 °C 2 MPa	1:3	13.7 1	75.59	1.93	[68]
B-Cu/ZrO <sub>2</sub>		27 Cu 3 B <sub>2</sub> O <sub>3</sub> 70 ZrO <sub>2</sub>	co-precipitation	250 °C 2 MPa	1:3	0	0	0	[68]
B-Cu/ZrO <sub>2</sub>		27 Cu 3 B <sub>2</sub> O <sub>3</sub> 70 ZrO <sub>2</sub>	deposition co-precipitation	250 °C 2 MPa	1:3	15.8 3	67.26	1.8	[68]
Cu/ZrO <sub>2</sub>		10 Cu	incipient wetness impregnation	230 °C 1MPa	1:3 (:1 N <sub>2</sub> )	4.2	39	1.2	[69]
Ag-Cu/ZrO <sub>2</sub>		10 Cu 1 Ag	incipient wetness impregnation	230 °C 1MPa	1:3 (:1 N <sub>2</sub> )	2.6	49	0.9	[69]
Cu/ZrO <sub>2</sub>	1 Cu 1 Zr		urea nitrate combustion	220 °C 3 MPa	1:3 (: 0.5 N <sub>2</sub> )	5.3	58	-	[70]
La-Cu/ZrO <sub>2</sub>	1 Cu 1 Zr 0.05 La		urea nitrate combustion	220 °C 3 MPa	1:3 (: 0.5 N <sub>2</sub> )	6.2	66	-	[70]

Portha *et al.* compared an Al<sub>2</sub>O<sub>3</sub>-supported and a ZrO<sub>2</sub>-supported Cu-ZnO catalyst for the hydrogenation of CO<sub>2</sub>. Despite the Al<sub>2</sub>O<sub>3</sub>-support led to a higher surface area and CO<sub>2</sub> conversion, the ZrO<sub>2</sub>-support was determined to elevate the methanol selectivity and simultaneously showed a lower selectivity for CO in the reverse water-gas shift reaction.[26]

Zirconium-supported copper catalysts were also tested by Liu *et al.* The physical properties of the catalysts changed with the copper content and the preparation method. Regarding the preparation method they figured out that deposition precipitation provided the largest specific surface area and smaller particles. The methanol selectivity depended on the CuO/ZrO<sub>2</sub> ratio.[64]

Copper was tested on ZrO<sub>2</sub>-supports with different Zr-phases such as amorphous zirconia, tetragonal zirconia and monoclinic zirconia. The XRD pattern indicated that on Cu/a-ZrO<sub>2</sub> and Cu/t-ZrO<sub>2</sub> CuO is well dispersed while Cu/m-ZrO<sub>2</sub> delivers bigger CuO particles which was verified by HR-TEM of the catalysts. Monoclinic zirconia showed a stronger adsorption of CO<sub>2</sub> than tetragonal. On amorphous and tetragonal zirconia much more H<sub>2</sub> could be adsorbed due to a strong interaction of copper with a-ZrO<sub>2</sub> and t-ZrO<sub>2</sub>, respectively. As the catalytic activity was tested Cu/a-ZrO<sub>2</sub> had the best methanol yield (2.56 mol<sub>MeOH</sub>/kg<sub>cat</sub>/h) and the highest CO<sub>2</sub> conversion (7.9 %) which is attributable to the large copper surface area. The methanol selectivity was highest using Cu/t-ZrO<sub>2</sub> (51 %).[65]

Arena *et al.* found only a difference smaller than 1 % in CO<sub>2</sub> conversion and methanol selectivity concerning the composition of Cu/ZrO<sub>2</sub> and Cu-ZnO/ZrO<sub>2</sub> catalysts. However, the space-time-yield of methanol did rapidly increase at low Zn content, showing a maximum at a Zn/Cu ratio between 0.3 and 0.5. Reverse co-precipitation under ultrasound irradiation was successfully applied, yielding in improved physical properties compared to conventionally prepared catalysts.[67]

Deposition precipitation on nanocrystalline zirconia yielded in a smaller CuO size than conventional precipitation which led to a better dispersion and a higher stability against sintering and agglomeration and further increased the CO<sub>2</sub> conversion and methanol yield. The effect of different promoters (Ga and B) was much lower than the effect of different preparation methods. It was concluded that nanocrystalline supports increase the interaction of the catalyst components and that Cu<sup>0</sup> and especially Cu<sup>+</sup> are important in the active sites.[68]

Tada *et al.* investigated Ag-promotion of CuO/ZrO<sub>2</sub> catalysts. Addition of Ag decreased the methanol production rate by 0.3 % and CO<sub>2</sub> conversion by 1.6 % but increased methanol selectivity by 10 % and lowered the CO<sub>2</sub> activation energy. Further on, silver-doped catalysts exhibited highly methanol-selective active sites. Silver was described to cover parts of the copper surface area and it promoted CuO growing.[69]

Guo *et al.* tested the promotional effect of La-doping on Cu/ZrO<sub>2</sub> catalysts and they found that La-promotion leads to decreasing CuO and ZrO<sub>2</sub> particle size with increasing La content. La acted positively regarding the thermal stability of the catalyst because the dispersed La works as a thermal insulation. As La-defects formed in the

ZrO<sub>2</sub>-phase and La<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> was formed, crystallization and grain growth were hindered. Further, La increased the number of basic sites. In terms of catalytic activity, increasing La loading yielded in increasing methanol selectivity and a volcano-shaped CO<sub>2</sub> conversion.[70]

ZrO<sub>2</sub>-supported catalysts are believed to be more stable and selective than ZnO-supported catalysts. Further, the kind of zirconia[65] and the preparation method[68] used have a great impact on the catalytic performance. Liu *et al.* proposed deposition precipitation to be the most effective method.[64] ZrO<sub>2</sub>-support was stated to improve the reducibility of copper.[63] Both, B<sub>2</sub>O<sub>3</sub> and Ga<sub>2</sub>O<sub>3</sub>, were proven to increase the catalytic performance of ZrO<sub>2</sub>-supported catalysts when using a suitable preparation method.[68] Also La-promotion had a positive effect on the catalytic activity.[70] Whereas, Ag-promotion did not deliver satisfactory results.[69] ZnO in a ZrO<sub>2</sub>-supported catalyst did not influence the CO<sub>2</sub> conversion and methanol selectivity but promoted the space-time-yield of methanol.[67]

#### 2.1.4.6. Graphene-oxide-supported catalysts

Table 6 summarizes the research on graphene-oxide (GO)-supported catalysts.

Table 6: GO-supported catalysts for the hydrogenation of CO<sub>2</sub> to methanol with composition, preparation method (unless otherwise stated the used precursors were nitrates), reaction conditions (temperature [°C] and pressure [MPa]), feed composition, CO<sub>2</sub> conversion X<sub>CO<sub>2</sub></sub> [%], methanol selectivity S<sub>MeOH</sub> [%], methanol activity (=space-time-yield STY) [mol<sub>MeOH</sub>/kg<sub>cat</sub>/h] and reference.

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO<sub>2</sub></sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Zn-Zr-Cu/GO		35.1 Cu 26.8 Zn 36.7 Zr 1.4 GO	reverse co-precipitation	240 °C 2 MPa	1:3 (: 0.3 N <sub>2</sub> )	15.8	35	8.43	[71]
Zn-Cu/redGO	1 Cu 1 Zn	5 Cu-Zn	incipient wetness impregnation	250 °C 1.5 MPa	1:3	14	2.8	6.87	[72]
Zn-Cu/redGO	1 Cu 1 Zn	10 Cu-Zn	incipient wetness impregnation	250 °C 1.5 MPa	1:3	26	5.1	13.2 3	[72]
Zn-Cu/redGO	1 Cu 1 Zn	20 Cu-Zn	incipient wetness impregnation	250 °C 1.5 MPa	1:3	19	8.5	7.62	[72]
Zn-Cu/redGO	1 Cu 1 Zn	30 Cu-Zn	incipient wetness impregnation	250 °C 1.5 MPa	1:3	20	15.6	7.62	[72]
Zn-Zr-Al-Cu/redGO		4 CuO 3 ZnO 1.5 ZrO <sub>2</sub> 1.5 Al <sub>2</sub> O <sub>3</sub> 40 redGO	co-precipitation	240 °C 2 MPa	1:3	14.7	78	9.7	[73]



Witoon *et al.* did experiments with graphene-oxide-supported Cu-ZnO-ZrO<sub>2</sub> catalysts. In the hydrogenation of CO<sub>2</sub> catalysts with small amounts of graphene-oxide (GO) (0.5-2.5 wt%) showed an increased conversion of CO<sub>2</sub> compared to a GO-free CuO-ZnO-ZrO<sub>2</sub> catalyst whereas at higher GO contents (5 wt%) the CO<sub>2</sub> conversion decreased drastically. Regarding the space-time-yield, the catalyst containing 1 wt% GO delivered the best results. The space-time-yield showed a volcano-shaped temperature dependency with a maximum at 240 °C. A long term test utilizing the catalyst with 1 wt% GO revealed that a GO-support is favorable for the long-term stability concerning the space-time-yield of methanol, whereas the CO yield decreased with time due to sintering or partial oxidation of copper.[71]

Bimetallic Cu-Zn/reduced graphene-oxide (redGO) catalysts showed the highest activity when containing 10 wt% Cu-Zn. At higher concentrations a lower dispersion and agglomeration of the active metal was observed and the performance got poorer.[72]

A reduced graphene-oxide-supported CuO-ZnO-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst showed a higher surface area and a higher dispersion of CuO than a CuO-ZnO-ZrO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst. The reduced graphene-oxide-supported catalyst was stated to have a better interaction between active component and CO<sub>2</sub> indicating a better adsorption of CO<sub>2</sub>. Additionally, the amount of adsorbed H<sub>2</sub> was higher. As expected, the catalytic performance of the reduced graphene-oxide-supported catalyst was higher, in particular about 1.1-fold, than for the catalyst without graphene.[73]

GO was found to promote the interaction between the mixed metals (Cu, Zn, Zr) to make the hydrogen spillover easier which leads to a high methanol space-time-yield[71] and increases the surface area leading to a better reducibility of copper and a higher adsorption capacity.[73] Cu-Zn supported on reduced graphene-oxide showed a remarkably high methanol yield at a content of 10 wt% Cu-Zn.[72]

#### **2.1.4.7. TiO<sub>2</sub>-supported catalysts**

Table 7 lists the research on TiO<sub>2</sub>-supported catalysts.

Table 7: TiO<sub>2</sub>-supported catalysts for the hydrogenation of CO<sub>2</sub> to methanol with composition, preparation method (unless otherwise stated the used precursors were nitrates), reaction conditions (temperature [°C] and pressure [MPa]), feed composition, CO<sub>2</sub> conversion X<sub>CO<sub>2</sub></sub> [%], methanol selectivity S<sub>MeOH</sub> [%], methanol activity (=space-time-yield STY) [mol<sub>MeOH</sub>/kg<sub>cat</sub>/h] and reference.

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO<sub>2</sub></sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Zn-Ce-Cu/TiO <sub>2</sub> -nanotubes	6 Cu 3 Zn 1 Ce	10 TiO <sub>2</sub> nanotubes	deposition precipitation	260 °C 3 MPa	1:3 (:1 N <sub>2</sub> )	23.3	59.8	9.33	[74]
Cu/TiO <sub>2</sub>		10 Cu	impregnation	220 °C 3 MPa	1:3 (:0.5 N <sub>2</sub> )	4.3	29.8	-	[75]
Mg-Cu/TiO <sub>2</sub>		10 Cu 1 MgO	impregnation	220 °C 3 MPa	1:3 (:0.5 N <sub>2</sub> )	5.2	37.9	-	[75]
Mg-Cu/TiO <sub>2</sub>		10 Cu 5 MgO	impregnation	220 °C 3 MPa	1:3 (:0.5 N <sub>2</sub> )	2.6	55.5	-	[75]

Using TiO<sub>2</sub>-nanotubes as supporting material provided catalysts with an enhanced CuO dispersion and a higher copper surface area compared to an unsupported Cu-ZnO-CeO<sub>2</sub> catalyst. The catalytic performance of the TiO<sub>2</sub>-nanotubes-supported catalysts was increased showing a maximum at a TiO<sub>2</sub> content of 10 wt%. The only side product that could be detected was CO.[74]

TiO<sub>2</sub>-supported catalysts were examined by Liu *et al.* They concluded that the supplementation of a small quantity of MgO gives a higher CO<sub>2</sub> conversion. At a loading of 3 % MgO the CO<sub>2</sub> conversion decreased in comparison to a Cu/TiO<sub>2</sub> catalyst without MgO. The TOF declined with an increasing MgO content owing to a lower copper activity due to less interaction between CuO and TiO<sub>2</sub>. The selectivity of methanol had a volcano-shaped profile with respect to an increasing MgO content on account of the increasing strong basic sites. The maximal selectivity of 55.5 % was observed at a MgO loading of 5 %.[75]

#### 2.1.4.8. CeO<sub>2</sub>-supported catalysts

Table 8 outlines the research work on CeO<sub>2</sub>-supported catalysts.

Table 8: CeO<sub>2</sub>-supported catalysts for the hydrogenation of CO<sub>2</sub> to methanol with composition, preparation method (unless otherwise stated the used precursors were nitrates), reaction conditions (temperature [°C] and pressure [MPa]), feed composition, CO<sub>2</sub> conversion X<sub>CO<sub>2</sub></sub> [%], methanol selectivity S<sub>MeOH</sub> [%], methanol activity (=space-time-yield STY) [mol<sub>MeOH</sub>/kg<sub>cat</sub>/h] and reference.

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO<sub>2</sub></sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
ZnO-Cu/CeO <sub>2</sub>		43 CuO 14 ZnO 43 CeO <sub>2</sub>	reverse co-precipitation	240 °C 5 MPa	1:3 (:0.3 N <sub>2</sub> )	8.5	80	-	[66]
Cu/CeO <sub>2</sub>	1 Cu 1 Ce		deposition precipitation	300 °C 5 MPa	1:4	29	10	-	[76]
Cu/CeO <sub>2</sub>		10 Cu	precipitation	230 °C 3 MPa	1:3	3.5	65.6	0.48	[77]
Pd-Cu/CeO <sub>2</sub>		10 Cu 0.5 Pd	precipitation	230 °C 3 MPa	1:3 (: 0.5 N <sub>2</sub> )	5.5	48.7	0.52	[77]
Pd-Cu/CeO <sub>2</sub>		10 Cu 1 Pd	precipitation	230 °C 3 MPa	1:3 (: 0.5 N <sub>2</sub> )	14.8	29.0	0.87	[77]
Cu/CeO <sub>2</sub>	1 Cu 1 Ce		co-precipitation	300 °C 5 MPa	1:4	30	28	-	[76]
Cu/CeO <sub>2</sub> -nanotubes			impregnation	260 °C 3 MPa	1:3 (: 1 N <sub>2</sub> )	3.5	85	4.2	[78]
Ni-Cu/CeO <sub>2</sub> -nanotubes	1 Cu 1 Ni		impregnation	260 °C 3 MPa	1:3 (: 1 N <sub>2</sub> )	11.9	74	12.0	[78]
Ni-Cu/CeO <sub>2</sub> -nanotubes	1 Cu 2 Ni		impregnation	260 °C 3 MPa	1:3 (: 1 N <sub>2</sub> )	17.8	79	18.1	[78]

Two different preparation methods for CeO<sub>2</sub>-supports were compared by Sripada *et al.* The preparation method had an impact on the surface area, the porosity, the dispersion of the active component and on support properties like the surface composition. Deposition precipitation provided catalysts with a higher methanol yield but a lower selectivity than co-precipitation.[76]

Pd-promotion was examined on a Cu/CeO<sub>2</sub> catalyst. Experiments indicated that Pd-promotion increases the space-time-yield and CO<sub>2</sub> conversion but decreases the methanol selectivity. The promotional effect of the highly dispersed Pd was due to more active Cu sites. However, Pd did not make more active sites available. Pd-promotion led to a higher surface concentration of copper and a higher copper dispersion through a strong interaction between Cu and Pd which prevented from aggregation of the copper particles.[77]

Tan *et al.* tried bimetallic Cu-Ni supported on CeO<sub>2</sub>-nanotubes for hydrogenation of CO<sub>2</sub> to methanol. They discovered that with increasing Ni content the CO<sub>2</sub> conversion

as well as methanol space-time-yield were rising to a maximum at a Ni/(Cu+Ni) atomic ratio of 2/3, thereafter they decreased. The methanol selectivity for a Ni-free Cu/CeO<sub>2</sub> catalyst was 10 % higher than for the Cu-Ni/CeO<sub>2</sub> catalysts where it was almost stable on a level around 75 %. The authors spoke of a Cu-Ni synergy where Cu segregates to the surface and Ni stabilizes the reaction intermediates. CeO<sub>2</sub> was described to promote the adsorption and activation of CO<sub>2</sub> and to favor the dispersion and stabilization of the Cu-Ni alloy.[78]

As mentioned before, also for CeO<sub>2</sub>-supported catalysts it was claimed that the preparation method influences the obtained catalyst in terms of morphology, surface area and other catalyst properties. Therefore, the catalytic performance is depending on the preparation method used.[76] Unpromoted Cu supported on CeO<sub>2</sub>-nanotubes prepared by impregnation showed a high methanol selectivity of 85 %.[78] Ni- and Pd-doping had a promotional effect on the catalytic performance compared to an unpromoted Cu/CeO<sub>2</sub> catalyst.[77][78]

#### 2.1.4.9. ZnO-ZrO<sub>2</sub>-supported catalysts

Table 9 gives a summary on ZnO-ZrO<sub>2</sub>-supported catalysts.

Table 9: ZnO-ZrO<sub>2</sub>-supported catalysts for the hydrogenation of CO<sub>2</sub> to methanol with composition, preparation method (unless otherwise stated the used precursors were nitrates), reaction conditions (temperature [°C] and pressure [MPa]), feed composition, CO<sub>2</sub> conversion X<sub>CO<sub>2</sub></sub> [%], methanol selectivity S<sub>MeOH</sub> [%], methanol activity (=space-time-yield STY) [mol<sub>MeOH</sub>/kg<sub>cat</sub>/h] and reference.

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO<sub>2</sub></sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Cu/ZnO-ZrO <sub>2</sub>	0.5 Cu 0.2 Zn 0.3 Zr		impregnation-sol-gel auto-combustion	250 °C 3 MPa	1:3 (: 0.4 N <sub>2</sub> )	0.5	33.31	0.31	[57]
Cu/ZnO-ZrO <sub>2</sub>	0.5 Cu 0.2 Zn 0.3 Zr		glycine nitrate combustion	220 °C 3 MPa	1:3	12.0	71.1	-	[79]
Cu/ZnO-ZrO <sub>2</sub>	0.5 Cu 0.2 Zn 0.3 Zr		urea nitrate combustion	240 °C 3 MPa	1:3	14.9	56.8	-	[80]
Cu/ZnO-ZrO <sub>2</sub>	0.5 Cu 0.2 Zn 0.3 Zr		solid-state reaction (solvent-free)	240 °C 3 MPa	1:3	15.7	58.0	-	[81]
Cu/ZnO-ZrO <sub>2</sub>	6 Cu 3 Zn 1 Zr	57.1 CuO 28.1 ZnO 14.8 ZrO <sub>2</sub>	carbonate co-precipitation	180 °C 3 MPa	3:9 (:1 N <sub>2</sub> )	2.9	92.4	2.65	[82]
Cu/ZnO-ZrO <sub>2</sub>	6 Cu 3 Zn 1 Zr	57.1 CuO 28.1 ZnO 14.8 ZrO <sub>2</sub>	carbonate co-precipitation	240 °C 3 MPa	3:9 (:1 N <sub>2</sub> )	16.0	48.7	7.96	[82]
Cu/ZnO-ZrO <sub>2</sub>	6 Cu 3 Zn 1 Zr	56.4 CuO 27.7 ZnO 15.9 ZrO <sub>2</sub>	complexation by citric acid	180 °C 3 MPa	3:9 (:1 N <sub>2</sub> )	1.9	0	1.87	[82]

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO2</sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Cu/ZnO-ZrO <sub>2</sub>	6 Cu 3 Zn 1 Zr	56.4 CuO 27.7 ZnO 15.9 ZrO <sub>2</sub>	complexation by citric acid	240 °C 3 MPa	3:9 (:1 N <sub>2</sub> )	12.5	48.2	6.74	[82]
Cu/ZnO-ZrO <sub>2</sub>	6 Cu 3 Zn 1 Zr	56.8 CuO 27.7 ZnO 15.5 ZrO <sub>2</sub>	gel oxalate co-precipitation	180 °C 3 MPa	3:9 (:1 N <sub>2</sub> )	3.6	11.0	3.37	[82]
Cu/ZnO-ZrO <sub>2</sub>	6 Cu 3 Zn 1 Zr	56.8 CuO 27.7 ZnO 15.5 ZrO <sub>2</sub>	gel oxalate co-precipitation	240 °C 3 MPa	3:9 (:1 N <sub>2</sub> )	18.0	48.6	9.52	[82]
Cu/ZnO-ZrO <sub>2</sub>	2.0 Cu 73.5 Zn 24.5 Zr		co-precipitation	220 °C 8 MPa	1:3	2	92	1.25	[83]
Cu/ZnO-ZrO <sub>2</sub>	62.5 Cu 28.125 Zn 9.375 Zr		co-precipitation	220 °C 8 MPa	1:3	21	68	5.65	[83]
Cu/ZnO-ZrO <sub>2</sub>	6 Cu 3 Zn 1 Zr		co-precipitation	230 °C 5 MPa	1:3	16.7	54.7	-	[84]
Cu/ZnO-ZrO <sub>2</sub>	6 Cu 3 Zn 1 Zr		co-precipitation	270 °C 5 MPa	1:3	22.5	51.8	-	[84]
Cu/ZnO-ZrO <sub>2</sub>	6 Cu 3 Zn 1 Zr		precipitation-reduction with NaBH <sub>4</sub> (B/Cu=5)	230 °C 5 MPa	1:3	15.4	66.8	-	[84]
Cu/ZnO-ZrO <sub>2</sub>	6 Cu 3 Zn 1 Zr		precipitation-reduction with NaBH <sub>4</sub> (B/Cu=5)	270 °C 5 MPa	1:3	23.0	56.8	-	[84]
Cu/ZnO-ZrO <sub>2</sub>		4 Cu 3 ZnO 3 ZrO <sub>2</sub>	co-precipitation	230 °C 3 MPa	1:3	19.3	48.6	2.51	[85]
Cu/ZnO-ZrO <sub>2</sub>	41.8 Cu 30.6 Zn 27.6 Zr		reverse co-precipitation	240 °C 2 MPa	1:3 (: 0.3 N <sub>2</sub> )	3.8	32	9.99	[86]
Si-Cu/ZnO-ZrO <sub>2</sub>	41.8 Cu 30.9 Zn 27.3 Zr	1.15 SiO <sub>2</sub>	reverse co-precipitation	240 °C 2 MPa	1:3 (: 0.3 N <sub>2</sub> )	5.0	37	11.5 5	[86]
Cu/ZnO-ZrO <sub>2</sub>		5 CuO 3 ZnO 2 ZrO <sub>2</sub>	co-precipitation	230 °C 3 MPa	1:3	19.6	44.4	2.3	[87]
La-Cu/ZnO-ZrO <sub>2</sub>		5 CuO 3 ZnO 1.5 ZrO <sub>2</sub> 0.5 La <sub>2</sub> O <sub>3</sub>	co-precipitation	230 °C 3 MPa	1:3	20.5	49.8	2.7	[87]
Ce-Cu/ZnO-ZrO <sub>2</sub>		5 CuO 3 ZnO 1.5 ZrO <sub>2</sub> 0.5 CeO <sub>2</sub>	co-precipitation	230 °C 3 MPa	1:3	22.8	53.0	3.2	[87]
Nd-Cu/ZnO-ZrO <sub>2</sub>		5 CuO 3 ZnO 1.5 ZrO <sub>2</sub> 0.5 Nd <sub>2</sub> O <sub>3</sub>	co-precipitation	230 °C 3 MPa	1:3	19.0	40.5	2.0	[87]
Pr-Cu/ZnO-ZrO <sub>2</sub>		5 CuO 3 ZnO 1.5 ZrO <sub>2</sub> 0.5 Pr <sub>6</sub> O <sub>11</sub>	co-precipitation	230 °C 3 MPa	1:3	19.3	42.0	2.2	[87]
Cu/ZnO-ZrO <sub>2</sub>	5 Cu 2 Zn 3 Zr		co-precipitation	240 °C 3 MPa	1:3 (: 0.5 N <sub>2</sub> )	18.2	41.6	-	[88]
W-Cu/ZnO-ZrO <sub>2</sub>	5 Cu 2 Zn 2.8 Zr 0.2 W		co-precipitation	240 °C 3 MPa	1:3 (: 0.5 N <sub>2</sub> )	19.7	49.3	-	[88]
W-Cu/ZnO-ZrO <sub>2</sub>	5 Cu 2 Zn 1 Zr 2 W		co-precipitation	240 °C 3 MPa	1:3 (: 0.5 N <sub>2</sub> )	5.6	64.0	-	[88]

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO2</sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Cu/ZnO-ZrO <sub>2</sub>	5 Cu 2 Zn 2.5 Zr		co-precipitation	240 °C 3 MPa	1:3	18.2	41.6	-	[89]
Cr-Cu/ZnO-ZrO <sub>2</sub>	5 Cu 2 Zn 2.5 Zr 0.5 Cr		co-precipitation	240 °C 3 MPa	1:3	18.1	40.0	-	[89]
Mo-Cu/ZnO-ZrO <sub>2</sub>	5 Cu 2 Zn 2.5 Zr 0.5 Mo		co-precipitation	240 °C 3 MPa	1:3	19.0	46.7	-	[89]
W-Cu/ZnO-ZrO <sub>2</sub>	5 Cu 2 Zn 2.5 Zr 0.5 W		co-precipitation	240 °C 3 MPa	1:3	19.4	47.8	-	[89]
Cu/ZnO-ZrO <sub>2</sub>		65 CuO 23 ZnO 12 ZrO <sub>2</sub>	co-precipitation	220 °C 8 MPa	1:3	-	68	5.62	[90]
Ga-Cu/ZnO-ZrO <sub>2</sub>		65 CuO 23 ZnO 9 ZrO <sub>2</sub> 3 Ga <sub>2</sub> O <sub>3</sub>	co-precipitation	220 °C 8 MPa	1:3	-	-	6.55	[90]
Mn-Cu/ZnO-ZrO <sub>2</sub>		65 CuO 23 ZnO 9 ZrO <sub>2</sub> 3 MnO	co-precipitation	220 °C 8 MPa	1:3	-	66	4.68	[90]
B-Cu/ZnO-ZrO <sub>2</sub>		65 CuO 23 ZnO 9 ZrO <sub>2</sub> 3 B <sub>2</sub> O <sub>3</sub>	co-precipitation	220 °C 8 MPa	1:3	-	-	5.31	[90]
In-Cu/ZnO-ZrO <sub>2</sub>		65 CuO 23 ZnO 9 ZrO <sub>2</sub> 3 In <sub>2</sub> O <sub>3</sub>	co-precipitation	220 °C 8 MPa	1:3	-	-	0.78	[90]
Gd-Cu/ZnO-ZrO <sub>2</sub>		65 CuO 23 ZnO 9 ZrO <sub>2</sub> 3 Gd <sub>2</sub> O <sub>3</sub>	co-precipitation	220 °C 8 MPa	1:3	-	-	4.84	[90]
Y-Cu/ZnO-ZrO <sub>2</sub>		65 Cu 23 ZnO 9 ZrO <sub>2</sub> 3 Y <sub>2</sub> O <sub>3</sub>	co-precipitation	220 °C 8 MPa	1:3	-	62	5.77	[90]
Cu/ZnO-ZrO <sub>2</sub>		65 CuO 23 ZnO 12 ZrO <sub>2</sub>	complexation with citric acid	220 °C 8 MPa	1:3	-	-	3.43	[90]
Ga-Cu/ZnO-ZrO <sub>2</sub>		65 CuO 23 ZnO 9 ZrO <sub>2</sub> 3 Ga <sub>2</sub> O <sub>3</sub>	complexation with citric acid	220 °C 8 MPa	1:3	-	70	6.55	[90]
Mg-Cu/ZnO-ZrO <sub>2</sub>		65 CuO 23 ZnO 9 ZrO <sub>2</sub> 3 MgO	complexation with citric acid	220 °C 8 MPa	1:3	-	63	2.81	[90]
Mn-Cu/ZnO-ZrO <sub>2</sub>		65 CuO 23 ZnO 9 ZrO <sub>2</sub> 3 MnO	complexation with citric acid	220 °C 8 MPa	1:3	-	67	4,84	[90]
Cu/ZnO-ZrO <sub>2</sub>		62.4 CuO 25.0 ZnO 12.6 ZrO <sub>2</sub>	thermal decomposition of citrates	220 °C 8 MPa	1:3	-	88	3.00	[91]
Mn-Cu/ZnO-ZrO <sub>2</sub>		65.8 CuO 26.6 ZnO 5.6 ZrO <sub>2</sub> 2 MnO	thermal decomposition of citrates	220 °C 8 MPa	1:3	-	91	4.31	[91]

A Cu/ZnO-ZrO<sub>2</sub> catalyst was prepared by glycine nitrate combustion. The glycine amount used during the preparation highly influenced the formation of the zirconia phases in a volcano-shaped form regarding the m-ZrO<sub>2</sub>/t-ZrO<sub>2</sub> ratio. It was stated that m-ZrO<sub>2</sub> has a higher catalytic activity than t-ZrO<sub>2</sub> with the same surface area and copper dispersion.[79]

The same was done with urea nitrate combustion, showing also a volcano-shaped form of the m-ZrO<sub>2</sub>/t-ZrO<sub>2</sub> ratio with increasing urea amount. The catalyst prepared by urea nitrate combustion had a higher catalytic activity compared to catalysts with the same compositions which were prepared using other methods, such as oxalic co-precipitation and Na<sub>2</sub>CO<sub>3</sub> co-precipitation, which could be explained by the better interaction between ZnO, ZrO<sub>2</sub> and copper after the short high temperature exposure during the combustion.[80]

The performance of Cu/ZnO-ZrO<sub>2</sub> catalysts was tested by Guo *et al.* The calcination temperature during the preparation affected the copper dispersion and simultaneously the CO<sub>2</sub> conversion so that it decreased at high calcination temperatures. Best results were obtained at a calcination temperature of 400 °C.[81]

Bonura *et al.* noticed a 5.5-times higher CO<sub>2</sub> conversion and 1.9-times lower methanol selectivity at high reaction temperatures because of favoring of the endothermic reverse water-gas shift reaction. Additionally, they investigated the influence of the preparation method on the catalytic performance. The catalyst prepared by complexation with citric acid turned out to perform worst in terms of CO<sub>2</sub> conversion and methanol selectivity due to the higher activation energy of the catalyst. In contrast to that, catalysts prepared by co-precipitation exhibited lower activation energies and easier reactivity of the adsorbed CO<sub>2</sub> in consequence of the lower particle size. The catalyst prepared *via* gel oxalate co-precipitation acted better regarding CO<sub>2</sub> conversion and space-time-yield compared to conventional co-precipitated catalysts. In addition to that, it was stated that there is a correlation between CO<sub>2</sub> conversion and methanol selectivity, particularly a high methanol selectivity is connected to a low CO<sub>2</sub> conversion and vice versa.[82]

Experiments using Cu/ZnO-ZrO<sub>2</sub> catalysts with varying copper content showed that the metal dispersion gets worse with increasing metal content due to a larger grain size. The catalytic activity decreased with increasing metal content regarding moles of

methanol produced by moles of copper in a certain time whereas the moles of methanol produced per kg catalyst and time unit increased. The adsorption of CO<sub>2</sub> on the catalyst was promoted by stabilized Cu<sup>+</sup> ions on the ZnO and ZrO<sub>2</sub> surface, respectively.[83]

The already discussed effect of reaction temperature was also proven by Dong *et al.* The often-used co-precipitation method for catalyst preparation was compared to a precipitation-reduction method using NaBH<sub>4</sub>. The precipitation-reduction method was evaluated to be advantageous considering methanol selectivity and space-time-yield. The Cu<sup>0</sup>/Cu<sup>+</sup> ratio had a volcano shaped curve with varying B/Cu molecular ratio and was presumed to influence the catalytic performance because it showed a relation to the space-time-yield.[84]

Phongamwong *et al.* investigated the promotional effect of SiO<sub>2</sub>-addition on Cu/ZnO-ZrO<sub>2</sub> catalysts. With increasing SiO<sub>2</sub> content the CuO crystal size decreased. The catalyst containing 1.15 wt% SiO<sub>2</sub> showed the best catalytic performance. When silica content got greater than 2.5 wt% the catalytic activity decreased due to segregation of silica particles. Addition of SiO<sub>2</sub> led to a higher long term stability.[86]

Rare-earth elements promoted Cu/ZnO/ZrO<sub>2</sub> catalysts performed differently. While La and Ce enhanced methanol selectivity and CO<sub>2</sub> conversion, Nd and Pr suppressed the hydrogenation reaction.[87]

Wang *et al.* tested various Cu/ZnO-ZrO<sub>2</sub> catalysts. The results indicated enhanced stability, CO<sub>2</sub> conversion and methanol selectivity for catalysts containing a small amount of WO<sub>3</sub>, like 2 or 5 mol%, due to a higher surface area and reducibility of the catalyst and a better copper dispersion. However, a high amount of WO<sub>3</sub> (20 mol%) led to a very low CO<sub>2</sub> conversion due to aggregation of the copper particles and coverage of the active copper by WO<sub>3</sub>. However noteworthy is the highly improved methanol selectivity which reached 64 %.[88]

Doping with Cr<sub>2</sub>O<sub>3</sub> led to a slightly lower catalytic activity, namely a 0.1 % lower CO<sub>2</sub> conversion and a 1.6 % lower methanol selectivity, compared to an unmodified Cu/ZnO-ZrO<sub>2</sub> catalyst because of less dispersion of the active components. MoO<sub>3</sub>- and WO<sub>3</sub>-doping had the opposite effect on the catalyst performance where WO<sub>3</sub>-promotion showed the best results with 19.4 % CO<sub>2</sub> conversion and 47.8 % CH<sub>3</sub>OH selectivity.[89]



Słoczyński *et al.* did an extensive study on the influence of various oxide additives on the catalytic performance of Cu/ZnO-ZrO<sub>2</sub> catalysts. Addition of Ga<sub>2</sub>O<sub>3</sub> led to the highest dispersion of CuO and ZnO and to a very positive effect on the catalytic performance. At first MnO and B<sub>2</sub>O<sub>3</sub> showed a high CuO dispersion but the catalyst tended to sintering. Indium oxide had a negative effect on the activity of the catalyst.[90]

A comparison of a CuO/ZnO-ZrO<sub>2</sub> catalyst with a Mn-promoted one showed that Mn-promotion is effective in terms of methanol yield and selectivity. Zirconium was stated to have a positive effect on the activity. Both catalysts did not produce higher alcohols or methane. The methanol yield did increase significantly with elevated pressure.[91]

In the Cu/ZnO-ZrO<sub>2</sub> system m-ZrO<sub>2</sub> was stated to have a higher catalytic activity than t-ZrO<sub>2</sub>. [79][80] This statement is contradictory to the proposal of Witoon *et al.* where t-ZrO<sub>2</sub> showed a higher activity in ZrO<sub>2</sub>-supported catalysts.[65] As it was already stated for other catalytic systems, the preparation method has a great impact on the activity as it influences the structure and properties of the catalyst. Best methanol yields were obtained using gel-oxalate co-precipitation, followed by carbonate co-precipitation which is the most used method. Unsatisfactory results were obtained by complexation with citric acid.[82] Precipitation-reduction delivered better results than conventional carbonate co-precipitation. The amount of NaBH<sub>4</sub> used for precipitation-reduction was another influencing factor regarding the catalytic performance.[84] It was found that the calcination temperature has a strong influence on the catalytic performance when using a solvent-free solid-state-reaction as preparation method.[81] Further, the copper content was proposed to be an important factor for catalytic activity. A high copper content results in a decreased activity concerning the methanol formation rate per mole of copper due to larger copper particles and a decreased copper dispersion.[83] Si-doping had a positive effect on Cu/ZnO-ZrO<sub>2</sub> systems in terms of stability and catalytic performance because it led to a better dispersion of the metal oxides.[86] La, Ce, Mo, W, Mn and Ga were found to be promoters in the CO<sub>2</sub> hydrogenation to methanol, whereas Nd, Pr, Cr and In are suppressors for this reaction.[87][89][90][91] Addition of a suitable amount of WO<sub>3</sub> was found to give stable catalysts with better catalytic performance than MoO<sub>3</sub>. [88][89]

### 2.1.4.10. ZnO-Al<sub>2</sub>O<sub>3</sub>-supported catalysts

Table 10 presents an overview on ZnO-Al<sub>2</sub>O<sub>3</sub>-supported catalysts.

Table 10: ZnO-Al<sub>2</sub>O<sub>3</sub>-supported catalysts for the hydrogenation of CO<sub>2</sub> to methanol with composition, preparation method (unless otherwise stated the used precursors were nitrates), reaction conditions (temperature [°C] and pressure [MPa]), feed composition, CO<sub>2</sub> conversion  $X_{CO_2}$  [%], methanol selectivity  $S_{MeOH}$  [%], methanol activity (=space-time-yield STY) [ $mol_{MeOH}/kg_{cat}/h$ ] and reference.

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	$X_{CO_2}$	$S_{MeOH}$	STY	Ref
	molar ratio	weight percent							
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>		67.5 CuO 25 ZnO 7.5 Al <sub>2</sub> O <sub>3</sub>	co-precipitation	250 °C 5 MPa	1:8 (:1 CO)	15.5 8	99.81	17.7 5	[54]
In <sub>2</sub> O <sub>3</sub> -Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>		67.5 CuO 25 ZnO 5 Al <sub>2</sub> O <sub>3</sub> 2.5 In <sub>2</sub> O <sub>3</sub>	co-precipitation	250 °C 5 MPa	1:8 (:1 CO)	15.2 4	99.34	14.9 7	[54]
In <sub>2</sub> O <sub>3</sub> -Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>		67.5 CuO 25 ZnO 2.5 Al <sub>2</sub> O <sub>3</sub> 5 In <sub>2</sub> O <sub>3</sub>	co-precipitation	250 °C 5 MPa	1:8 (:1 CO)	14.9 8	99.72	8.98	[54]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>		40 Cu	commercial	250 °C 4.1 MPa	24:72 (:4 Ar)	18.4	27	0.17	[60]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>		35 CuO 33 ZnO 32 Al <sub>2</sub> O <sub>3</sub>	commercial	240 °C 5 MPa	1:3 (:0.3 N <sub>2</sub> )	19.5	61	-	[66]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>		4 Cu 3 ZnO 3 Al <sub>2</sub> O <sub>3</sub>	co-precipitation	230 °C 3MPa	1:3	18.7	43.0	2.15	[85]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	6 Cu 2.5 Zn 1.5 Al Citric acid/salt=0.5		mechanical milling and direct combustion with citric acid (solvent-free)	240 °C 3 MPa	1:3	5.6	62.3	1.40	[92]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	6 Cu 2.5 Zn 1.5 Al Citric acid/salt=0.75		mechanical milling and direct combustion with citric acid (solvent-free)	240 °C 3 MPa	1:3	8.9	62.9	2.25	[92]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	6 Cu 2.5 Zn 1.5 Al Citric acid/salt=1		mechanical milling and direct combustion with citric acid (solvent-free)	240 °C 3 MPa	1:3	14.6	63.6	3.75	[92]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	6 Cu 2.5 Zn 1.5 Al Citric acid/salt=1.25		mechanical milling and direct combustion with citric acid (solvent-free)	240 °C 3 MPa	1:3	16.2	83.8	4.06	[92]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	6 Cu 2.5 Zn 1.5 Al oxalic acid/salt=1		mechanical milling and direct combustion with oxalic acid (solvent-free)	240 °C 3 MPa	1:3	12.1	42.6	3.12	[92]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	6 Cu 2.5 Zn 1.5 Al urea/salt=1		mechanical milling and direct combustion with urea (solvent-free)	240 °C 3 MPa	1:3	3.2	53.9	0.69	[92]

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO2</sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	6 Cu 2.5 Zn 1.5 Al		carbonate co-precipitation	240 °C 3 MPa	1:3	8.1	63.3	2.06	[92]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	45 Cu 45 Zn 10 Al		gel-network co-precipitation	240 °C 2 MPa	1:3	20.1	31.3	-	[93]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	45 Cu 45 Zn 10 Al		oxalate co-precipitation	240 °C 2 MPa	1:3	19.3	22.3	-	[93]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	45 Cu 45 Zn 10 Al		carbonate co-precipitation	240 °C 2 MPa	1:3	15.8	22.8	-	[93]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	2 Cu 1 Zn 1 Al		co-precipitation (precursor: HTIs)	230 °C 5 MPa	1:3	12.5	50.3	-	[94]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	2 Cu 1 Zn 1 Al		co-precipitation (precursor: HTIs)	270 °C 5 MPa	1:3	23.8	39.8	-	[94]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>		5 CuO 4 ZnO 1 Al <sub>2</sub> O <sub>3</sub>	co-precipitation	260 °C 2.6 MPa	1:3	15.8 1	23.32	-	[95]
Si-Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>		5 CuO 4 ZnO 1 Al <sub>2</sub> O <sub>3</sub> 0.02 SiO <sub>2</sub>	co-precipitation	260 °C 2.6 MPa	1:3	20.2 4	27.15	-	[95]
Ti-Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>		5 CuO 4 ZnO 1 Al <sub>2</sub> O <sub>3</sub> 0.02 TiO <sub>2</sub>	co-precipitation	260 °C 2.6 MPa	1:3	16.1 0	25.29	-	[95]
Si-Ti-Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>		5 CuO 4 ZnO 1 Al <sub>2</sub> O <sub>3</sub> 0.01 SiO <sub>2</sub> 0.01 TiO <sub>2</sub>	co-precipitation	260 °C 2.6 MPa	1:3	40.7 0	41.17	-	[95]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	50 Cu 25 Zn 25 Al		co-precipitation <i>via</i> HTIs	250 °C 5 MPa	1:3	19.7	39.7	10.6 1	[96]
Mn-Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	50 Cu 25 Zn 22.5 Al 2.5 Mn		co-precipitation <i>via</i> HTIs	250 °C 5 MPa	1:3	22.3	43.0	13.1 1	[96]
La-Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	50 Cu 25 Zn 22.5 Al 2.5 La		co-precipitation <i>via</i> HTIs	250 °C 5 MPa	1:3	23.3	43.8	13.7 3	[96]
Ce-Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	50 Cu 25 Zn 22.5 Al 2.5 Ce		co-precipitation <i>via</i> HTIs	250 °C 5 MPa	1:3	23.6	45.9	14.0 4	[96]
Zr-Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	50 Cu 25 Zn 22.5 Al 2.5 Zr		co-precipitation <i>via</i> HTIs	250 °C 5 MPa	1:3	24.7	58.0	15.2 9	[96]
Y-Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	50 Cu 25 Zn 22.5 Al 2.5 Y		co-precipitation <i>via</i> HTIs	250 °C 5 MPa	1:3	26.9	47.1	16.2 3	[96]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	55 Cu 30 Zn 15 Al		co-precipitation	200 °C 4 MPa	1:3	3.9	90	8	[97]
Pd-Cu/ZnO-Al <sub>2</sub> O <sub>3</sub>	55 Cu 30 Zn 15 Al	4 Pd	co-precipitation and impregnation of Pd	200 °C 4 MPa	1:3	3.0	95	7	[97]

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO2</sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
<b>Pd-Cu/ZnO-Al<sub>2</sub>O<sub>3</sub></b>	55 Cu 30 Zn 15 Al	10 Pd	co-precipitation and impregnation of Pd	200 °C 4 MPa	1:3	2.2	93	4	[97]
<b>Cu/ZnO-Al<sub>2</sub>O<sub>3</sub></b>	2 Cu 1 Zn 1 Al		co-precipitation (precursor: HTIs)	270 °C 5 MPa	1:3	23.8	39.8	-	[98]
<b>F-Cu/ZnO-Al<sub>2</sub>O<sub>3</sub></b>	2 Cu 1 Zn 1 Al 0.1 F		co-precipitation (precursor: HTIs)	270 °C 5 MPa	1:3	23.7	43.7	-	[98]

Despite addition of In<sub>2</sub>O<sub>3</sub> to a Cu/ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst resulted in a higher copper surface area, the catalytic activity did not increase compared to a catalyst without In<sub>2</sub>O<sub>3</sub>. This may be explained by the strong adsorption of CO<sub>2</sub>. However, the stability of the catalyst was enhanced when containing In<sub>2</sub>O<sub>3</sub>. [54]

Using a Cu/ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst prepared by solvent-free mechanical milling and direct combustion Lei *et al.* determined only methanol and CO as products. Different fuels were tested where citric acid turned out to deliver catalysts with the highest activity, followed by oxalic acid. Urea delivered the lowest performance. When comparing different fuel to salt atomic ratios using citric acid as fuel the ratio 1 showed the best performance, probably due to smaller CuO particles and a larger Cu surface. [92]

Gel-network co-precipitation was contrasted to oxalate and carbonate co-precipitation. The gel-network co-precipitation method generated smaller particles, a higher copper dispersion and a higher surface area than the other two methods. As expected from these parameters, also the catalytic activity and performance was higher for the gel-network co-precipitated catalysts with the same composition as the oxalate and carbonate co-precipitated catalysts. In particular a carbon dioxide conversion of 20.1 % and a methanol selectivity of 31.3 % could be reached. More precisely, the oxalate method led to a higher CO<sub>2</sub> conversion as the carbonate method, whereas the methanol selectivity was similar. A 100 h on-stream test showed that using the gel-network method generated a more stable catalyst. [93]

The promotional effect of SiO<sub>2</sub> and TiO<sub>2</sub> on a Cu/ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst was investigated by Zhang *et al.* They provided data of the catalytic activity which shows that SiO<sub>2</sub> has a better effect on the catalytic performance than TiO<sub>2</sub>. Moreover, promotion with both,

SiO<sub>2</sub> and TiO<sub>2</sub>, led to the best results. All promoters did improve the CuO and ZnO dispersion in the catalyst and hence, enhanced the surface area and interaction between CuO and ZnO which is accountable for the higher catalytic activity.[95]

Cu/ZnO-Al<sub>2</sub>O<sub>3</sub> catalysts with different modifiers were checked for their performance in CO<sub>2</sub> hydrogenation to methanol. The CO<sub>2</sub> conversion and methanol selectivity of Cu/ZnO-Al<sub>2</sub>O<sub>3</sub> catalysts could be significantly improved by addition of modifiers such as Mn, La, Ce, Zr and Y. All modifiers obtained a higher copper surface area, metal dispersion and amount of basic sites, especially Zr and Y performed very good.[96]

The effect of Pd-promotion was tested on Cu/ZnO-Al<sub>2</sub>O<sub>3</sub> catalysts. Pd-doping was stated to decrease the copper dispersion and the exposed copper area due to coverage of copper by palladium or the formation of a Pd-Cu alloy and leads to smaller copper particles. Catalysts containing Pd had a lower methanol yield. Moreover, with increasing Pd content the catalytic activity was decreasing. For that, Melián-Cabrera *et al.* assumed that Pd has no promotional effect on Cu/ZnO-Al<sub>2</sub>O<sub>3</sub> catalysts. But measuring the intrinsic methanol yield per mole of exposed copper showed a promoting effect of Pd. The authors could not exactly qualify this intrinsic promotional effect because palladium interferes in N<sub>2</sub>O chemisorption experiments, where the exposed copper surface is determined.[97]

Gao *et al.* investigated the influence of fluorine modification on Cu/ZnO-Al<sub>2</sub>O<sub>3</sub> catalysts. The CO<sub>2</sub> conversion was slightly lower (0.1 %) for the fluorine modified catalyst due to the smaller exposed copper surface area, whereas the TOF, methanol selectivity and yield were higher for this catalyst. The methanol selectivity was stated to be dependent on the basic sites, namely strongly basic sites favor methanol production.[98]

As the preparation method is an important parameter for the catalytic activity, a combustion method with different fuels and different amounts of fuel was tested. Activity tests showed the following results: citric acid > oxalic acid > urea. The activity increased with increasing amount of citric acid.[92] Different co-precipitation methods were compared giving results that showed the following activity: gel-network co-precipitation > oxalate co-precipitation > carbonate co-precipitation.[93] Compared to the combustion method, all co-precipitation methods had a fairly lower methanol selectivity. SiO<sub>2</sub> and TiO<sub>2</sub> promoted the hydrogenation of CO<sub>2</sub> to methanol, where SiO<sub>2</sub> was the better promoter. A combination of SiO<sub>2</sub> and TiO<sub>2</sub> strongly enhanced the

catalytic performance.[95] Other promoters were Mn, La, Ce, Zr and Y. Regarding the space-time-yield of methanol and the CO<sub>2</sub> conversion the promotional effect was: Y > Zr > Ce > La > Mn. The only difference in this order regarding the methanol selectivity was that Zr showed a higher selectivity than Y.[96] In<sub>2</sub>O<sub>3</sub>-doping had promotional effects on the catalyst structure but it lowered the catalytic activity.[54] F-modification decreased the CO<sub>2</sub> conversion but elevated the methanol selectivity and yield.[98] Pd-promotion was stated to lower the catalytic activity but the intrinsic methanol yield enhanced.[97] Remarkably, all catalysts, Pd-promoted, In<sub>2</sub>O<sub>3</sub>-promoted and unpromoted, tested by Melián-Cabrera *et al.*[97] and Sadeghinia *et al.*[54] showed a very high methanol selectivity above 90 % compared to all other Cu/ZnO-Al<sub>2</sub>O<sub>3</sub> catalysts mentioned before which mostly show a selectivity in the range of 20-65 %.

#### 2.1.4.11. ZnO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-supported catalysts

Table 11 provides a summary of ZnO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-supported catalysts.

Table 11: ZnO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-supported catalysts for the hydrogenation of CO<sub>2</sub> to methanol with composition, preparation method (unless otherwise stated the used precursors were nitrates), reaction conditions (temperature [°C] and pressure [MPa]), feed composition, CO<sub>2</sub> conversion X<sub>CO<sub>2</sub></sub> [%], methanol selectivity S<sub>MeOH</sub> [%], methanol activity (=space-time-yield STY) [mol<sub>MeOH</sub>/kg<sub>cat</sub>/h] and reference.

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO<sub>2</sub></sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>		4 CuO 3 ZnO 1.5 ZrO <sub>2</sub> 1.5 Al <sub>2</sub> O <sub>3</sub>	co-precipitation	240 °C 2 MPa	1:3	13.2	72	8.2	[73]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>		4 Cu 3 ZnO 1.5 Al <sub>2</sub> O <sub>3</sub> 1.5 ZrO <sub>2</sub>	co-precipitation	230 °C 3 MPa	1:3	23.2	60.3	3.75	[85]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	2 Cu 1 Zn 0.7 Al 0.3 Zr		co-precipitation (precursor: HTIs)	230 °C 5 MPa	1:3	15.5	54.5	-	[94]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	2 Cu 1 Zn 0.7 Al 0.3 Zr		co-precipitation (precursor: HTIs)	270 °C 5 MPa	1:3	26.6	43.1	-	[94]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	2 Cu 1 Zn 0.3 Al 0.7 Zr		co-precipitation (precursor: HTIs)	230 °C 5 MPa	1:3	8.6	41.7	-	[94]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	2 Cu 1 Zn 0.3 Al 0.7 Zr		co-precipitation (precursor: HTIs)	270 °C 5 MPa	1:3	20.9	31.4	-	[94]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	6 Cu 3 Zn 0.7 Al 0.3 Zr		co-precipitation (precursor: HT containing)	250 °C 5 MPa	1:3	23.9	55.0	-	[99]

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO2</sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	9 Cu 3 Zn 0.7 Al 0.3 Zr		co-precipitation (precursor: HT containing)	250 °C 5 MPa	1:3	22.1	51.6	-	[99]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	6 Cu 3 Zn 0.7 Al 0.3 Zr		co-precipitation (precursor: phase-pure HTIs)	250 °C 5 MPa	1:3	21.2	48.8	-	[99]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	6 Cu 3 Zn 0.7 Al 0.3 Zr		co-precipitation (precursor: rosasite)	250 °C 5 MPa	1:3	23.0	52.5	-	[99]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	2 Cu 1 Zn 0.6 Al 0.1 Zr		co-precipitation (precursor: HTIs)	250 °C 5 MPa	24:73 (:3 N <sub>2</sub> )	23.0	47.6	4.37	[100]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	2 Cu 1 Zn 0.9 Al 0.1 Zr		co-precipitation (precursor: HTIs)	250 °C 5 MPa	24:73 (:3 N <sub>2</sub> )	24.1	55.7	5.93	[100]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	2 Cu 1 Zn 1.2 Al 0.1 Zr		co-precipitation (precursor: HTIs)	250 °C 5 MPa	24:73 (:3 N <sub>2</sub> )	25.6	61.3	8.74	[100]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	2 Cu 1 Zn 1.5 Al 0.1 Zr		co-precipitation (precursor: HTIs)	250 °C 5 MPa	24:73 (:3 N <sub>2</sub> )	23.8	56.9	5.93	[100]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	6 Cu 3 Zn 5 Al 5 Zr		co-precipitation	240 °C 4 MPa	1:3	20.5 1	61.01	-	[101]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>			commercial	240 °C 4 MPa	1:3	16.2 5	42.61	-	[101]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	2 Cu 1 Zn 0.92 Al 0.08 Zr		co-precipitation (precursor: HTIs)	250 °C 5 MPa	1:3	21.9	45.3	12.1 7	[102]
Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	2 Cu 1 Zn 0.76 Al 0.24 Zr		co-precipitation (precursor: HTIs)	250 °C 5 MPa	1:3	22.5	46.9	12.8 0	[102]
F-Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	2 Cu 1 Zn 0.92 Al 0.08 Zr	0.77 F	co-precipitation (precursor: HTIs)	250 °C 5 MPa	1:3	20.5	52.3	13.4 2	[102]
F-Cu/ZnO-Al <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	2 Cu 1 Zn 0.76 Al 0.24 Zr	0.59 F	co-precipitation (precursor: HTIs)	250 °C 5 MPa	1:3	21.1	53.5	13.7 3	[102]

Cu/ZnO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalysts showed a maximum in CO<sub>2</sub> conversion as well as CH<sub>3</sub>OH selectivity with varying zirconia content. The opposite, namely a minimum, happened for CO selectivity. With increasing Zr<sup>4+</sup>/(Al<sup>3+</sup>+Zr<sup>4+</sup>) atomic ratio a maximum in Cu surface area and Cu dispersion was demonstrated. Best results were obtained using an atomic ratio of 0.3.[94]

Gao *et al.* found besides methanol also carbon monoxide, water and small amounts of methane and higher hydrocarbons as by-products. With increasing copper content of the Cu/ZnO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalysts they found a maximum of CO<sub>2</sub> conversion, methanol selectivity as well as methanol yield at a copper content of 55 wt%. The decrease after the maximum was referred to a coverage of the active centers with unreducible Cu<sup>2+</sup>. The catalytic performance of a catalyst prepared with a hydrotalcite-containing precursor was better than that of catalysts prepared with a phase-pure HTI precursor having a general formula of [M<sup>2+</sup><sub>1-x</sub>M<sup>3+</sup><sub>x</sub>(OH)<sub>2</sub>]<sup>x+</sup>(A<sup>n-</sup>)<sub>x/n</sub>·mH<sub>2</sub>O or with a rosasite precursor.[99]

Gao *et al.* declared that when using a Cu/ZnO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst for CO<sub>2</sub> hydrogenation the maximum CO<sub>2</sub> conversion, methanol selectivity and yield can be achieved for an Al content of 1.2 relative to the Zn content (Cu<sup>2+</sup>/Zn<sup>2+</sup>/Al<sup>3+</sup>/Zr<sup>4+</sup> = 2/1/1.2/0.1). The amount of copper surface played an important role in the activity of the catalyst. Further the effect of the reaction temperature was tested. The results indicated that with increasing reaction temperature from 170 to 310 °C the methanol selectivity decreased from 86 to 26 %, the CO<sub>2</sub> conversion increased from 5 to 32 % and the methanol yield raised to a maximum of 8.74 mol<sub>MeOH</sub>/kg<sub>cat</sub>/h at 250 °C thereafter it decreased again. Additionally, the impact of elevating reaction pressure was checked in the range of 1 to 9 MPa, emerging that all three performance parameters mentioned above increased but it was mentioned that too high pressures require better equipment and is a safety problem.[100]

A fibrous Cu/ZnO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalyst was compared to a commercial one. The catalytic activity of the fibrous catalyst was higher than that of the commercial catalyst. Further, the catalyst stability was tested by exposing the catalysts at 400 °C for 3 h as Cu tends to sinter at high temperatures. The fibrous catalyst showed a very good thermal stability compared to the commercial catalyst.[101]

Fluorine-modification had an impact on the properties of Cu/ZnO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalysts. While the copper surface area was decreased, the proportion of strongly basic sites was increased. Therefore, these catalysts obtained marginally lower (about 6 %) carbon dioxide conversions but CH<sub>3</sub>OH selectivity and yield increased significantly (about 15 and 10 %, respectively) compared to catalysts without fluorine.[102]



Cu/ZnO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> had a high thermal stability[101] and produced also CO, water, methane and higher hydrocarbons besides methanol. The copper content which delivered the best results was 55 wt% with a Cu<sup>2+</sup>/Zn<sup>2+</sup> ratio of 2.[99] Some authors stated that the Zr content in Cu/ZnO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalysts was ideal at a Zr<sup>4+</sup>/(Al<sup>3+</sup>+Zr<sup>4+</sup>) ratio of 0.3.[94] While others proposed the optimal Al content to be 27.9 mol%[100] and the best Zr content to be 5 mol%.[101] F-promotion led to a slightly lower CO<sub>2</sub> conversion but increased the methanol selectivity and yield.[102]

### 2.1.4.12. Others

Table 12 contains research work on copper-based catalysts in compositions that were not mentioned yet.

Table 12: Other catalysts for the hydrogenation of CO<sub>2</sub> to methanol with composition, preparation method (unless otherwise stated the used precursors were nitrates), reaction conditions (temperature [°C] and pressure [MPa]), feed composition, CO<sub>2</sub> conversion X<sub>CO<sub>2</sub></sub> [%], methanol selectivity S<sub>MeOH</sub> [%], methanol activity (=space-time-yield STY) [mol<sub>MeOH</sub>/kg<sub>cat</sub>/h] and reference.

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO<sub>2</sub></sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Cu/MnO	6 Cu 1.5 Mn		citric acid impregnation	180 °C 4 MPa	1:3	1.8	98.8	11.8	[59]
Cu/Ga <sub>2</sub> O <sub>3</sub>		2 Cu	impregnation	250 °C 3 MPa	22:75 (:3 He)	1.09	58	2.6	[63]
Cu/Ga <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>		2 Cu 6 Ga	ion-exchange	250 °C 3 MPa	22:75 (:3 He)	1.05	72	4.0	[63]
Cu/Ga <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>		2 Cu 6 Ga	ion-exchange + additional drying	250 °C 3 MPa	22:75 (:3 He)	0.65	75	2.6	[63]
Cu/Ga <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>		2 Cu 6 Ga	impregnation	250 °C 3 MPa	22:75 (:3 He)	0.94	78	4.1	[63]
Cu-ZnO-TiO <sub>2</sub> -ZrO <sub>2</sub>	4 Cu 4 Zn 1 Ti 1 Zr		sol-gel with citric acid	240 °C 3 MPa	1:3	17.0	44.0	-	[103]
Cu-ZnO-TiO <sub>2</sub> -ZrO <sub>2</sub>	4 Cu 4 Zn 1 Ti 1 Zr		solid-state reaction with citric acid	240 °C 3 MPa	1:3	16.2	43.7	-	[103]
Cu-ZnO-TiO <sub>2</sub> -ZrO <sub>2</sub>	4 Cu 4 Zn 1 Ti 1 Zr		solution-combustion	240 °C 3 MPa	1:3	15.6	41.9	-	[103]
Zr-Cu/CNT (oxygen containing groups)		10 CU 40 ZrO <sub>2</sub> 50 CNT	deposition precipitation	260 °C 3 MPa	1:3	14.4	36.5	1.94	[104]
Zr-Cu/CNT (few oxygen containing groups)		10 CU 40 ZrO <sub>2</sub> 50 CNT	deposition precipitation	260 °C 3 MPa	1:3	24.9	40.1	2.21	[104]

Catalyst	Composition		Preparation method	Reaction conditions	Feed CO <sub>2</sub> : H <sub>2</sub>	X <sub>CO2</sub>	S <sub>MeOH</sub>	STY	Ref
	molar ratio	weight percent							
Zr-Cu/CNT (nitrogen containing groups)		10 Cu 40 ZrO <sub>2</sub> 50 CNT	deposition precipitation	260 °C 3 MPa	1:3	16.3	43.5	2.62	[104]
Cu/ZnO-Ga <sub>2</sub> O <sub>3</sub>		14.2 Cu 4.2 Ga	incipient wetness impregnation	250 °C 3 MPa	1:3	3.37	35.4	1.00	[115]
Cu/ZnO-Ga <sub>2</sub> O <sub>3</sub>		14.2 Cu 4.2 Ga	incipient wetness impregnation	270 °C 3 MPa	1:3	6.01	28.2	1.44	[115]
(CuZnGa) <sub>MW</sub>		16.6 Cu 4.9 Ga	MW-assisted precipitation	250 °C 3 MPa	1:3	10.3	38.3	3.50	[115]
(CuZnGa) <sub>MW</sub>		16.6 Cu 4.9 Ga	MW-assisted precipitation	270 °C 3 MPa	1:3	15.8	29.3	4.23	[115]
Cu/LaCrO <sub>3</sub>		13 Cu	wet impregnation	250 °C 2 MPa	1:3	4.8	46.6	-	[116]
LaCr <sub>0.5</sub> Cu <sub>0.5</sub> O <sub>3</sub>		13 Cu	sol-gel with citric acid	250 °C 2 MPa	1:3	10.4	90.8	-	[116]
La-Cu-Zn-O	1 La 0.7 Cu 0.3 Zn		sol gel with citric acid	250 °C 5 MPa	1:3	6.4	57.9	1.56	[117]
La-Y-Cu-Zn-O	0.8 La 0.2 Y 0.7 Cu 0.3 Zn		sol gel with citric acid	250 °C 5 MPa	1:3	5.0	59.6	1.25	[117]
La-Ce-Cu-Zn-O	0.8 La 0.2 Ce 0.7 Cu 0.3 Zn		sol gel with citric acid	250 °C 5 MPa	1:3	8.1	63.3	2.50	[117]
La-Mg-Cu-Zn-O	0.8 La 0.2 Mg 0.7 Cu 0.3 Zn		sol gel with citric acid	250 °C 5 MPa	1:3	9.1	65.2	2.81	[117]
La-Zr-Cu-Zn-O	0.8 La 0.2 Zr 0.7 Cu 0.3 Zn		sol gel with citric acid	250 °C 5 MPa	1:3	12.6	59.6	1.25	[117]
YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	1 Y 2 B 3 Cu 7 O		Grinding, heating, pressing, crushing, sieving, calcination	240 °C 3 MPa	1:3	3.4	50.7	-	[118]

Cu-ZnO-TiO<sub>2</sub>-ZrO<sub>2</sub> catalysts were prepared using three different preparation methods, namely a sol-gel method, a solid-state reaction method and solution combustion. The sol-gel method yielded in the highest CO<sub>2</sub> conversion (17 %) and methanol selectivity (44 %), followed by the solid-state reaction method. This result was explained by the high Cu surface area and hence, high copper dispersion and by the high adsorption capacity for H<sub>2</sub>. [103]

Carbon nanotubes (CNT) supports were examined on Cu/ZrO<sub>2</sub>. The kind of functional groups on CNTs played a major role on the metal dispersion such that nitrogen

containing groups ensured a high dispersion and good reduction to form small copper particles. Small copper particles were stated to be advantageous for the separation of H<sub>2</sub>. This led to a high methanol yield of 2.62 mol<sub>MeOH</sub>/kg<sub>cat</sub>/h when using nitrogen containing groups.[104]

For Cu/Zn-Ga catalysts the influence of increasing reaction temperature was also tested which yielded in a higher CO<sub>2</sub> conversion and methanol yield but in a lower methanol selectivity. Catalysts prepared using a microwave (MW)-assisted method showed better performance than conventionally prepared catalysts.[115]

The catalytic performance of a LaCr<sub>0.5</sub>Cu<sub>0.5</sub>O<sub>3</sub> catalyst was determined to have a better catalytic performance than a Cu/LaCrO<sub>3</sub> catalyst with the same copper amount. The LaCr<sub>0.5</sub>Cu<sub>0.5</sub>O<sub>3</sub> catalyst showed a lower CO and CH<sub>4</sub> selectivity and simultaneously a high CH<sub>3</sub>OH selectivity of 90.8 % which makes the LaCr<sub>0.5</sub>Cu<sub>0.5</sub>O<sub>3</sub> perovskite structure a well applicable catalyst material.[116]

Perovskite-type catalysts (La-Cu-Zn-O) were tested with yttrium, cerium, magnesium and zirconium. Adding Ce, Mg and Zr resulted in smaller particles, a higher Cu dispersion and further increased the catalytic performance. Notable, the catalyst containing zirconium displayed the highest CO<sub>2</sub> conversion and methanol yield (12.6 % and 1.25 mol<sub>MeOH</sub>/kg<sub>cat</sub>/h, respectively) but the lowest methanol selectivity (59.6 %). Addition of yttrium lowered the CO<sub>2</sub> conversion and methanol yield.[117]

Tests on a YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> catalyst showed that after H<sub>2</sub> reduction at 250 °C the non-active orthorhombic structure turned to a tetragonal structure, which is active for CO<sub>2</sub> hydrogenation. Best results for the production of methanol could be obtained at a high pressure, a high space velocity and a low temperature. For CO<sub>2</sub> conversion a high pressure, a high temperature and a low space velocity were preferable.[118]

### **2.1.5. Summary**

#### **Supports**

The selectivity of Al<sub>2</sub>O<sub>3</sub>-supported catalysts is rather low but Cu/Al<sub>2</sub>O<sub>3</sub> catalysts lead to a better methanol yield than Cu/SiO<sub>2</sub> catalysts.[114] Silica-supported catalysts stand out with their high thermal stability.[17] Cu/Al<sub>2</sub>O<sub>3</sub> catalysts give a higher CO<sub>2</sub> conversion, while Cu/ZrO<sub>2</sub> catalysts have a higher methanol selectivity.[26] ZrO<sub>2</sub>-

supports provide a higher basicity of the catalyst, a better copper dispersion and stability than  $\text{Al}_2\text{O}_3$ -supports.[29] In a  $\text{Cu}/\text{Ga}_2\text{O}_3\text{-ZrO}_2$  catalyst the  $\text{ZrO}_2$  contributes to a better reducibility of copper whereas  $\text{Ga}_2\text{O}_3$  improves the metal dispersion leading to better catalytic performance.[63] Various supports for Cu-Zn catalysts were compared, showing that Zr-oxide delivers the highest activity, followed by Al. The worst results were given by Ce-oxide catalysts due to a low carbon dioxide conversion. Summarizing, it is stated that the oxide carrier influences the adsorption properties and structure of the catalyst. Methanol is believed to be the main product if the reaction temperature is low and the  $\text{CO}_2$  conversion is high.[66]  $\text{ZnO}$  is an often-used supporting material due to the synergy between copper and zinc yielding in a highly selective catalyst.[55] A comparison of  $\text{Cu}/\text{ZnO-Al}_2\text{O}_3$ ,  $\text{Cu}/\text{ZnO-ZrO}_2$  and  $\text{Cu}/\text{ZnO-Al}_2\text{O}_3\text{-ZrO}_2$  catalysts shows that the  $\text{Cu}/\text{ZnO-Al}_2\text{O}_3$  catalysts have the highest copper surface area, followed by the  $\text{Cu}/\text{ZnO-Al}_2\text{O}_3\text{-ZrO}_2$  catalyst. Since the  $\text{Cu}/\text{ZnO-Al}_2\text{O}_3\text{-ZrO}_2$  catalyst has the best catalytic performance the exposed copper surface cannot be the only influencing factor.  $\text{Al}_2\text{O}_3$ -promotion is stated to enhance the  $\text{CuO}$  dispersion and hinders the  $\text{CuO}$  reduction while  $\text{ZrO}_2$ -addition promotes the reduction leading to a higher catalytic stability.[85]  $\text{CeO}_2$  as supporting material gives highly selective catalysts but it is not stable in the presence of water.[29]  $\text{TiO}_2$  and  $\text{Ga}_2\text{O}_3$  are also stated to be applicable supporting materials which can lead to satisfying results in the presence of promoters.[75] To combine the advantages of each support also combinations of  $\text{ZnO}$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$  are used.[103] Further supports are CNT with functional groups which have a positive effect on the catalytic properties.[104]

### **Promoters**

Using  $\text{ZnO}$  as a promotor results in a high copper dispersion and surface area.  $\text{ZnO}$  promotes the reaction of  $\text{CO}_2$  and  $\text{H}_2$  through interaction with copper.[41][59][61][67]  $\text{ZrO}_2$ -promotion gives highly selective, active and stable catalysts for the desired reaction.[57][41][42][48][49][62][96] Positive effects on the copper particle size and dispersion are given by Mn-addition but also sintering could be observed.[23][59][90][91][96] The main promotional effect of  $\text{Ga}_2\text{O}_3$  is the improved metal dispersion on the catalyst surface leading to an enhanced performance for the  $\text{CO}_2$  hydrogenation to methanol. Gallium was also attributed to increase the stability of the catalyst.[50][51][52][49][90] Mg increases the copper dispersion and metal surface as well as the strong basic sites.[41][75] There exist very contradictory opinions on Pd-

promotion. While there is agreement that there forms a strong interaction between copper and palladium researcher disagree on the effect of this alloy on the catalytic performance. Some speak of an enhanced methanol formation and a stable catalyst due to the Pd-Cu alloy[60][77] while others declare that the copper gets covered by the palladium leading to a decreased catalytic activity whereas the intrinsic methanol yield is enhanced.[97] Barium has a great impact on the methanol selectivity. It increases the exposed copper area and hinders from sintering. Since potassium favors the reverse water-gas shift reaction it is not promoting the methanol formation.[43] TiO<sub>2</sub> is often reported as a well performing promoter for the hydrogenation reaction to methanol. It is said to have a positive impact on the Cu-Zn interaction in Zn containing catalysts, on the copper dispersion and on the crystal size.[44][48][53][95] But there exists also a study claiming that TiO<sub>2</sub> has no influence on the copper dispersion.[62] Yttrium, aluminum, molybdenum and tungsten have a highly positive effect on the catalyst properties and hence on the catalytic performance.[46][49][88][89][96] B<sub>2</sub>O<sub>3</sub> was also tested for the promotion of the hydrogenation of CO<sub>2</sub> yielding in a positive result concerning the catalytic activity.[68][90] Silver promotes the formation of methanol-selective active sites but lowers the methanol production due to coverage of the exposed copper area.[69] Iron, Cobalt and Gadolinium are suppressors for the CO<sub>2</sub> reduction to methanol. Moreover, addition of cobalt leads to methane production.[23][87] While some researchers state that chromium has a positive effect on the catalytic performance of a catalyst[23][49], others assume a negative influence.[89] Varying opinions exist on the impact of nickel. As some scientists say nickel hinders the catalytic activity[23], whereas others speak of a promoting effect of nickel on the CO<sub>2</sub> conversion and methanol formation rate.[78] Agreement persists on the lower methanol selectivity when using nickel. Praseodymium and neodymium have a slightly negative effect on catalysts concerning the catalytic performance.[87] While indium has no or a negative effect on the catalytic performance, it raises the stability of the catalyst.[54][90] Lanthanum, cerium as well as silicon are good promoters for the desired reaction.[86][46][70][87][95][96] Doping with fluorine leads to a smaller copper surface area which results in a lower carbon dioxide conversion, while the methanol selectivity and yield are enhanced.[98][102]

In general, it can be said that high temperatures lead to a high CO<sub>2</sub> conversion rate and methanol yield but to a low methanol selectivity due to favoring of the reverse water-gas shift reaction.[56][82][115] Besides the right composition a high catalytic

performance can be achieved by catalysts with highly dispersed, small particles which are well reduceable and have a high surface area. The preparation method has a high impact on these important properties of the catalyst.[103][80][68][64][76][82]

### 3. Reaction mechanism of Cu-based catalysts

The reaction mechanism of the hydrogenation of carbon dioxide to form methanol is a strongly debated topic among researchers. Scientists do not agree about key reaction intermediates. Knowledge about the reaction mechanism is very important for an efficient catalyst design. In the following section the reaction pathways that can be found in literature are discussed. The formate pathway and the RWGS reaction and CO hydrogenation pathway are the two mostly proposed reaction mechanisms but also a hydrocarboxyl pathway is mentioned.[119]

#### 3.1. Formate pathway

The formate pathway is often considered as the reaction route for CO<sub>2</sub> hydrogenation to methanol on copper-based catalysts. This path is characterized by the formation of a formate (HCOO) intermediate. Nevertheless, researchers proposed various reaction routes containing different reaction intermediates in addition to formate as pictured in Figure 4.

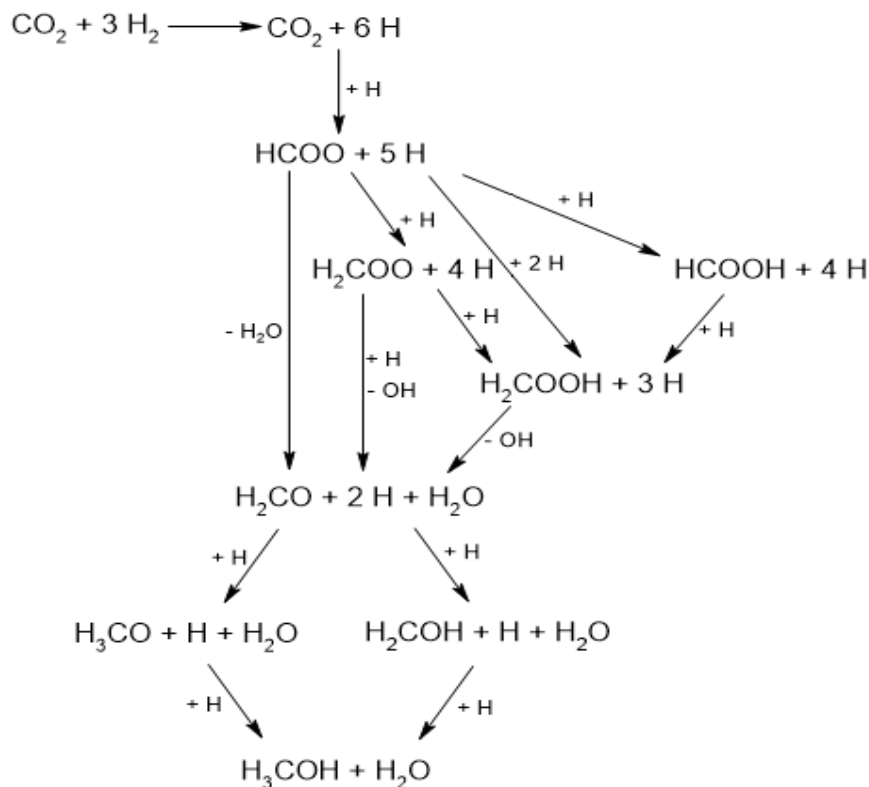


Figure 4: Formate pathway for methanol synthesis from CO<sub>2</sub>[120][121][122][123][124][125][126][127][128][129][130][131][132][133]

Kourtelesis *et al.* investigated the mechanism of CO<sub>2</sub> hydrogenation on La<sub>2</sub>O<sub>3</sub>-promoted Cu/ZnO-Al<sub>2</sub>O<sub>3</sub> catalysts with the help of in situ diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) experiments. They found that the reaction runs *via* the formate pathway with the formation of a methoxy (H<sub>3</sub>CO) species being the rate-determining step. Hydrogen adsorbs on copper and provides atomic hydrogen by spillover, whereas CO<sub>2</sub> adsorbs on the support. CO was proposed to be a by-product which is produced by the RWGS reaction *via* a formate intermediate.[120]

Grabow and Mavrikakis did density functional theory (DFT) calculations on a Cu(111) surface with reaction rates that are similar to reaction rates on Cu/ZnO and merged the data with experimental data from a Cu/ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst. They concluded that methanol is formed by CO<sub>2</sub> reduction through the formate pathway with the methoxy hydrogenation being the rate-limiting step. CO was stated to be promotional for CO<sub>2</sub> hydrogenation because it may support the hydrogenation of intermediates in the CO<sub>2</sub> hydrogenation pathway through a HCO (formyl) intermediate and it removes H<sub>2</sub>O and shifts the equilibrium to CO<sub>2</sub> and H<sub>2</sub> *via* the water-gas shift reaction.[121]

A DFT calculation was done by Qiu *et al.* to analyze the reaction mechanism on a Co-promoted Cu(100) surface. They came to the result that carbon dioxide undergoes the formate pathway to form methanol. The hydrogenation of CO<sub>2</sub> follows an Eley-Rideal (ER)-mechanism. The hydrogenation of an OH-group to form water is the rate-limiting step. The impact of Co-promotion was investigated showing that the hydrogenation of the OH group is the only different step compared to an unpromoted Cu(100) surface. Hence, the rate-limiting step has changed. Adding Co leads to a Co-O bond which is stronger than the Cu-O bond and promotes the formation of key intermediates. Thus, the methanol selectivity and efficiency on a Cu(110) surface is enhanced by Co-doping.[122]

Studt *et al.* did microkinetic modelling and DFT studies on Cu/ZnO catalysts. They spoke of a formate intermediate, hence the formate pathway was considered. All intermediates in CO<sub>2</sub> hydrogenation form an oxygen bond on the catalyst surface and are therefore stabilized by ZnO whereas carbon bonds which occur in CO hydrogenation would be destabilized by ZnO. Thus, ZnO promotes CO<sub>2</sub> hydrogenation and suppresses CO hydrogenation. The researchers compared different CO/CO<sub>2</sub> feed compositions and came to the conclusion that high contents of CO<sub>2</sub> lead to a high formate coverage of the catalyst surface which lowers the activity for CO



hydrogenation but supports CO<sub>2</sub> hydrogenation because formate is an intermediate in this mechanism.[134]

Kattel *et al.* did x-ray photoelectron spectroscopy measurements, DFT calculations and kinetic Monte Carlo simulations for Cu/ZnO and ZnCu catalysts. They considered the formate pathway and the RWGS reaction to form CO followed by CO hydrogenation *via* an HCO intermediate. The favored pathway for both catalysts was stated to be the formate route. The RWGS reaction and CO hydrogenation route was proposed to mainly produce CO because only a small amount of CO is further hydrogenated to methanol.[123]

Karelovic *et al.* proposed the formate pathway to be the route for methanol synthesis from H<sub>2</sub> and CO<sub>2</sub>. They did kinetic experiments, H/D isotopic substitution and in situ DRIFTS to examine the mechanism on SiO<sub>2</sub>-supported copper-based catalysts and came to the result that the reaction proceeds *via* the formate pathway. The hydrogenation of formic acid is the rate-limiting step. Two products are formed under the reaction conditions. The formate intermediate was stated to lead to methanol while the carboxyl intermediate results in carbon monoxide as side product *via* the RWGS reaction.[124]

Nie *et al.* investigated Pd-Cu bimetallic catalysts using DFT calculations. The mechanism was stated to follow the formate path. The formation of the HCOO (formate) intermediate was found to be energetically more favored than the formation of the COOH (hydrocarboxyl) intermediate since HCOO is thermodynamically more stable. The step with the highest barrier was found to be the hydrogenation of HCOO. Water was observed to have a promoting effect on the reaction.[125]

Fujitani *et al.* stated that on a Zn-deposited Cu(111) surface a formate and a methoxy species can be found as reaction intermediates with formate hydrogenation being the rate-limiting step indicating the reaction to proceed *via* the formate pathway.[135]

Wu *et al.* compared the formate pathway and the RWGS reaction and CO hydrogenation pathway applying spin-polarized DFT calculations on Cu/ZnO. The scientists came to the conclusion that the formate path is favored. The rate-limiting steps were found to be the HCOO and H<sub>3</sub>CO hydrogenation forming HCOOH (formic acid) and H<sub>3</sub>COH, respectively.[126]

Wang *et al.* did research on copper-cerium-zirconium catalysts using in situ DRIFTS. They found that the monodentate as well as the bidentate form of the HCOO intermediate contribute to the formation of methanol. While the bidentate HCOO directly reacts to H<sub>3</sub>COH or forms the monodentate HCOO, the monodentate form concentrates slowly on the surface before further hydrogenation to methanol.[136]

Liu *et al.* did DFT calculations and kinetic Monte Carlo simulations on Cu<sub>2</sub>O(111) and Cu(111). Mono-HCOO was considered to be a more favorable reaction intermediate than *cis*-COOH or *trans*-COOH. On Cu<sub>2</sub>O(111) further hydrogenation leads to HCOOH, H<sub>2</sub>COOH (hydroxymethoxy), H<sub>2</sub>CO (formaldehyde), H<sub>2</sub>COH (hydroxymethyl) and finally results in H<sub>3</sub>COH, whereas on Cu(111) H<sub>3</sub>CO is built instead of H<sub>2</sub>COH. HCOOH hydrogenation was regarded as the rate-limiting step on both surfaces.[127]

Hong and Liu did DFT calculations and kinetic Monte Carlo simulations on Cu/m-ZrO<sub>2</sub>. According to their research CO<sub>2</sub> adsorbs on ZrO<sub>2</sub>, while H<sub>2</sub> dissociatively adsorbs on Cu. The reaction proceeds mainly through the formate route. The results indicate that CO is not produced directly from CO<sub>2</sub> but by the decomposition of the HCO intermediate. Rate-limiting steps are mainly the adsorption of CO<sub>2</sub> and the hydrogenation of the H<sub>2</sub>CO intermediate. CO<sub>2</sub> adsorption could be supported by lowering of the temperature but the H<sub>2</sub>CO hydrogenation requires higher temperatures.[128]

Xu *et al.* examined the CO<sub>2</sub> hydrogenation on a Cu/ZnO catalyst through <sup>13</sup>C-labeled CO and came to the result that CO<sub>2</sub> is the only carbon source in methanol synthesis from CO<sub>2</sub> and H<sub>2</sub> meaning that no CO is built through the reverse water-gas shift reaction and further hydrogenated to methanol. Further, they proposed that the reaction proceeds *via* a formate intermediate with the formation of formaldehyde from formate being the key step.[137]

Kakumoto *et al.* did DFT calculations on Cu/ZnO and Cu/CuO catalysts. The results indicated that methanol synthesis occurs on the boundary of Cu to CuO and ZnO, respectively. At first, CO<sub>2</sub> adsorbs linearly on the Cu<sup>+</sup>, whereas H<sub>2</sub> adsorbs on the metallic copper, whereafter the hydrogen attacks the carbon to form bidentate formate. Further formaldehyde, methoxy and methanol are formed.[129]

Nakatsuji and Hu did some research on the reaction mechanism on Cu(100) and Zn/Cu(100) using the dipped adcluster model combined with ab initio Hartree-Fock and

second-order Møller-Plesset calculations. The scientists state that H<sub>2</sub> as well as CO<sub>2</sub> adsorb on the catalyst before they react with each other. The reaction proceeds according to the formate pathway. The rate-limiting step was determined to be the hydrogenation of formate to dioxomethylene and the further hydrogenation to formaldehyde. On Cu(100) the reaction occurs on the Cu-Cu sites. Whereas on Zn/Cu(100) the Cu-Cu sites as well as the Cu-Zn sites play an important role. Moreover, on Zn/Cu(100) the activation barriers of the rate-determining steps are lower and the dioxomethylene intermediate is stabilized which leads to a higher reactivity in CO<sub>2</sub> hydrogenation to methanol.[130]

DFT calculations on Cu nanoparticles and on Cu(111) were done by Yang *et al.* Their research revealed that the reaction runs *via* the formate path where the H<sub>2</sub>COO (dioxomethylene) intermediate is energetically favored over the HCOOH intermediate. The reaction of hydrogen with carbon dioxide proceeds in an ER-mechanism. Dioxomethylene hydrogenation is the rate-limiting step. In comparison to Cu(111) intermediates and transition states are more stable on Cu nanoparticles and hence, Cu nanoparticles exhibit a higher activity.[131]

Hu *et al.* studied the formate pathway on a Cu(100) surface with the dipped adcluster model. According to the authors the reactants hydrogen and carbon dioxide follow a Langmuir-Hinshelwood (LH)-mechanism. The rate-determining step was found to be the hydrogenation of formate to dioxomethylene. Since the backward reaction has a low energy barrier and is exothermic the dioxomethylene intermediate can easily react back to the formate intermediate. Therefore, the presence of adsorbed hydrogen is important to ensure that the dioxomethylene intermediate is converted to the formaldehyde intermediate according to the proposed reaction sequence.[132]

As formate is the most abundant intermediate on the surface Wu and Yang discussed the influence of formate surface coverage over Cu(211) on the reaction path. They found that a high formate coverage leads to a weaker adsorption of many intermediates. The adsorbed formate intermediate does not only participate in methanol formation but also acts as a spectator. Surface coverage also affects the turnover frequency.[133]

In situ DRIFTS studies on Cu/ZrO<sub>2</sub> showed that methanol is produced by the formate pathway with the hydrogenation of formate being the rate-limiting step. In the beginning

H<sub>2</sub> dissociatively adsorbs on the copper surface and migrates to the ZrO<sub>2</sub> surface by hydrogen spillover. The hydrogen spillover plays an important role and depends on the interaction between Cu and ZrO<sub>2</sub>. CO<sub>2</sub> adsorbs on the oxygen vacancies of the ZrO<sub>2</sub> surface forming a carbonate species. Wang *et al.* proposed a formate pathway with carbonate (CO<sub>3</sub>), formate and methoxy being the intermediates before the final product methanol is formed.[138]

### 3.2. RWGS reaction and CO hydrogenation pathway

Figure 5 shows that a possible reaction path to generate methanol from CO<sub>2</sub> starts with the reverse water-gas shift reaction where carbon dioxide is converted to carbon monoxide *via* a hydrocarboxyl intermediate. CO is then hydrogenated to finally produce methanol and water.

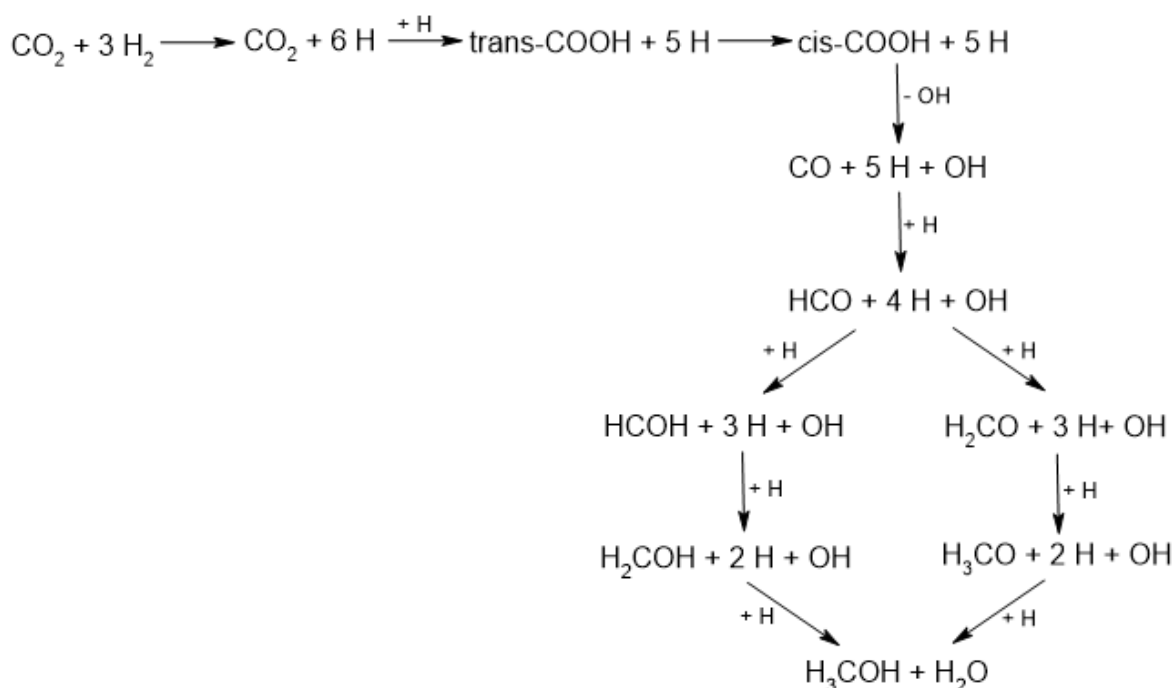


Figure 5: RWGS reaction and CO hydrogenation pathway for methanol synthesis from CO<sub>2</sub>[139][140][141][142]

Yang *et al.* discussed not only the formate path but also the RWGS reaction and CO hydrogenation path on Cu nanoparticles besides the more plausible formate path. CO formation through the RWGS reaction occurs two orders of magnitude faster than methanol production. In the CO hydrogenation path the HCO intermediate seemed more likely than the COH (hydroxymethylidyne) intermediate but the HCO intermediate is not stable and dissociates to CO and H. Therefore, this path leads solely to CO as

by-product in CO<sub>2</sub> hydrogenation to methanol and methanol is exclusively produced *via* the formate route. To increase the methanol yield methanol formation through the CO hydrogenation path has to be achieved. Therefore, a catalyst which stabilizes the formyl intermediate is necessary.[131]

Liu *et al.* studied the RWGS reaction followed by CO hydrogenation path on Cu-Pd bimetallic catalysts using periodic DFT calculations. The presence of Pd causes an increase of the adsorption energies and activation barriers. On Cu(111) and PdCu hydrogenation of carbon dioxide to trans-COOH is considered as the rate-limiting step as it shows the highest activation barrier whereas on a Pd monolayer on copper cis-COOH decomposition is the rate-limiting step due to a stronger adsorption of COOH.[139]

DFT calculations and kinetic Monte Carlo simulations on metal-doped Cu(111) surfaces were done by Yang, White and Liu. They compared the formate route, which runs *via* a H<sub>2</sub>COO intermediate with its hydrogenation being the rate-limiting step, and the RWGS reaction and CO hydrogenation path for Au-, Ni-, Pt-, Pd- and Rh-doped copper surfaces. It was stated that the reaction proceeds *via* both pathways. The Au-doped surface and the undoped surfaces were found to produce methanol mainly through the formate route, whereas the other dopants lead to methanol by the RWGS reaction and CO hydrogenation path. Furthermore, Au turned out to suppress methanol formation, whereas the other dopants promote methanol production on a Cu(111) surface by stabilization of the CO and HCO intermediate.[140]

Kattel *et al.* demonstrated that the RWGS reaction and CO hydrogenation path is more favored than the formate route on Cu/TiO<sub>2</sub> and Cu/ZrO<sub>2</sub> catalysts using DFT calculations, KMC simulations and in-situ DRIFTS measurements. Even though the HCOO formation is favored, it tends to accumulate on the surface and hence poisons the catalyst which makes the RWGS reaction and CO hydrogenation path more likely.[141]

Liu *et al.* investigated the RWGS and CO hydrogenation path on Cu(111) and Rh-doped Cu(111) surfaces with the help of DFT calculations. On Cu(111) and Rh<sub>3</sub>Cu<sub>6</sub>(111) surfaces the rate-limiting step is the formation of trans-COOH, whereas on Rh<sub>6</sub>Cu<sub>3</sub>(111) surfaces as well as on Rh monolayer surfaces the rate-determining

step is the CO hydrogenation because of the enhanced interaction between the surface and trans-COOH.[142]

### 3.3. Hydrocarboxyl pathway

As in the RWGS reaction and CO hydrogenation path there exists a second pathway in which a COOH intermediate is formed. Here, the hydrocarboxyl is hydrogenated to dihydroxycarbene (COHOH) and after some intermediate steps methanol is generated as shown in Figure 6.

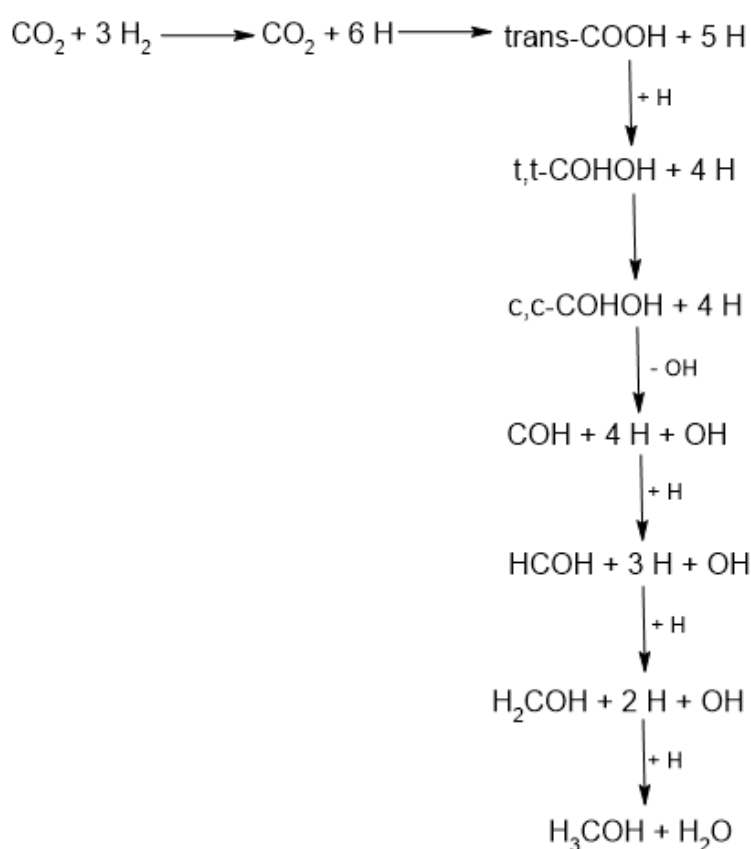


Figure 6: Hydrocarboxyl pathway for methanol synthesis from CO<sub>2</sub>[119]

Zhao *et al.* considered all possible steps for the hydrogenation of CO<sub>2</sub> on Cu(111) to form methanol using periodic plane-wave DFT. One possibility is the formate pathway proceeding *via* an ER-mechanism. The rate limiting steps in the formate path were stated to be the hydrogenation of formate and the formation of H<sub>2</sub>CO which is even harder. The authors came to the conclusion that the formate pathway is unlikely at the usual low operating temperatures because of the high activation energies of a few elementary steps and the absence of H<sub>2</sub>CO as side product. The second possibility is the RWGS reaction followed by CO hydrogenation path where CO<sub>2</sub> is converted to CO

through the formation of COOH. The H<sub>2</sub>CO intermediate of this pathway is only weakly bound to the surface and may desorb. As H<sub>2</sub>CO is not detected as side product on Cu(111) Zhao *et al.* assume that methanol formation does not happen through this pathway. The third possibility is the hydrocarboxyl pathway. After the dissociative adsorption of H<sub>2</sub> on the copper surface it reacts with CO<sub>2</sub> most likely through an ER-mechanism and forms trans-COOH which can be further transformed to cis-COOH. In the most likely route the trans-COOH is hydrogenated to dihydrocarbene (t,t-COHOH) which can be transformed to its isomers t,c- and c,c-COHOH. The dihydrocarbenes dissociate into COH and OH. The COH intermediate is hydrogenated to HCOH (hydroxymethylene). Followed by another three hydrogenation steps first HCOH, then H<sub>2</sub>COH and then H<sub>3</sub>COH are formed. Zhao *et al.* proposed the COOH pathway to be more plausible than the formate route and RWGS reaction and CO hydrogenation path. The key-step in the hydrocarboxyl route is the formation of trans-COOH. The methanol formation from H<sub>2</sub>COH in the COOH route is more likely than from H<sub>3</sub>CO in the formate pathway. The authors also studied the influence of water on the reaction mechanism and found that water acts as an inhibitor in the formate pathway whereas the COOH pathway is promoted by the presence of water due to a hydrogen transfer mechanism during the formation of trans-COOH. In the presence of water the rate limiting step is the decomposition of COHOH.[119]

### 3.4. Summary

Despite many years of research on the reaction mechanism of CO<sub>2</sub> hydrogenation to methanol on copper-based catalysts the main reaction path is still not known. While many researchers suggest the formate pathway, others propose the reverse water-gas shift reaction followed by CO hydrogenation. Another potential way for methanol formation is the hydrocarboxyl pathway. Not only the main pathway is debated but also the reaction intermediates as well as the rate-limiting step. It is well known that hydrogen dissociatively adsorbs on the copper surface.[119] Many researchers propose an Eley-Rideal-mechanism where gaseous CO<sub>2</sub> reacts with the adsorbed hydrogen[119][122][131], whereas others state that CO<sub>2</sub> adsorbs on the catalyst before it reacts with the adsorbed hydrogen in a Langmuir-Hinshelwood-mechanism.[132] The reaction route may also depend on the support. To gain more insight into the

reaction mechanism further research is necessary in order to develop more efficient and effective catalysts.



## 4. Conclusion and outlook

It can be said that the hydrogenation of carbon dioxide to methanol is an important research topic especially concerning environmental issues. The transformation of carbon dioxide to methanol is a promising approach to reduce CO<sub>2</sub> emissions to the atmosphere in order to counteract global warming and therefore has aroused wide interest among scientist. The obtained methanol can be used in various applications for example as fuel or solvent. In the past decades extensive studies have been carried out regarding this topic.

The reaction starting from carbon dioxide and hydrogen to produce methanol is an exothermic reaction and requires low temperatures and high pressure to reach ideal reaction conditions for high conversions at equilibrium. Further a catalyst is necessary to activate the carbon dioxide, accelerate the desired reaction and eliminate the formation of side products like carbon monoxide or methane. The composition of the catalyst is crucial as it determines the properties of the catalyst such as activity, stability, and selectivity. This work summarizes the research status with respect to heterogeneous copper-based catalysts as they showed satisfactory methanol formation in experiments. As discussed in the previous chapters various supports and promoters were tested in combination with copper acting as an active metal. Tested supports were for example Al<sub>2</sub>O<sub>3</sub>, ZnO, SiO<sub>2</sub>, ZrO<sub>2</sub>, graphene-oxide, TiO<sub>2</sub>, CeO<sub>2</sub>. Remarkably good results were gained using mixtures of supports to combine the positive features of each material for example ZnO-Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>. Nearly each element of the periodic table was tested as promoter for the catalyst. Good results were obtained using gallium, aluminum, zirconium, yttrium, molybdenum and tungsten. Not only the catalyst composition and reaction conditions have a big influence on the catalytic properties but also the preparation method has a great impact on the catalytic performance of the catalyst.

Another discussed topic is the reaction mechanism of the CO<sub>2</sub> hydrogenation to methanol. Knowledge about the reaction route would make it easier to find the ideal catalyst composition. The considered supporting material should be taken into account when discussing the reaction mechanism since it can influence the reaction route by stabilization or destabilization of the reaction intermediates. By now a few different reaction pathways were proposed. Often mentioned are the formate pathway as well

as the reverse water-gas shift reaction and CO hydrogenation pathway. Also published is a hydrocarboxyl pathway. Further, the activation of CO<sub>2</sub> is still unclear. Both, a Langmuir-Hinshelwood-mechanism and an Eley-Rideal-mechanism are mentioned in literature. The impact of the presence of water on the reaction is unclear, too. While some scientists state that water deactivates the catalyst and inhibits the reaction, others propose a promoting effect of water on the reaction. By now the reaction mechanism is an unsolved problem. Further research and experiments are necessary to gain more insight into the reaction path that is proceeded.

The hydrogenation of carbon dioxide can be a significant step against global warming. Speaking of environmental issues, prospective challenges are the waste treatment or perhaps even recycling of spent catalysts. Hence, in research a focus should be laid on the disposal of the catalysts to develop a reaction cycle that is as environmentally friendly as possible. At the same time more research has to be done concerning the reaction mechanism, catalyst composition and catalyst preparation to be able to create a highly active, selective and stable catalyst. The optimization of the catalyst and the operating conditions are important to transform carbon dioxide effectively and selectively to methanol. As a result, carbon dioxide is removed from the atmosphere and transformed into a valuable and versatile chemical that can be reused in many applications.

## 5. References

- [1] O. Deutschmann, H. Knözinger, K. Kochloefl, and T. Turek, 'Heterogeneous Catalysis and Solid Catalysts', in *Ullmann's encyclopedia of industrial chemistry*, 2012, pp. 457–481.
- [2] R. Schlögl, 'Heterogeneous Catalysis', *Angew. Chemie - Int. Ed.*, vol. 54, no. 11, pp. 3465–3520, 2015, doi: 10.1002/anie.201410738.
- [3] J. G. De Vries and S. D. Jackson, 'Homogeneous and heterogeneous catalysis in industry', *Catal. Sci. Technol.*, vol. 2, no. 10, p. 2009, 2012, doi: 10.1039/c2cy90039d.
- [4] X. M. Liu, G. Q. Lu, Z. F. Yan, and J. Beltramini, 'Recent Advances in Catalysts for Methanol Synthesis via Hydrogenation of CO and CO<sub>2</sub>', *Ind. Eng. Chem. Res.*, vol. 42, no. 25, pp. 6518–6530, 2003, doi: 10.1021/ie020979s.
- [5] H. S. Taylor, 'Catalysis', *Encyclopaedia Britannica*. [Online]. Available: <https://www.britannica.com/science/catalysis>. [Accessed: 01-Mar-2020].
- [6] J. Ma *et al.*, 'A short review of catalysis for CO<sub>2</sub> conversion', *Catal. Today*, vol. 148, pp. 221–231, 2009, doi: 10.1016/j.cattod.2009.08.015.
- [7] J. R. H. Ross, 'Heterogeneous Catalysis – Chemistry in Two Dimensions', in *Heterogeneous Catalysis*, 2012, pp. 1–15.
- [8] A. Álvarez *et al.*, 'Challenges in the Greener Production of Formates/Formic Acid, Methanol, and DME by Heterogeneously Catalyzed CO<sub>2</sub> Hydrogenation Processes', *Chem. Rev.*, vol. 117, no. 14, pp. 9804–9838, 2017, doi: 10.1021/acs.chemrev.6b00816.
- [9] H. Ritchie and M. Roser, 'CO<sub>2</sub> and Greenhouse Gas Emissions', *Our World in Data*. [Online]. Available: <https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions#citation>. [Accessed: 02-Mar-2020].
- [10] 'Trends in Atmospheric Carbon Dioxide', *ESRL - Global Monitoring Division*. [Online]. Available: <https://www.esrl.noaa.gov/gmd/ccgg/trends/global.html>. [Accessed: 02-Mar-2020].
- [11] B. Metz, O. Davidson, L. Meyer, P. Bosch, and R. Dave, *Climate Change 2007: Mitigation of Climate Change*. 2007.
- [12] X. Jiang, X. Nie, X. Guo, C. Song, and J. G. Chen, 'Recent Advances in Carbon Dioxide Hydrogenation to Methanol via Heterogeneous Catalysis', *Chem. Rev.*, doi: 10.1021/acs.chemrev.9b00723.
- [13] S. Dang *et al.*, 'A review of research progress on heterogeneous catalysts for methanol synthesis from carbon dioxide hydrogenation', *Catal. Today*, vol. 330, no. April 2018, pp. 61–75, 2019, doi: 10.1016/j.cattod.2018.04.021.
- [14] E. Alper and O. Yuksel Orhan, 'CO<sub>2</sub> utilization: Developments in conversion processes', *Petroleum*, vol. 3, pp. 109–126, 2017, doi: 10.1016/j.petlm.2016.11.003.
- [15] 'Carbon dioxide', *Sigma Aldrich*. [Online]. Available: <https://www.sigmaaldrich.com/catalog/product/aldrich/295108?lang=de&region>

=AT. [Accessed: 03-Mar-2020].

- [16] S. G. Jadhav, P. D. Vaidya, B. M. Bhanage, and J. B. Joshi, 'Catalytic carbon dioxide hydrogenation to methanol: A review of recent studies', *Chem. Eng. Res. Des.*, vol. 92, pp. 2557–2567, 2014, doi: 10.1016/j.cherd.2014.03.005.
- [17] I. Din, M. S. Shaharun, M. A. Alotaibi, and A. I. Alharthi, 'Recent developments on heterogeneous catalytic CO<sub>2</sub> reduction to methanol', *J. CO<sub>2</sub> Util.*, vol. 34, no. June, pp. 20–33, 2019, doi: 10.1016/j.jcou.2019.05.036.
- [18] G. A. Olah, 'Beyond Oil and Gas: The Methanol Economy', *Angew. Chemie - Int. Ed.*, vol. 44, no. 18, pp. 2636–2639, 2005, doi: 10.1002/anie.200462121.
- [19] H. Yang *et al.*, 'A review of the catalytic hydrogenation of carbon dioxide into value-added hydrocarbons', *Catal. Sci. Technol.*, vol. 7, no. 20, pp. 4580–4598, 2017, doi: 10.1039/c7cy01403a.
- [20] M. Bowker, 'Methanol Synthesis from CO<sub>2</sub> Hydrogenation', *ChemCatChem*, vol. 11, no. 17, pp. 4238–4246, 2019, doi: 10.1002/cctc.201900401.
- [21] 'What is methanol?', *Methanol Institute*. [Online]. Available: <https://www.methanol.org/about-methanol/>.
- [22] 'Methanol', *Sigma Aldrich*. [Online]. Available: <https://www.sigmaaldrich.com/chemistry/solvents/methanol-center.html>. [Accessed: 03-Mar-2020].
- [23] M. K. Koh, M. M. Zain, and A. R. Mohamed, 'Exploring transition metal (Cr, Mn, Fe, Co, Ni) promoted copper-catalyst for carbon dioxide hydrogenation to methanol', *AIP Conf. Proc.*, vol. 2124, no. July, p. 020006, 2019, doi: 10.1063/1.5117066.
- [24] 'Production', *Methanol Institute*. [Online]. Available: <https://www.methanol.org/production/>. [Accessed: 03-Mar-2020].
- [25] J. Ott *et al.*, 'Methanol', in *Ullmann's encyclopedia of industrial chemistry*, 2012, pp. 1–27.
- [26] J. F. Portha *et al.*, 'Kinetics of Methanol Synthesis from Carbon Dioxide Hydrogenation over Copper-Zinc Oxide Catalysts', *Ind. Eng. Chem. Res.*, vol. 56, no. 45, pp. 13133–13145, 2017, doi: 10.1021/acs.iecr.7b01323.
- [27] E. Jwa, S. B. Lee, H. W. Lee, and Y. S. Mok, 'Plasma-assisted catalytic methanation of CO and CO<sub>2</sub> over Ni-zeolite catalysts', *Fuel Process. Technol.*, vol. 108, pp. 89–93, 2013, doi: 10.1016/j.fuproc.2012.03.008.
- [28] J. Wu, M. Saito, M. Takeuchi, and T. Watanabe, 'The stability of Cu/ZnO-based catalysts in methanol synthesis from a CO<sub>2</sub>-rich feed and from a CO-rich feed', *Appl. Catal. A Gen.*, vol. 218, pp. 235–240, 2001, doi: 10.1016/S0926-860X(01)00650-0.
- [29] R. Guil-Lopez *et al.*, 'Methanol Synthesis from CO<sub>2</sub>: A Review of the Latest Developments in Heterogeneous Catalysis', *Materials (Basel)*, vol. 12, p. 3902, 2019.
- [30] W. Wang, S. Wang, X. Ma, and J. Gong, 'Recent advances in catalytic hydrogenation of carbon dioxide', *Chem. Soc. Rev.*, vol. 40, no. 7, pp. 3703–

3727, 2011, doi: 10.1039/c1cs15008a.

- [31] R. Raudaskoski, E. Turpeinen, R. Lenkkeri, E. Pongrácz, and R. L. Keiski, 'Catalytic activation of CO<sub>2</sub>: Use of secondary CO<sub>2</sub> for the production of synthesis gas and for methanol synthesis over copper-based zirconia-containing catalysts', *Catal. Today*, vol. 144, no. 3–4, pp. 318–323, 2009, doi: 10.1016/j.cattod.2008.11.026.
- [32] K. Scott and R. Hughes, *Industrial Membrane Separation Technology*. Springer Science & Business Media, 1996.
- [33] S. Saeidi, N. A. S. Amin, and M. R. Rahimpour, 'Hydrogenation of CO<sub>2</sub> to value-added products - A review and potential future developments', *J. CO<sub>2</sub> Util.*, vol. 5, pp. 66–81, 2014, doi: 10.1016/j.jcou.2013.12.005.
- [34] K. G. dos Santos *et al.*, 'Hydrogen production in the electrolysis of water in Brazil, a review', *Renew. Sustain. Energy Rev.*, vol. 68, pp. 563–571, 2017, doi: 10.1016/j.rser.2016.09.128.
- [35] K. Zeng and D. Zhang, 'Recent progress in alkaline water electrolysis for hydrogen production and applications', *Prog. Energy Combust. Sci.*, vol. 36, no. 3, pp. 307–326, 2010, doi: 10.1016/j.pecs.2009.11.002.
- [36] Y. N. Li, R. Ma, L. N. He, and Z. F. Diao, 'Homogeneous hydrogenation of carbon dioxide to methanol', *Catal. Sci. Technol.*, vol. 4, no. 6, pp. 1498–1512, 2014, doi: 10.1039/c3cy00564j.
- [37] J. Wu, Y. Huang, W. Ye, and Y. Li, 'CO<sub>2</sub> Reduction: From the Electrochemical to Photochemical Approach', *Adv. Sci.*, vol. 4, no. 11, pp. 1–29, 2017, doi: 10.1002/advs.201700194.
- [38] O. Tursunov, L. Kustov, and A. Kustov, 'A Brief Review of Carbon Dioxide Hydrogenation to Methanol Over Copper and Iron Based Catalysts', *Oil Gas Sci. Technol.*, vol. 72, no. 5, p. 30, 2017, doi: 10.2516/ogst/2017027.
- [39] N. A. M. Razali, K. T. Lee, S. Bhatia, and A. R. Mohamed, 'Heterogeneous catalysts for production of chemicals using carbon dioxide as raw material: A review', *Renew. Sustain. Energy Rev.*, vol. 16, pp. 4951–4964, 2012, doi: 10.1016/j.rser.2012.04.012.
- [40] T. Witton, S. Bumrungsalee, M. Chareonpanich, and J. Limtrakul, 'Effect of hierarchical meso-macroporous alumina-supported copper catalyst for methanol synthesis from CO<sub>2</sub> hydrogenation', *Energy Convers. Manag.*, vol. 103, pp. 886–894, 2015, doi: 10.1016/j.enconman.2015.07.033.
- [41] H. Ren, C. H. Xu, H. Y. Zhao, Y. X. Wang, J. Y. J. Liu, and J. Y. J. Liu, 'Methanol synthesis from CO<sub>2</sub> hydrogenation over Cu/γ-Al<sub>2</sub>O<sub>3</sub> catalysts modified by ZnO, ZrO<sub>2</sub> and MgO', *J. Ind. Eng. Chem.*, vol. 28, pp. 261–267, 2015, doi: 10.1016/j.jiec.2015.03.001.
- [42] Y. Zhang, J. Fei, Y. Yu, and X. Zheng, 'Methanol synthesis from CO<sub>2</sub> hydrogenation over Cu based catalyst supported on zirconia modified γ-Al<sub>2</sub>O<sub>3</sub>', *Energy Convers. Manag.*, vol. 47, pp. 3360–3367, 2006, doi: 10.1016/j.enconman.2006.01.010.
- [43] A. Bansode, B. Tidona, P. R. Von Rohr, and A. Urakawa, 'Impact of K and Ba

- promoters on CO<sub>2</sub> hydrogenation over Cu/Al<sub>2</sub>O<sub>3</sub> catalysts at high pressure', *Catal. Sci. Technol.*, vol. 3, no. 3, pp. 767–778, 2013, doi: 10.1039/c2cy20604h.
- [44] G. X. Qi, X. M. Zheng, J. H. Fei, and Z. Y. Hou, 'Low-temperature methanol synthesis catalyzed over Cu/γ-Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> for CO<sub>2</sub> hydrogenation', *Catal. Letters*, vol. 72, no. 3–4, pp. 191–196, 2001, doi: 10.1023/A:1009049523210.
- [45] Y. Zhang, J. Fei, Y. Yu, and X. Zheng, 'Study of CO<sub>2</sub> Hydrogenation to Methanol over Cu-V/γ-Al<sub>2</sub>O<sub>3</sub> Catalyst', *J. Nat. Gas Chem.*, vol. 16, pp. 12–15, 2007, doi: 10.1016/S1003-9953(07)60019-X.
- [46] J. B. Wang, H. K. Lee, and T. J. Huang, 'Synergistic catalysis of carbon dioxide hydrogenation into methanol by yttria-doped ceria/γ-alumina-supported copper oxide catalysts: Effect of support and dopant', *Catal. Letters*, vol. 83, no. 1–2, pp. 79–86, 2002, doi: 10.1023/A:1020613700495.
- [47] R. Raudaskoski, M. V. Niemelä, and R. L. Keiski, 'The effect of ageing time on co-precipitated Cu/ZnO/ZrO<sub>2</sub> catalysts used in methanol synthesis from CO<sub>2</sub> and H<sub>2</sub>', *Top. Catal.*, vol. 45, no. 1–4, pp. 57–60, 2007, doi: 10.1007/s11244-007-0240-9.
- [48] J. Xiao, D. Mao, X. Guo, and J. Yu, 'Effect of TiO<sub>2</sub>, ZrO<sub>2</sub>, and TiO<sub>2</sub>-ZrO<sub>2</sub> on the performance of CuO-ZnO catalyst for CO<sub>2</sub> hydrogenation to methanol', *Appl. Surf. Sci.*, vol. 338, pp. 146–153, 2015, doi: 10.1016/j.apsusc.2015.02.122.
- [49] M. Saito, T. Fujitani, M. Takeuchi, and T. Watanabe, 'Development of copper/zinc oxide-based multicomponent catalysts for methanol synthesis from carbon dioxide and hydrogen', *Appl. Catal. A Gen.*, vol. 138, pp. 311–318, 1996, doi: 10.1016/0926-860X(95)00305-3.
- [50] J. Toyir, P. Ramírez De La Piscina, J. L. G. Fierro, and N. Homs, 'Highly effective conversion of CO<sub>2</sub> to methanol over supported and promoted copper-based catalysts: Influence of support and promoter', *Appl. Catal. B Environ.*, vol. 29, pp. 207–215, 2001, doi: 10.1016/S0926-3373(00)00205-8.
- [51] J. Toyir, P. R. De la Piscina, J. L. G. Fierro, and N. Homs, 'Catalytic performance for CO<sub>2</sub> conversion to methanol of gallium-promoted copper-based catalysts: Influence of metallic precursors', *Appl. Catal. B Environ.*, vol. 34, pp. 255–266, 2001, doi: 10.1016/S0926-3373(01)00203-X.
- [52] M. M. J. Li, Z. Zeng, F. Liao, X. Hong, and S. C. E. Tsang, 'Enhanced CO<sub>2</sub> hydrogenation to methanol over CuZn nanoalloy in Ga modified Cu/ZnO catalysts', *J. Catal.*, vol. 343, pp. 157–167, 2016, doi: 10.1016/j.jcat.2016.03.020.
- [53] J. Xiao, D. Mao, X. Guo, and J. Yu, 'Methanol Synthesis from CO<sub>2</sub> Hydrogenation over CuO-ZnO-TiO<sub>2</sub> Catalysts: The Influence of TiO<sub>2</sub> Content', *Energy Technol.*, vol. 3, no. 1, pp. 32–39, 2015, doi: 10.1002/ente.201402091.
- [54] M. Sadeghinia, M. Rezaei, A. Nemati Kharat, M. Namayandeh Jorabchi, B. Nematollahi, and F. Zareiekordshouli, 'Effect of In<sub>2</sub>O<sub>3</sub> on the structural properties and catalytic performance of the CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst in CO<sub>2</sub> and CO hydrogenation to methanol', *Mol. Catal.*, vol. 484, p. 110776, 2020, doi: 10.1016/j.mcat.2020.110776.
- [55] A. Le Valant, C. Comminges, C. Tisseraud, C. Canaff, L. Pinard, and Y.

- Pouilloux, 'The Cu-ZnO synergy in methanol synthesis from CO<sub>2</sub>, Part 1: Origin of active site explained by experimental studies and a sphere contact quantification model on Cu + ZnO mechanical mixtures', *J. Catal.*, vol. 324, pp. 41–49, 2015, doi: 10.1016/j.jcat.2015.01.021.
- [56] T. Witoon, T. Permsirivanich, W. Donphai, A. Jaree, and M. Chareonpanich, 'CO<sub>2</sub> hydrogenation to methanol over Cu/ZnO nanocatalysts prepared via a chitosan-assisted co-precipitation method', *Fuel Process. Technol.*, vol. 116, pp. 72–78, 2013, doi: 10.1016/j.fuproc.2013.04.024.
- [57] M. Mureddu, F. Ferrara, and A. Pettinau, 'Highly efficient CuO/ZnO/ZrO<sub>2</sub>@SBA-15 nanocatalysts for methanol synthesis from the catalytic hydrogenation of CO<sub>2</sub>', *Appl. Catal. B Environ.*, vol. 258, p. 117941, 2019, doi: 10.1016/j.apcatb.2019.117941.
- [58] M. K. Koh, M. Khavarian, S. P. Chai, and A. R. Mohamed, 'The morphological impact of siliceous porous carriers on copper-catalysts for selective direct CO<sub>2</sub> hydrogenation to methanol', *Int. J. Hydrogen Energy*, vol. 43, pp. 9334–9342, 2018, doi: 10.1016/j.ijhydene.2018.03.202.
- [59] M. K. Koh, Y. J. Wong, S. P. Chai, and A. R. Mohamed, 'Carbon dioxide hydrogenation to methanol over multi-functional catalyst: Effects of reactants adsorption and metal-oxide(s) interfacial area', *J. Ind. Eng. Chem.*, vol. 62, pp. 156–165, 2018, doi: 10.1016/j.jiec.2017.12.053.
- [60] X. Jiang, N. Koizumi, X. Guo, and C. Song, 'Bimetallic Pd-Cu catalysts for selective CO<sub>2</sub> hydrogenation to methanol', *Appl. Catal. B Environ.*, vol. 170–171, pp. 173–185, 2015, doi: 10.1016/j.apcatb.2015.01.010.
- [61] H. Yang *et al.*, 'Core-shell structured Cu@m-SiO<sub>2</sub> and Cu/ZnO@m-SiO<sub>2</sub> catalysts for methanol synthesis from CO<sub>2</sub> hydrogenation', *Catal. Commun.*, vol. 84, pp. 56–60, 2016, doi: 10.1016/j.catcom.2016.06.010.
- [62] T. C. Schilke, I. A. Fisher, and A. T. Bell, 'In Situ Infrared Study of Methanol Synthesis from CO<sub>2</sub>/H<sub>2</sub> on Titania and Zirconia Promoted Cu/SiO<sub>2</sub>', *J. Catal.*, vol. 184, pp. 144–156, 1999, doi: 10.1006/jcat.1999.2434.
- [63] P. B. Sanguineti, M. A. Baltanás, and A. L. Bonivardi, 'Copper-gallia interaction in Cu-Ga<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalysts for methanol production from carbon oxide(s) hydrogenation', *Appl. Catal. A Gen.*, vol. 504, pp. 476–481, 2015, doi: 10.1016/j.apcata.2014.11.021.
- [64] J. Liu *et al.*, 'Surface active structure of ultra-fine Cu/ZrO<sub>2</sub> catalysts used for the CO<sub>2</sub> + H<sub>2</sub> to methanol reaction', *Appl. Catal. A Gen.*, vol. 218, pp. 113–119, 2001, doi: 10.1016/S0926-860X(01)00625-1.
- [65] T. Witoon, J. Chalorngtham, P. Dumrongbunditkul, M. Chareonpanich, and J. Limtrakul, 'CO<sub>2</sub> hydrogenation to methanol over Cu/ZrO<sub>2</sub> catalysts: Effects of zirconia phases', *Chem. Eng. J.*, vol. 293, pp. 327–336, 2016, doi: 10.1016/j.cej.2016.02.069.
- [66] F. Arena, G. Mezzatesta, G. Zafarana, G. Trunfio, F. Frusteri, and L. Spadaro, 'How oxide carriers control the catalytic functionality of the Cu-ZnO system in the hydrogenation of CO<sub>2</sub> to methanol', *Catal. Today*, vol. 210, pp. 39–46, 2013, doi: 10.1016/j.cattod.2013.02.016.

- [67] F. Arena, K. Barbera, G. Italiano, G. Bonura, L. Spadaro, and F. Frusteri, 'Synthesis, characterization and activity pattern of Cu-ZnO/ZrO<sub>2</sub> catalysts in the hydrogenation of carbon dioxide to methanol', *J. Catal.*, vol. 249, pp. 185–194, 2007, doi: 10.1016/j.jcat.2007.04.003.
- [68] X. M. Liu, G. Q. Lu, and Z. F. Yan, 'Nanocrystalline zirconia as catalyst support in methanol synthesis', *Appl. Catal. A Gen.*, vol. 279, pp. 241–245, 2005, doi: 10.1016/j.apcata.2004.10.040.
- [69] S. Tada and S. Satokawa, 'Effect of Ag loading on CO<sub>2</sub>-to-methanol hydrogenation over Ag/CuO/ZrO<sub>2</sub>', *Catal. Commun.*, vol. 113, pp. 41–45, 2018, doi: 10.1016/j.catcom.2018.05.009.
- [70] X. Guo, D. Mao, G. Lu, S. Wang, and G. Wu, 'The influence of La doping on the catalytic behavior of Cu/ZrO<sub>2</sub> for methanol synthesis from CO<sub>2</sub> hydrogenation', *J. Mol. Catal. A Chem.*, vol. 345, pp. 60–68, 2011, doi: 10.1016/j.molcata.2011.05.019.
- [71] T. Witoon *et al.*, 'Enhanced activity, selectivity and stability of a CuO-ZnO-ZrO<sub>2</sub> catalyst by adding graphene oxide for CO<sub>2</sub> hydrogenation to methanol', *Chem. Eng. J.*, vol. 334, pp. 1781–1791, 2018, doi: 10.1016/j.cej.2017.11.117.
- [72] V. Deerattrakul, P. Dittanet, M. Sawangphruk, and P. Kongkachuichay, 'CO<sub>2</sub> hydrogenation to methanol using Cu-Zn catalyst supported on reduced graphene oxide nanosheets', *J. CO<sub>2</sub> Util.*, vol. 16, pp. 104–113, 2016, doi: 10.1016/j.jcou.2016.07.002.
- [73] Y. J. Fan and S. F. Wu, 'A graphene-supported copper-based catalyst for the hydrogenation of carbon dioxide to form methanol', *J. CO<sub>2</sub> Util.*, vol. 16, no. March, pp. 150–156, 2016, doi: 10.1016/j.jcou.2016.07.001.
- [74] Z. Shi, Q. Tan, and D. Wu, 'Enhanced CO<sub>2</sub> hydrogenation to methanol over TiO<sub>2</sub> nanotubes-supported CuO-ZnO-CeO<sub>2</sub> catalyst', *Appl. Catal. A Gen.*, vol. 581, pp. 58–66, 2019, doi: 10.1016/j.apcata.2019.05.019.
- [75] C. Liu, X. Guo, Q. Guo, D. Mao, J. Yu, and G. Lu, 'Methanol synthesis from CO<sub>2</sub> hydrogenation over copper catalysts supported on MgO-modified TiO<sub>2</sub>', *J. Mol. Catal. A Chem.*, vol. 425, pp. 86–93, 2016, doi: 10.1016/j.molcata.2016.09.032.
- [76] P. Sripada, J. Kimpton, A. Barlow, T. Williams, S. Kandasamy, and S. Bhattacharya, 'Investigating the dynamic structural changes on Cu/CeO<sub>2</sub> catalysts observed during CO<sub>2</sub> hydrogenation', *J. Catal.*, vol. 381, pp. 415–426, 2020, doi: 10.1016/j.jcat.2019.11.017.
- [77] E. J. Choi, Y. H. Lee, D. W. Lee, D. J. Moon, and K. Y. Lee, 'Hydrogenation of CO<sub>2</sub> to methanol over Pd-Cu/CeO<sub>2</sub> catalysts', *Mol. Catal.*, vol. 434, pp. 146–153, 2017, doi: 10.1016/j.mcat.2017.02.005.
- [78] Q. Tan, Z. Shi, and D. Wu, 'CO<sub>2</sub> Hydrogenation to Methanol over a Highly Active Cu-Ni/CeO<sub>2</sub>-Nanotube Catalyst', *Ind. Eng. Chem. Res.*, vol. 57, no. 31, pp. 10148–10158, 2018, doi: 10.1021/acs.iecr.8b01246.
- [79] X. Guo, D. Mao, G. Lu, S. Wang, and G. Wu, 'Glycine-nitrate combustion synthesis of CuO-ZnO-ZrO<sub>2</sub> catalysts for methanol synthesis from CO<sub>2</sub> hydrogenation', *J. Catal.*, vol. 271, pp. 178–185, 2010, doi: 10.1016/j.jcat.2010.01.009.



- [80] X. Guo, D. Mao, S. Wang, G. Wu, and G. Lu, 'Combustion synthesis of CuO-ZnO-ZrO<sub>2</sub> catalysts for the hydrogenation of carbon dioxide to methanol', *Catal. Commun.*, vol. 10, pp. 1661–1664, 2009, doi: 10.1016/j.catcom.2009.05.004.
- [81] X. Guo, D. Mao, G. Lu, S. Wang, and G. Wu, 'CO<sub>2</sub> hydrogenation to methanol over Cu/ZnO/ZrO<sub>2</sub> catalysts prepared via a route of solid-state reaction', *Catal. Commun.*, vol. 12, pp. 1095–1098, 2011, doi: 10.1016/j.catcom.2011.03.033.
- [82] G. Bonura, M. Cordaro, C. Cannilla, F. Arena, and F. Frusteri, 'The changing nature of the active site of Cu-Zn-Zr catalysts for the CO<sub>2</sub> hydrogenation reaction to methanol', *Appl. Catal. B Environ.*, vol. 152–153, pp. 152–161, 2014, doi: 10.1016/j.apcatb.2014.01.035.
- [83] J. Słoczyński *et al.*, 'Catalytic activity of the M/(3ZnO·ZrO<sub>2</sub>) system (M = Cu, Ag, Au) in the hydrogenation of CO<sub>2</sub> to methanol', *Appl. Catal. A Gen.*, vol. 278, pp. 11–23, 2004, doi: 10.1016/j.apcata.2004.09.014.
- [84] X. Dong, F. Li, N. Zhao, F. Xiao, J. Wang, and Y. Tan, 'CO<sub>2</sub> hydrogenation to methanol over Cu/ZnO/ZrO<sub>2</sub> catalysts prepared by precipitation-reduction method', *Appl. Catal. B Environ.*, vol. 191, pp. 8–17, Aug. 2016, doi: 10.1016/j.apcatb.2016.03.014.
- [85] C. Li, X. Yuan, and K. Fujimoto, 'Development of highly stable catalyst for methanol synthesis from carbon dioxide', *Appl. Catal. A Gen.*, vol. 469, pp. 306–311, 2014, doi: 10.1016/j.apcata.2013.10.010.
- [86] T. Phongamwong *et al.*, 'CO<sub>2</sub> hydrogenation to methanol over CuO–ZnO–ZrO<sub>2</sub>–SiO<sub>2</sub> catalysts: Effects of SiO<sub>2</sub> contents', *Chem. Eng. J.*, vol. 316, pp. 692–703, 2017, doi: 10.1016/j.cej.2017.02.010.
- [87] H. Ban, C. Li, K. Asami, and K. Fujimoto, 'Influence of rare-earth elements (La, Ce, Nd and Pr) on the performance of Cu/Zn/Zr catalyst for CH<sub>3</sub>OH synthesis from CO<sub>2</sub>', *Catal. Commun.*, vol. 54, pp. 50–54, 2014, doi: 10.1016/j.catcom.2014.05.014.
- [88] G. Wang, D. Mao, X. Guo, and J. Yu, 'Enhanced performance of the CuO-ZnO-ZrO<sub>2</sub> catalyst for CO<sub>2</sub> hydrogenation to methanol by WO<sub>3</sub> modification', *Appl. Surf. Sci.*, vol. 456, pp. 403–409, 2018, doi: 10.1016/j.apsusc.2018.06.090.
- [89] G. Wang, D. Mao, X. Guo, and J. Yu, 'Methanol synthesis from CO<sub>2</sub> hydrogenation over CuO-ZnO-ZrO<sub>2</sub>-M<sub>x</sub>O<sub>y</sub> catalysts (M=Cr, Mo and W)', *Int. J. Hydrogen Energy*, vol. 44, pp. 4197–4207, 2019, doi: 10.1016/j.ijhydene.2018.12.131.
- [90] J. Słoczyński *et al.*, 'Effect of metal oxide additives on the activity and stability of Cu/ZnO/ZrO<sub>2</sub> catalysts in the synthesis of methanol from CO<sub>2</sub> and H<sub>2</sub>', *Appl. Catal. A Gen.*, vol. 310, pp. 127–137, 2006, doi: 10.1016/j.apcata.2006.05.035.
- [91] M. Lachowska and J. Skrzypek, 'Methanol synthesis from carbon dioxide and hydrogen over Mn-promoted copper/zinc/zirconia catalysts', *React. Kinet. Catal. Lett.*, vol. 83, no. 2, pp. 269–273, 2004, doi: 10.1023/B:REAC.0000046086.93121.36.
- [92] H. Lei, Z. Hou, and J. Xie, 'Hydrogenation of CO<sub>2</sub> to CH<sub>3</sub>OH over CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts prepared via a solvent-free routine', *Fuel*, vol. 164, pp. 191–198, 2016, doi: 10.1016/j.fuel.2015.09.082.

- [93] Z. S. Hong, Y. Cao, J. F. Deng, and K. N. Fan, 'CO<sub>2</sub> hydrogenation to methanol over Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalysts prepared by a novel gel-network-coprecipitation method', *Catal. Letters*, vol. 82, no. 1–2, pp. 37–44, 2002, doi: 10.1023/A:1020531822590.
- [94] P. Gao *et al.*, 'Influence of Zr on the performance of Cu/Zn/Al/Zr catalysts via hydrotalcite-like precursors for CO<sub>2</sub> hydrogenation to methanol', *J. Catal.*, vol. 298, pp. 51–60, 2013, doi: 10.1016/j.jcat.2012.10.030.
- [95] L. Zhang, Y. Zhang, and S. Chen, 'Effect of promoter SiO<sub>2</sub>, TiO<sub>2</sub> or SiO<sub>2</sub>-TiO<sub>2</sub> on the performance of CuO-ZnO-Al<sub>2</sub>O<sub>3</sub> catalyst for methanol synthesis from CO<sub>2</sub> hydrogenation', *Appl. Catal. A Gen.*, vol. 415–416, pp. 118–123, 2012, doi: 10.1016/j.apcata.2011.12.013.
- [96] P. Gao *et al.*, 'Influence of modifier (Mn, La, Ce, Zr and Y) on the performance of Cu/Zn/Al catalysts via hydrotalcite-like precursors for CO<sub>2</sub> hydrogenation to methanol', *Appl. Catal. A Gen.*, vol. 468, pp. 442–452, 2013, doi: 10.1016/j.apcata.2013.09.026.
- [97] I. Melián-Cabrera, M. López Granados, and J. L. G. Fierro, 'Reverse Topotactic Transformation of a Cu-Zn-Al catalyst during Tet Pd Impregnation: Relevance for the Performance in Methanol Synthesis from CO<sub>2</sub>/H<sub>2</sub> Mixtures', *J. Catal.*, vol. 210, pp. 273–284, 2002, doi: 10.1006/jcat.2002.3676.
- [98] P. Gao *et al.*, 'Influence of fluorine on the performance of fluorine-modified Cu/Zn/Al catalysts for CO<sub>2</sub> hydrogenation to methanol', *J. CO<sub>2</sub> Util.*, vol. 2, pp. 16–23, 2013, doi: 10.1016/j.jcou.2013.06.003.
- [99] P. Gao *et al.*, 'Preparation and activity of Cu/Zn/Al/Zr catalysts via hydrotalcite-containing precursors for methanol synthesis from CO<sub>2</sub> hydrogenation', *Catal. Sci. Technol.*, vol. 2, no. 7, pp. 1447–1454, 2012, doi: 10.1039/c2cy00481j.
- [100] P. Gao *et al.*, 'Cu/Zn/Al/Zr catalysts via phase-pure hydrotalcite-like compounds for methanol synthesis from carbon dioxide', *J. CO<sub>2</sub> Util.*, vol. 11, pp. 41–48, 2015, doi: 10.1016/j.jcou.2014.12.008.
- [101] X. An, J. Li, Y. Zuo, Q. Zhang, D. Wang, and J. Wang, 'A Cu/Zn/Al/Zr fibrous catalyst that is an improved CO<sub>2</sub> hydrogenation to methanol catalyst', *Catal. Letters*, vol. 118, no. 3–4, pp. 264–269, 2007, doi: 10.1007/s10562-007-9182-x.
- [102] P. Gao *et al.*, 'Fluorine-modified Cu/Zn/Al/Zr catalysts via hydrotalcite-like precursors for CO<sub>2</sub> hydrogenation to methanol', *Catal. Commun.*, vol. 50, pp. 78–82, 2014, doi: 10.1016/j.catcom.2014.03.006.
- [103] D. Chen, D. Mao, J. Xiao, X. Guo, and J. Yu, 'CO<sub>2</sub> hydrogenation to methanol over CuO-ZnO-TiO<sub>2</sub>-ZrO<sub>2</sub>: a comparison of catalysts prepared by sol-gel, solid-state reaction and solution-combustion', *J. Sol-Gel Sci. Technol.*, vol. 86, no. 3, pp. 719–730, 2018, doi: 10.1007/s10971-018-4680-4.
- [104] G. Wang, L. Chen, Y. Sun, J. Wu, M. Fu, and D. Ye, 'Carbon dioxide hydrogenation to methanol over Cu/ZrO<sub>2</sub>/CNTs: Effect of carbon surface chemistry', *RSC Adv.*, vol. 5, no. 56, pp. 45320–45330, 2015, doi: 10.1039/c5ra04774a.
- [105] S. Li, L. Guo, and T. Ishihara, 'Hydrogenation of CO<sub>2</sub> to methanol over Cu/AlCeO catalyst', *Catal. Today*, vol. 339, pp. 352–361, 2020, doi:

10.1016/j.cattod.2019.01.015.

- [106] J. Haber, J. H. Block, and B. Delmon, 'Manual of methods and procedures for catalyst characterization (technical report)', *Pure Appl. Chem.*, vol. 67, no. 8–9, pp. 1257–1306, 1995, doi: 10.1351/pac199567081257.
- [107] N. M. Deraz, 'The comparative jurisprudence of catalysts preparation methods: I. precipitation and impregnation methods.', *J. Ind. Environ. Chem.*, vol. 2, no. 1, pp. 19–21, 2018.
- [108] N. M. Deraz, 'The comparative jurisprudence of catalysts preparation methods: II. Deposition-precipitation and adsorption methods.', *J Ind Env. Chem*, vol. 2, no. 2, pp. 1–3, 2018.
- [109] R. D. Gonzalez, T. Lopez, and R. Gomez, 'Sol-gel preparation of supported metal catalysts', *Catal. Today*, 1997, doi: 10.1016/S0920-5861(96)00162-9.
- [110] M. A. Cauqui and J. M. Rodríguez-Izquierdo, 'Application of the sol-gel methods to catalyst preparation', *J. Non. Cryst. Solids*, vol. 147–148, no. C, pp. 724–738, 1992, doi: 10.1016/S0022-3093(05)80707-0.
- [111] P. Bera, 'Solution Combustion Synthesis as a Novel Route to Preparation of Catalysts', *Int. J. Self-Propagating High-Temperature Synth.*, vol. 28, no. 2, pp. 77–109, 2019, doi: 10.3103/S106138621902002X.
- [112] K. C. Patil, S. T. Aruna, and T. Mimani, 'Combustion synthesis: an update', *Curr. Opin. Solid State Mater. Sci.*, vol. 6, no. 6, pp. 507–512, 2002, doi: 10.1016/S1359-0286(02)00123-7.
- [113] J. A. Schwarz, C. Contescu, and A. Contescu, 'Methods for Preparation of Catalytic Materials', *Chem. Rev.*, vol. 95, no. 3, pp. 477–510, 1995, doi: 10.1021/cr00035a002.
- [114] E. Lam *et al.*, 'CO<sub>2</sub> Hydrogenation on Cu/Al<sub>2</sub>O<sub>3</sub>: Role of the Metal/Support Interface in Driving Activity and Selectivity of a Bifunctional Catalyst', *Angew. Chemie*, vol. 131, no. 39, pp. 14127–14134, 2019, doi: 10.1002/ange.201908060.
- [115] W. Cai, P. R. De La Piscina, J. Toyir, and N. Homs, 'CO<sub>2</sub> hydrogenation to methanol over CuZnGa catalysts prepared using microwave-assisted methods', *Catal. Today*, vol. 242, pp. 193–199, 2015, doi: 10.1016/j.cattod.2014.06.012.
- [116] L. Jia, J. Gao, W. Fang, and Q. Li, 'Carbon dioxide hydrogenation to methanol over the pre-reduced LaCr<sub>0.5</sub>Cu<sub>0.5</sub>O<sub>3</sub> catalyst', *Catal. Commun.*, vol. 10, pp. 2000–2003, 2009, doi: 10.1016/j.catcom.2009.07.017.
- [117] H. Zhan *et al.*, 'Methanol synthesis from CO<sub>2</sub> hydrogenation over La-M-Cu-Zn-O (M = Y, Ce, Mg, Zr) catalysts derived from perovskite-type precursors', *J. Power Sources*, vol. 251, pp. 113–121, 2014, doi: 10.1016/j.jpowsour.2013.11.037.
- [118] L. Z. Gao and C. T. Au, 'CO<sub>2</sub> Hydrogenation to Methanol on a YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> Catalyst', *J. Catal.*, vol. 189, pp. 1–15, 2000, doi: 10.1006/jcat.1999.2682.
- [119] Y. F. Zhao, Y. Yang, C. Mims, C. H. F. F. Peden, J. Li, and D. Mei, 'Insight into methanol synthesis from CO<sub>2</sub> hydrogenation on Cu(1 1 1): Complex reaction network and the effects of H<sub>2</sub>O', *J. Catal.*, vol. 281, no. 2, pp. 199–211, 2011,

doi: 10.1016/j.jcat.2011.04.012.

- [120] M. Kourtelesis, K. Kousi, and D. I. Kondarides, 'CO<sub>2</sub> Hydrogenation to Methanol over La<sub>2</sub>O<sub>3</sub>-promoted CuO/ZnO/Al<sub>2</sub>O<sub>3</sub> Catalysts: A Kinetic and Mechanistic Study', *Catalysts*, vol. 10, pp. 1–17, 2020, doi: 10.3390/catal10020183.
- [121] L. C. Grabow and M. Mavrikakis, 'Mechanism of Methanol Synthesis on Cu through CO<sub>2</sub> and CO Hydrogenation', *ACS Catal.*, vol. 1, no. 4, pp. 365–384, 2011, doi: 10.1021/cs200055d.
- [122] M. Qiu *et al.*, 'Insight into the mechanism for the methanol synthesis via the hydrogenation of CO<sub>2</sub> over a Co-modified Cu(100) surface: A DFT study', *J. Chem. Phys.*, vol. 145, no. 13, p. 134701, 2016, doi: 10.1063/1.4963384.
- [123] S. Kattel, P. J. Ramírez, J. G. Chen, J. A. Rodriguez, and P. Liu, 'Active sites for CO<sub>2</sub> hydrogenation to methanol on Cu/ZnO catalysts', *Science (80-. )*, vol. 355, pp. 1296–1299, 2017, doi: 10.1126/science.aan8074.
- [124] A. Karelovic, G. Galdames, J. C. Medina, C. Yévenes, Y. Barra, and R. Jiménez, 'Mechanism and structure sensitivity of methanol synthesis from CO<sub>2</sub> over SiO<sub>2</sub>-supported Cu nanoparticles', *J. Catal.*, vol. 369, pp. 415–426, 2019, doi: 10.1016/j.jcat.2018.11.012.
- [125] X. Nie *et al.*, 'Mechanistic Understanding of Alloy Effect and Water Promotion for Pd-Cu Bimetallic Catalysts in CO<sub>2</sub> Hydrogenation to Methanol', *ACS Catal.*, vol. 8, no. 6, pp. 4873–4892, 2018, doi: 10.1021/acscatal.7b04150.
- [126] X. K. Wu *et al.*, 'Mechanistic insight into the catalytically active phase of CO<sub>2</sub> hydrogenation on Cu/ZnO catalyst', *Appl. Surf. Sci.*, vol. 525, no. November 2019, p. 146481, 2020, doi: 10.1016/j.apsusc.2020.146481.
- [127] Y. M. Liu *et al.*, 'Reaction mechanisms of methanol synthesis from CO/CO<sub>2</sub> hydrogenation on Cu<sub>2</sub>O(111): Comparison with Cu(111)', *J. CO<sub>2</sub> Util.*, vol. 20, no. May, pp. 59–65, 2017, doi: 10.1016/j.jcou.2017.05.005.
- [128] Q. J. Hong and Z. P. Liu, 'Mechanism of CO<sub>2</sub> hydrogenation over Cu/ZrO<sub>2</sub>(2'12) interface from first-principles kinetics Monte Carlo simulations', *Surf. Sci.*, vol. 604, no. 21–22, pp. 1869–1876, 2010, doi: 10.1016/j.susc.2010.07.018.
- [129] T. Kakumoto and T. Watanabe, 'A theoretical study for methanol synthesis by CO<sub>2</sub> hydrogenation', *Catal. Today*, vol. 36, no. 1, pp. 39–44, 1997, doi: 10.1016/S0920-5861(96)00194-0.
- [130] H. Nakatsuji and Z. Hu, 'Mechanism of Methanol Synthesis on Cu(100) and Zn/Cu(100) Surfaces: Comparative Dipped Adcluster Model Study', *Int. J. Quantum Chem.*, vol. 77, no. 100, pp. 341–349, 2000.
- [131] Y. Yang, J. Evans, J. A. Rodriguez, M. G. White, and P. Liu, 'Fundamental studies of methanol synthesis from CO<sub>2</sub> hydrogenation on Cu(111), Cu clusters, and Cu/ZnO(0001)', *Phys. Chem. Chem. Phys.*, vol. 12, no. 33, pp. 9909–9917, 2010, doi: 10.1039/c001484b.
- [132] Z. M. Hu, K. Takahashi, and H. Nakatsuji, 'Mechanism of the hydrogenation of CO<sub>2</sub> to methanol on a Cu(100) surface: dipped adcluster model study', *Surf. Sci.*, vol. 442, no. 1, pp. 90–106, 1999, doi: 10.1016/S0039-6028(99)00900-0.
- [133] P. Wu and B. Yang, 'Significance of Surface Formate Coverage on the Reaction

- Kinetics of Methanol Synthesis from CO<sub>2</sub> Hydrogenation over Cu', *ACS Catal.*, vol. 7, no. 10, pp. 7187–7195, 2017, doi: 10.1021/acscatal.7b01910.
- [134] F. Studt *et al.*, 'The Mechanism of CO and CO<sub>2</sub> Hydrogenation to Methanol over Cu-Based Catalysts', *ChemCatChem*, vol. 7, no. 7, pp. 1105–1111, 2015, doi: 10.1002/cctc.201500123.
- [135] T. Fujitani, I. Nakamura, T. Uchijima, and J. Nakamura, 'The kinetics and mechanism of methanol synthesis by hydrogenation of CO<sub>2</sub> over a Zn-deposited Cu(111) surface', *Surf. Sci.*, vol. 383, no. 2–3, pp. 285–298, 1997, doi: 10.1016/S0039-6028(97)00192-1.
- [136] W. Wang, Z. Qu, L. Song, and Q. Fu, 'Probing into the multifunctional role of copper species and reaction pathway on copper-cerium-zirconium catalysts for CO<sub>2</sub> hydrogenation to methanol using high pressure in situ DRIFTS', *J. Catal.*, vol. 382, pp. 129–140, 2020, doi: 10.1016/j.jcat.2019.12.022.
- [137] Z. Xu, Z. Qian, and H. Hattori, 'Mechanistic Study of the Hydrogenation of Carbon Dioxide to Methanol over Supported Rhenium and Copper–Zinc Catalysts', *Bull. Chem. Soc. Jpn.*, vol. 64, no. 11, pp. 3432–3437, 1991, doi: 10.1246/bcsj.64.3432.
- [138] Y. H. Wang, W. G. Gao, H. Wang, Y. E. Zheng, W. Na, and K. Z. Li, 'Structure-activity relationships of Cu-ZrO<sub>2</sub> catalysts for CO<sub>2</sub> hydrogenation to methanol: interaction effects and reaction mechanism', *RSC Adv.*, vol. 7, no. 14, pp. 8709–8717, 2017, doi: 10.1039/c6ra28305e.
- [139] L. Liu, F. Fan, Z. Jiang, X. Gao, J. Wei, and T. Fang, 'Mechanistic Study of Pd-Cu Bimetallic Catalysts for Methanol Synthesis from CO<sub>2</sub> Hydrogenation', *J. Phys. Chem. C*, vol. 121, no. 47, pp. 26287–26299, 2017, doi: 10.1021/acs.jpcc.7b06166.
- [140] Y. Yang, M. G. White, and P. Liu, 'Theoretical Study of Methanol Synthesis from CO<sub>2</sub> Hydrogenation on Metal-Doped Cu(111) Surfaces', *J. Phys. Chem. C*, vol. 116, no. 1, pp. 248–256, 2012, doi: 10.1021/jp208448c.
- [141] S. Kattel, B. Yan, Y. Yang, J. G. Chen, and P. Liu, 'Optimizing Binding Energies of Key Intermediates for CO<sub>2</sub> Hydrogenation to Methanol over Oxide-Supported Copper', *J. Am. Chem. Soc.*, vol. 138, no. 38, pp. 12440–12450, 2016, doi: 10.1021/jacs.6b05791.
- [142] L. Liu *et al.*, 'Mechanistic study of methanol synthesis from CO<sub>2</sub> hydrogenation on Rh-doped Cu(111) surfaces', *Mol. Catal.*, vol. 466, no. 28, pp. 26–36, 2019, doi: 10.1016/j.mcat.2019.01.009.

## 6. List of abbreviations

ALE	Atomic layer epitaxy
CH <sub>3</sub> OH	Methanol
CNT	Carbon nanotubes
CO	Carbon monoxide
CO <sub>2</sub>	Carbon dioxide
DFT	Density functional theory
DME	Dimethyl ether
DRIFTS	Diffuse reflectance infrared fourier transform spectroscopy
ER	Eley-Rideal
GO	Graphene-oxide
HAI	Hierarchical meso-macroporous alumina
HD	High dispersible
HR-TEM	High resolution transmission electron microscopy
HS	High surface
HTIs	Hydrotalcite-like compounds
LH	Langmuir-Hinshelwood
LS	Low surface
MW	Micro-wave
MeOH	Methanol
redGO	Reduced graphene-oxide
RWGS	Reverse water-gas shift
STY	Space-time-yield
TOF	Turn-over frequency
UAI	Unimodal mesoporous alumina
XRD	X-ray diffraction

## 7. List of figures

Figure 1: Annual CO <sub>2</sub> emissions from 1751-2017. Statistical differences means the difference between global estimate and the sum of the world regions.[9] .....	2
Figure 2: Chemical structure of carbon dioxide .....	2
Figure 3: Chemical structure of methanol (MeOH) .....	3
Figure 4: Formate pathway for methanol synthesis from CO <sub>2</sub> [120][121][122][123][124][125][126][127][128][129][130][131][132][133].....	49
Figure 5: RWGS reaction and CO hydrogenation pathway for methanol synthesis from CO <sub>2</sub> [139][140][141][142].....	54
Figure 6: Hydrocarboxyl pathway for methanol synthesis from CO <sub>2</sub> [119].....	56