



Review Article

Short Review: Mitigation of Current Environmental Concerns from Methanol Synthesis

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Abstract

Methanol has become a widely used and globally distributed product. Methanol is very important due to the current depletion of fossil fuels. Industrially, methanol was produced from the catalytic reaction of synthetic gas composed of hydrogen, carbon monoxide, and carbon dioxide. Methanol production has brought great attention due to the carbon dioxide as the main source of greenhouse gas emissions. Combined of reducing CO₂ emissions and supplying an alternative fuel source has created the idea of a carbon neutral cycle called "the methanol economy". The best catalyst for the methanol economy leads to a high CO₂ conversion and high selectivity for methanol production. This paper investigates a research focused on catalyst development for efficient methanol synthesis from hydrogenation of carbon dioxide through added various supports and additives such as silica, zirconium, and palladium. Catalysts that displayed the highest activity included a zirconia and silicon-titanium oxide promoted Cu/Zn/Al₂O₃ catalyst. Alternative method of catalyst preparation, including the oxalate-gel, solid-state reaction, co-precipitation and combustion method, also investigated. © 2013 BCREC UNDIP. All rights reserved

Keywords: Methanol; methanol synthesis; carbon dioxide; carbon dioxide hydrogenation; carbon dioxide conversion; methanol selectivity

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1. Introduction

Methanol has become an exceptionally flexible worldwide commodity. Over 90 plants of methanol with a total production capacity of roughly 75 million metric tons [1]. The methanol industry driven by traditional derivative and energy related appli-

cations. These include products used for producing adhesives, textiles, solvents and alternative fuels. Table 1 displays a list of methanol applications and description of their uses [2-7,8,9]. The demand for methanol reached 45.6 million metric tons and experienced a demand growth of 7% to 49 million tons in 2011 [10]. Methanol production as an alternative fuel has also coincided with the fossil fuel depletion.

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Fossil fuels cover roughly 80% of the energy needed worldwide and are not renewable on a human timescale [9]. Over-consumption of fossil fuels has also become a major concern. The global population will reach about 9 billion by 2050, leading to a severe depletion of fossil fuels [11]. It is estimated that oil, coal and natural gas reserves will last 35, 107 and 37 years respectively [12]. It has led to a search for an alternative to fossil fuels.

Excellent fuel source in internal combustion engines and direct methanol fuel cells (DMFC) has proven a methanol. Methanol and methanol blends also contain a higher octane rating than gasoline. This results in higher fuel efficiency [9,13]. In particular, methanol is regarded as the most suitable choice, because it has a high hydrogen-to-carbon ratio and, in comparison with alkane or higher alcohol reforming, methanol reforming shows lower selectivity to by-products, such as carbon monoxide and methane. Also, methanol has no C-C bonds, which reduces the risk of catalyst coking [14]. Methanol is conventionally obtained from syngas (CO+H₂), which can originate from non-renewable (fossil fuels) or renewable (biomass) feedstocks. Besides, the use of CO₂ as reactant is beneficial and particularly attractive among the viable strategies to valorize anthropogenic carbon dioxide emissions [15]. The establishment of the methanol plant lately has attracted attention to reducing greenhouse gas emissions through carbon recycling.

The burning of fossil fuels has led to climate change due to global warming or the greenhouse gas effect. Carbon dioxide (CO₂) has become the biggest source with six billion tons of carbon re-

leased as CO₂ every year [16]. Currently, the main producers of carbon dioxide emissions are natural gas (30%), coal/petroleum (43%) and oil (37%) [17].

It is predicted that CO₂ emission from natural gas, coal/petroleum, and oil will rise to 8.4 Gt, 14.4 Gt, and 12.6 Gt in 2035 from 5.6 Gt, 12.5 Gt, and 10.6 Gt in 2009 respectively [17]. The total world carbon dioxide emission predicted to reach 35.4 Gt by 2035 result an increase in the average temperature of the world 2.4 °C to 6.4 °C by 2100 [17]. The real growth of CO₂ emissions requires a need for carbon recycling technology.

A carbon neutral cycle provides a possible solution to the fossil fuel depletion and CO₂ emission crisis. CO₂ released upon combustion of fossil fuels. Available energy sources (solar, wind, geothermal, atomic) can offer the hydrogen to convert the released CO₂ into methanol. George Olah refers to this catalytic regenerative process as “the methanol economy” [9]. A highly selective catalyst for methanol formation and carbon dioxide conversion desired to reduce CO₂ emissions as well as offer an alternative fuel source and chemical feedstock. Currently the industrial methanol’s production is via synthetic gas. Synthetic gas composition included carbon monoxide, carbon dioxide, and hydrogen. Methanol synthesis used copper-based catalyst (Cu/ZnO/Al₂O₃) with co-precipitation method for preparation catalysts [18].

The author aims to provide a fundamental understanding of the methanol synthesis reaction, involved reaction, process parameters, as well as a summary of the of the latest catalyst discovery used for methanol synthesis by researchers.

Table 1. Applications of methanol

Applications	Description	References
Formaldehyde	Production of plastic, plywood, paint, and textiles.	[2]
Methyl Tertiary Butyl Ether (MTBE)	An additive in motor gasoline. To reduces harmful emission by vehicles.	[3]
Acetic acid	Raw material for production of monomer. It also used in coating, adhesive and ink.	[4]
Methylamines	Produce intermediates for chemicals agricultural.	[5]
Fuel source	Fuel in internal combustion engines and flexible fuel vehicles. Use in direct methanol fuel cells.	[6,9]
Dimethyl terephthalate (DMT)	Intermediate compound manufactured into polyester fibers, resin for bottles and other packaging applications.	[7]
Olefins	Feed reactant for ethylene/propylene production.	[8,9]

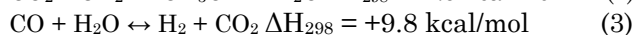
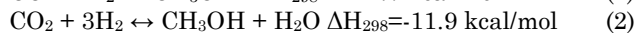
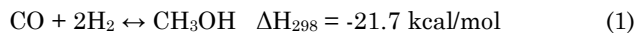
2. Materials and Method

The first industrial process was created by BASF in 1923 with the “high pressure” process to synthesize methanol. This process operated at 250-350 bar and 320-450 °C via zinc-based catalyst (ZnO/Cr₂O₃) [19]. The “high pressure” process dominated methanol production until the 1960s when Imperial Chemical Industries (ICI) found Zn as an optimal compound to disperse a copper-based catalyst. This enhanced catalyst allowed for a “low pressure” process operating at less severe conditions of 33-55 bar and 200-300 °C [19]. The only significant change to the industrial catalyst composition since the 1960s has been added with alumina [20]. Alumina was founded increase catalytic stability and led to create the dominant catalyst in worldwide methanol production [21].

Imperial Chemical Industries process low-pressure methanol synthesis [22]. Synthetic gas sent through a compressor where it heated and split off into two steams. One steam used to cool down the reactor and the other to offer the reagents for methanol synthesis. The effluent leaving the reactor then cooled by water to produce high-pressured steam and cooled further by running it counter currently with the inlet streams. The effluent is then cooled with air once more and sent into a separator where crude methanol and un-reacted gas can be separated. The un-reacted gas is recycled back into the inlet synthetic gas stream and crude methanol sent for further purification. Table 2 lists the locations and compositions of the commercial Cu/Zn/Al₂O₃ catalyst for key industrial companies [20,23].

3. Methanol synthesis

The principal reactions in methanol synthesis are as follows [9,20,21] :



The reactions include the hydrogenation of carbon monoxide (1), hydrogenation of carbon dioxide (2) and a reverse water gas shift reaction (3) (RWGS). Both hydrogenation reactions (1,2) are exothermic and result in volume reduction. The reaction favors high pressure and low temperature. Current synthesis processes use low pressures due to gas compression being costly and requiring high-energy input. Modern processes also use high temperature ranges to enable catalytic activity and efficient used the heat of reaction. Heat removal has become an important part of the process design [19].

There has been controversy on whether the formation of methanol is due to the reaction (1) or (2). Methanol formed from hydrogenated CO₂ which CO had RWGS reaction to produce H₂ and forming CO₂ henceforward converted to methanol [9,21]. Chinchin and co-workers [24] use isotopic labeling to locate a ¹⁴Carbon in the methanol product that was introduced in the carbon dioxide feed. It concluded that methanol synthesis must be directed by the hydrogenation of CO₂. Graaf and co-workers [25] conducted experiments on the methanol synthesis over a commercial catalyst. However, water produced more than accounted for thermodynamically. It is due to the reaction (3) is slower than another, so the direct hydrogenation of CO₂ into methanol must be the source of the excess water. Liu and co-workers [26] investigated the effect of feed composition on methanol synthesis over a Cu/ZnO catalyst. The rate of methanol production increased linearly with the CO₂/CO feed ratio. Water as byproduct can inhibited methanol production. However, small amounts of CO₂ or water is helpful to maintain the catalyst activity. The de-

Table 2. Location, reactor type, and compositions of industrial catalysts in wt% [20,23]

Company	Location	Reactor Type	CuO (wt%)	ZnO (wt%)	Al ₂ O ₃ (wt%)
BASF	Ludwigshafen, Germany	-	38.5	48.8	12.9
Dupont	Wilmington, Delaware (US)	-	50	19	31
Haldor Topsoe	Ravnholm, Denmark	Mutliple Bed Converter	>55	21 to 25	8 to 10
ICI	Millbank, London	Single Catalyst Bed	20 to 35	15 to 50	4 to 20
IFP	Rueil-Malmaison, France	-	45 to 70	15 to 35	4 to 20
Lurgi	Frankfurt, Germany	Shell and Tube Single Bed	60 to 70	20 to 30	5 to 15
Shell	Houston, Texas (US)	-	71	24	-
Sud Chemie	Munich, Germany	Slurry Reactor	65	22	12

bate over the mechanism has also led to an investigation on the performance of commercial catalysts from CO₂ hydrogenation.

The Cu/Zn/Al catalyst has been widely used and studied in the industry. However, the industrial catalyst has shown high methanol selectivity for CO-rich feed gas and not CO₂-rich feed gas. Table 3 shows the equilibrium data for carbon monoxide and carbon dioxide conversion via synthetic gas. The conversion of CO is substantially higher than CO₂ at all temperatures and pressures.

Schack and co-workers [30] claims that under industrial conditions carbon monoxide proceeds as the dominant reactant while under low temperature and pressure CO₂ hydrogenation. Studies have also shown that water produced from methanol synthesis from a CO₂-rich feed over commercial catalysts have led to the accelerated crystalline growth of copper and zinc [31]. The water produced from the RWGS reaction essentially accelerates oxidation and deactivation of active sites on the catalyst surface. [32] This crystalline growth known as sintering and has become the only considerable type of deactivation in methanol synthesis plants. Sintering results in a loss of the copper metal surface area, which is proportional to catalyst activity during industrial production [33].

Catalyst morphology does not affect the reaction mechanism but the rate of reaction [34]. A catalyst capable of converting a CO₂-rich feed with high methanol selectivity has become of utmost importance due to the greenhouse gas emission and fossil fuel problems. This has proven to research on a variety of additives and supports of the copper-based catalyst and preparation methods to meet the desired catalytic activity.

4. Catalysts

Methanol produced from the hydrogenation of carbon dioxide and carbon monoxide. However, this reaction favors higher alcohols as products rather than methanol. In order to optimize the methanol production, a specified catalyst is required with high methanol selectivity [35]. The current Cu/ZnO/Al₂O₃ catalyst (Table 4) has shown high activity for the carbon monoxide conversion and methanol selectivity. Therefore, alternative additive and supports have been investigated that show high activity for carbon dioxide conversion methanol selectivity.

4.1 Copper

Copper-based catalysts have been popular in reactions involving hydrogen. Copper-based catalyst utilized for hydrogenation, including the hydrogenation of carbon oxides such as methanol [36]. A key to a highly active catalyst is to have a large copper surface area. Karelavic and co-workers [34] claims that the rate of methanol formation increases linearly with the amount of copper surface atoms. In the case of CO formation through the reverse water gas shift reaction, the rate does not depend directly on the amount of copper atoms exposed. This illustrates the fact that CO formation is highly favored in some special sites that would account for a small fraction of the exposed copper atoms [34].

This high dispersion and small particle size of the active site is favorable for catalyst activity. Kakumoto and co-workers [37] suggested methanol synthesis exists on a Cu⁺ active site and follows the reaction pathway. However, there has been debate on whether metallic copper alone acts as an active site or copper-zinc interaction induces activity [38].

Table 3. Conversion of CO and CO₂ at equilibrium conditions using Cu/ZnO/Al₂O₃ catalyst

Pressure (bar)	20		25		40		50		70		150		300		References
Temperature (°C)	CO	CO ₂	CO	CO ₂	CO	CO ₂	CO	CO ₂	CO	CO ₂	CO	CO ₂	CO	CO ₂	
275	-	-	14.4	3.91	-	-	39.1	4.18	53.9	4.47	81.9	6.23	95.8	13.5	[27]
300	-	-	5.94	5.55	-	-	21.7	5.68	35.1	5.88	69.2	7.13	90.1	11.6	[27]
325	-	-	-	-	-	-	10.4	7.63	19.5	7.76	53.2	8.64	81.8	11.7	[27]
350	-	-	-	-	-	-	-	-	9.41	10.1	36.4	10.7	70.1	12.8	[27]
260	-	-	-	-	89.2	31.9	-	-	-	-	-	-	-	-	[28]
260	-	-	-	-	67.2	25.5	-	-	-	-	-	-	-	-	[28]
260	-	-	-	-	59.2	22.4	-	-	-	-	-	-	-	-	[28]
260	-	-	-	-	87.9	31.2	-	-	-	-	-	-	-	-	[28]
225	25	5.4	-	-	-	-	-	-	-	-	-	-	-	-	[29]
225	26	6.1	-	-	-	-	-	-	-	-	-	-	-	-	[29]
225	32.8	2.8	-	-	-	-	-	-	-	-	-	-	-	-	[29]
225	28.8	6.5	-	-	-	-	-	-	-	-	-	-	-	-	[29]
225	26.3	5.3	-	-	-	-	-	-	-	-	-	-	-	-	[29]

Due to a negative effect of water in the presence of the hydrophilic alumina carrier, is pressing the discovery of alternative catalyst formulations including copper as active phase and various oxide carriers and promoters [39] like Al_2O_3 [39, 40, 41, 42], CeO_2 [39], ZnO [39, 40, 41, 42], ZrO_2 [43, 44].

Al_2O_3 is one of the best-known catalyst-support materials frequently used in both research and industrial applications. Addition of Al_2O_3 improved the catalyst stability but the methanol conversion rate reduced considerably [45].

CeO_2 carrier promotes the surface functionality of the Cu–ZnO system though a negative influence on catalyst texture and metal surface area in comparison to ZrO_2 [39]. ZnO plays a fundamental role as promoter of both dispersion and catalytic functionality of the metal copper phase [39].

A number of researchers have reported positive effects from incorporating ZrO_2 in copper catalysts as a promoter or support. Zirconium has recently emerged as a particularly interesting support material. ZrO_2 presents special characteristics such as high fracture toughness, ionic conductivity, and stability even under reducing conditions. Moreover, the possession of both amphoteric and redox functions makes it appealing as a more suitable carrier for a number of catalytic applications [45].

4.2 Zinc

There have been various roles assigned to zinc during the methanol synthesis reaction. Some researchers believe zinc used to increase the dispersion of the Cu active site. Burch and co-workers [46] claimed ZnO may provide a reservoir for hydrogen atoms to spill over onto copper to hydrogenate an adsorbed formate species. However, Choi and co-workers [47] suggested ZnO migrates to the copper for create Cu-Zn active sites and promote methanol synthesis. Fujitani and co-workers [48] indicated the role of Zn as to promote the hydrogenation of formate into a methoxy intermediate. They also claimed ZnO to disperse Cu particles along with creating an active site. Although there was debate, the research has shown that ZnO had a beneficiary effect on methanol synthesis.

4.3 Zirconium

The promoter such as Zr is known to enhance the Cu/Zn dispersion and thus improve the catalytic activity of methanol synthesis catalysts. [49] Zirconium Oxide (ZrO_2) utilized as an effective carrier or an additive for methanol synthesis from CO_2 hydrogenation. ZrO_2 exhibits high ion exchange capacity, abundant oxygen vacancies, required properties of alkalinity/acidity and oxidation/reduction [43]. It was suggest that the role of

ZrO_2 during methanol synthesis is dependent on strong interactions between the copper and zirconia particles. Zirconium oxide also acts as a P-semiconductor and may make copper electron deficient [43]. This increases the copper ability to adsorbed hydrogen molecules as well as dissociated them [50]. Arenas and co-workers [50] suggested the reaction pathway for copper-based catalyst utilizing zirconium oxide. This synergistic interaction between zirconium and copper has made it a highly researched topic.

Zhuang and co-workers [43] investigated the structure and performance of Cu/ ZrO_2 catalyst for methanol synthesis from CO_2 hydrogenation through different preparation techniques. A fractional precipitation method led to higher surface area and pore volume but low catalyst activity. The impregnation precipitation method exhibited activity and lower surface area. The Cu $2p_{3/2}$ bond energies were also higher in the impregnation precipitation method. It was concluded that catalytic performance of Cu/ ZrO_2 should be depended greatly on the interaction between Cu and ZrO_2 rather than surface area.

Liu and co-workers [51] reported the effect of nanocrystalline zirconia support on the interparticle interactions of a copper/metal oxide based catalyst. The nanocrystalline zirconia exhibited 50% higher surface area than a conventionally prepared zirconium induced catalyst. This high dispersion of the metal species, CuO, leads to less sintering and agglomeration on the catalyst surface. The incorporation of nanocrystalline zirconia changed the physical structure of the catalyst. The isomorphous substitution of copper into the zirconia framework allowed for a higher surface energy and interaction between the metal components.

Yang and co-workers [41] conducted a comparative study on the effects of a ZrO_2 -doped Cu/ZnO catalyst versus the conventional Cu/ZnO catalyst. The ZrO_2 -doped catalyst existed fine particles that were more highly dispersed than the reference Cu/ZnO catalyst. The catalytic performance of Cu/ZnO from CO hydrogenation was higher at lower temperatures, but became almost equal at reaction temperatures above 523 K. The ZrO_2 -doped catalyst showed a higher CO_2 conversion from CO_2 rich syngas at all temperatures (483-543 K). However, the methanol selectivity started to decrease once the temperature reached 543 K. The maximum in methanol yield was observed at 523 K where the CO_2 conversion was 26.41% and methanol selectivity was 60.45%. The ZrO_2 -doped catalyst also exhibited very high catalytic stability running for 1000 h.

Zirconia shortcomings include low surface area

and poor thermal stability. Zhang and co-workers [44] examined the effects of modifying a high surface area γ -Al₂O₃ as supported copper-based catalyst with added Zirconia. Temperatures were investigated included 240 °C and 260 °C. Added 10 wt% of zirconium into Cu-based catalyst showed higher carbon dioxide conversion and methanol selectivity. It was verified that the added of zirconia enhanced the dispersion and interactions between CuO and the γ -Al₂O₃ species.

4.4 Silica

Silica is introduced to Cu/ZnO based catalysts in order to improve their physical properties. It was found that the addition of small amounts of silica helped suppress the crystallization of Cu and ZnO and also reduced their crystallite size [31,32].

Wu and co-workers [31] suggests that small particles of silica hinder the agglomeration of Cu and ZnO particles by covering their surfaces in the catalyst. Samei and co-workers [32] also investigated the effects of small amounts of silica (0.6 wt%) on the stability and activity of Cu/ZnO/Al₂O₃ catalysts from a CO₂-rich feed. It was observed that methanol space time yield (STY) and temperature increased dependently. It showed that the silicon oxide also induces the re-dispersion of copper at high temperatures.

Zhang and co-workers [40] examined the catalytic performance of the ternary CuO/ZnO/Al₂O₃ catalyst promoted with SiO₂, TiO₂ and SiO₂ combined with TiO₂ prepared by the co-precipitation method. The modified ternary catalysts increased the copper surface area and showed a better catalytic performance than without the promoters. Methanol formation hindered at high temperatures while low temperatures could not run the catalyst. The optimal reaction temperature indicated at 260 °C. The maximum CO₂ conversion (40.7%) and methanol selectivity (41.17%) were seen on the 2 wt% SiO₂-TiO₂/CuO-ZnO-Al₂O₃ catalyst. The combination of SiO₂ and TiO₂ led to weaker acid strength and higher acid concentration on the catalyst surface. This enhanced adsorption and dissociation of hydrogen molecules and weakened the adsorption of CO₂.

4.5 Palladium

The Pd catalysts would be potential candidate for the low-temperature CH₃OH synthesis from CO₂ and H₂ as well as CO and H₂ [52,53,54]. The effect of the use of palladium is very profitable for the synthesis of methanol via hydrogenation of CO₂, and also considered works as a reservoir for spillover hydrogen.

Sahibzada and co-workers [55] and Cabrera

and co-workers [56] both investigated the effects of palladium on Cu/ZnO/Al₂O₃ catalyst from CO₂ hydrogenation. The addition of palladium increased the activity of the catalyst. However, methanol formation had no dependency on Pd-loading. Pd not act as a catalytic site for methanol synthesis. Promotion effect of palladium was able to increase the reduction of copper oxide, whereas to enhance the activity of the methanol synthesis, hydrogen flows into Pd shared via hydrogen spillover to Cu. so it explained that the spillover effect against oxidizing effects of CO₂ or H₂O on the surface of copper [55,56].

Fujitana and co-workers [42] examined the support effects of palladium on various metal oxides for methanol synthesis from CO₂ hydrogenation. Low activity on Pd/SiO₂ indicated that palladium alone could not catalyze the reverse water gas shift (RWGS) reaction, which accounts for the spillover of hydrogen atoms onto the metal oxide surface to hydrogenate CO₂. The highest activity indicated by Pd/Ga₂O₃ with a yield of 10.1% as opposed to the conventional Cu/ZnO at 4.2%. This super-active catalyst was due to an optimal amount of Pd species and the stabilizing effect Ga_xO_y on the surface of the catalyst.

Collins and co-workers [57] reported that the formation of Pd-Ga bimetallic particles was identified by means of a combination of quasi-in situ transmission electron microscopy techniques and CO adsorption experiments. A progressive change in selectivity during the CO₂ reaction with H₂, increasing the yield of methanol at the expense of the undesired CO, was observed under typical process conditions.

4.6 Gallia

Chiavassa and co-workers [58] claimed the hydrogenation of CO₂/H₂ mixtures on Ga₂O₃-Pd/silica catalysts. The supported palladium crystallites, due the high H₂ dissociation capability of the metal, generate active H_s species which then migrate to surface Ga₂O₃ patches, thereby hydrogenating the chemisorbed CO₂; a bifunctional mechanism seems to be fully operational here.

The bifunctional synthesis pathway that leads to CH₃OH and CO on Ga₂O₃-Pd/silica catalysts using CO₂/H₂ mixtures operates through dissociation of molecular hydrogen on the palladium crystallites and further migration of atomic hydrogen to GaO_x, where a sequence of hydrogenation steps of the carbonaceous species operates [58].

Whenever the supply of atomic hydrogen to the gallia surface is sufficient, the most likely rate determining steps for the methanol synthesis and the RWGS reactions are the hydrogenation of formate

Table 4. Influenced of catalyst compositions, temperature of calcinations, temperature of drying, temperature of the reaction, H₂O/CH₃OH (S/M), O₂/CH₃OH (O/M) on the performance of different Cu and Zn based catalysts for autothermal reforming reaction of methanol

Catalyst	T _{reaction} (°C)	GHSV (h ⁻¹)	Pressure (MPa)	CO ₂ conversion (%)	CH ₃ OH selectivity (%)	CH ₃ OH yield (%)	References
Cu/ZnO/Al ₂ O ₃	220	3600	2.6	5.17	34.99	1.81	[40]
Cu/ZnO/Al ₂ O ₃	240	3600	2.6	8.32	30.86	2.57	[40]
Cu/ZnO/Al ₂ O ₃	260	3600	2.6	15.81	23.31	3.69	[40]
Cu/ZnO/Al ₂ O ₃	280	3600	2.6	16.69	12.74	2.13	[40]
Cu/ZnO/Al ₂ O ₃	300	3600	2.6	21.37	7.68	1.64	[40]
2wt% SiO ₂ /Cu/ZnO/Al ₂ O ₃	260	3600	2.6	20.24	27.15	5.5	[40]
2wt% TiO ₂ /Cu/ZnO/Al ₂ O ₃	260	3600	2.6	16.1	25.29	4.07	[40]
2wt% SiO ₂ -TiO ₂ /Cu/ZnO/Al ₂ O ₃	260	3600	2.6	40.7	41.17	16.76	[40]
Zr-Cu/ZnO	210	4000	5	17.31	55.29	-	[41]
Zr-Cu/ZnO	230	4000	5	23.46	58.88	-	[41]
Zr-Cu/ZnO	250	4000	5	26.41	60.45	-	[41]
Zr-Cu/ZnO	270	4000	5	27.91	51.12	-	[41]
CuZnO	210	4000	5	9.67	55.18	-	[41]
CuZnO	230	4000	5	13.61	49.08	-	[41]
CuZnO	250	4000	5	16.03	47.53	-	[41]
CuZnO	270	4000	5	20.47	40.12	-	[41]
Pd/Al ₂ O ₃	250	-	5	3.4	29.9	1	[42]
Pd/Cr ₂ O ₃	250	-	5	2.1	22.4	0.5	[42]
Pd/Ga ₂ O ₃	250	-	5	19.6	51.5	10.1	[42]
Pd/SiO ₂	250	-	5	0.05	100	0.05	[42]
Pd/TiO ₂	250	-	5	15.5	3.9	0.6	[42]
Pd/ZnO	250	-	5	13.8	37.5	5.2	[42]
Pd/ZrO ₂	250	-	5	0.4	4.3	0.02	[42]
Cu/ZnO	240	-	5	11.7	36.1	4.2	[42]
Cu/ZrO ₂ (FP)	250	5400	2	3.2	59.57	-	[43]
Cu/ZrO ₂ (IP)	250	5400	2	13.6	83.48	-	[43]
Cu/ZrO ₂ (SR)	250	5400	2	13.8	62.05	-	[43]
12Cu/γ- Al ₂ O ₃	240	1800	3	13.1	13.6	-	[44]
12Cu5Zr/γ- Al ₂ O ₃	240	1800	3	13.9	15.1	-	[44]
12Cu10Zr/γ- Al ₂ O ₃	240	1800	3	14.3	17.1	-	[44]
12Cu15Zr/γ- Al ₂ O ₃	240	1800	3	14.1	16	-	[44]
12Cu/γ- Al ₂ O ₃	240	3600	3	10.7	16.9	-	[44]
12Cu5Zr/γ- Al ₂ O ₃	240	3600	3	11.3	16.7	-	[44]
12Cu10Zr/γ- Al ₂ O ₃	240	3600	3	11.3	20.3	-	[44]
12Cu15Zr/γ- Al ₂ O ₃	240	3600	3	12	18.9	-	[44]
12Cu/γ- Al ₂ O ₃	260	3600	3	15.6	10.7	-	[44]
12Cu5Zr/γ- Al ₂ O ₃	260	3600	3	15.9	12.1	-	[44]
12Cu10Zr/γ- Al ₂ O ₃	260	3600	3	16.5	14.6	-	[44]
12Cu15Zr/γ- Al ₂ O ₃	260	3600	3	16.1	13	-	[44]
Cu/ZnO/Al ₂ O ₃ 01	240	3600	2	19.3	22.3	1.73	[60]
Cu/ZnO/Al ₂ O ₃ 01	240	10000	2	16.8	23.4	4.35	[60]
Cu/ZnO/Al ₂ O ₃ 02	240	3600	2	19.3	36.3	2.81	[60]
Cu/ZnO/Al ₂ O ₃ 02	240	10000	2	17.6	37.9	7.37	[60]
Cu/ZnO/Al ₂ O ₃ 03	240	3600	2	15.8	22.8	1.45	[60]
Cu/ZnO/Al ₂ O ₃ 03	240	10000	2	15.1	21.9	3.68	[60]
Cu/ZnO/ZrO ₂ 01	240	3600	2	18.5	36.3	6.7	[61]
Cu/ZnO/ZrO ₂ 01	240	7800	2	12.3	40.5	5	[61]
Cu/ZnO/ZrO ₂ 02	240	3600	2	17.1	36.6	6.3	[61]
Cu/ZnO/ZrO ₂ 02	240	7800	2	9.5	45.5	4.3	[61]
Cu/ZnO/ZrO ₂ 03	240	3600	2	18.5	38.4	7.1	[61]
Cu/ZnO/ZrO ₂ 03	240	7800	2	14	41.5	5.8	[61]
Cu/ZnO/ZrO ₂ 04	240	3600	2	18.7	36.7	6.9	[61]
Cu/ZnO/ZrO ₂ 04	240	7800	2	13.1	43	5.6	[61]
Cu/ZnO/ZrO ₂ 05	240	3600	2	17.53	33.08	5.8	[61]
Cu/ZnO/ZrO ₂ 05	240	7800	2	9.62	37.56	3.6	[61]
Cu/Zn/Zr-400	240	3600	3	15.7	58	9.1	[62]
Cu/Zn/Zr -500	240	3600	3	14.5	57.7	8.4	[62]
Cu/Zn/Zr -600	240	3600	3	14	56	7.8	[62]
Cu/Zn/Zr -700	240	3600	3	10.2	56.2	5.7	[62]
Cu/Zn/Zr -800	240	3600	3	5.1	63.3	3.2	[62]
Cu/ZnO/Al ₂ O ₃ 1	240	3600	2	18.8	34.7	6.5	[63]
Cu/ZnO/Al ₂ O ₃ 2	240	3600	2	18.6	37.3	6.9	[63]
Cu/ZnO/Al ₂ O ₃ 3	240	3600	2	18.9	38.2	7.2	[63]
Cu/ZnO/Al ₂ O ₃ 4	240	3600	2	15.5	30.7	4.8	[63]

to the fast reacting methylenebisoxo species, and the decomposition/ dehydroxylation of formate to give CO_(g), respectively [58].

A competitive adsorption mechanism, where adsorbed atomic hydrogen competes on the gallia for the same active sites occupied by the other surface intermediates, was found to be the most satisfactory, in terms of the physicochemical significance of the parameter estimates. Minimal residuals were found-for a wide range of process conditions- considering as kinetically relevant the simultaneous surface occupancy by formate, methylenebisoxo, hydroxyl and atomic hydrogen intermediates [58].

5. Preparation methods

Along with a change in the composition of a catalyst, hence the variations in the methods of preparation having a significant impact on the structure and activity of a catalyst for the synthesis of methanol of hydrogenated CO₂. The oxalate-gel precipitation, solid-state reaction and combustion methods provide an alternative approach to the conventional carbonate co-precipitation method.

5.1 Co-precipitation

Co-precipitation has been the conventional method in preparing current industrial catalysts. It utilizes a cation and an anion solution with a mixture of the desired metal nitrates and generally sodium carbonate. Wu and co-workers [59] investigated the optimal co-precipitation conditions for methanol synthesis from CO₂ hydrogenation. Cu/ZnO/ZrO₂/Al₂O₃/Ga₂O₃ and Cu/ZnO/ZrO₂/Al₂O₃ catalysts were prepared using Na₂CO₃ as a precipitant. They observed that the temperature of the preparation is the only variable that showed significant effects of the preparation on a catalyst. There is no difference in activity between the temperatures 273-313 K. However, activity was 7% lower at 333 K. This suggests temperatures should be lower than 313 K in order to prepare a highly active catalyst. Wu and co-workers [59] also noted that washing of sodium left on the catalyst after filtration of the precipitate is an important step. If sodium still remaining on the catalyst during calcinations, it will cause crystallization on the surface and reduce the activity of the catalytic.

5.2 Oxalate-gel precipitation

The oxalate-gel precipitation method begins with aqueous solutions of metal nitrates (generally 0.1 M each) dissolved in a specified solvent mixed with an aqueous solution (1 M) of 20% excess of oxalic acid. The mixture stirred vigorously at room

temperature (298 K). The precipitates separated through a centrifuge, dried and calcined under specific conditions [60,61]. Jingfa and co-workers [60] conducted experiments to analyzing the effects of the oxalate-gel precipitation method versus conventional oxalate and carbonate co-precipitation methods on the ternary Cu/ZnO/Al₂O₃ catalyst. Ethanol used as a solvent in gel-precipitation method [60]. The gel precipitation method exhibited ultrafine quasi-spherical particles as opposed to the conventional method, which produced larger particles. After calcinations, the gel precipitation method had a copper surface area of 28.8 m² g⁻¹ and pore volume of 0.23 ml g⁻¹ [60].

This result was much higher than the conventional method, which exhibited a copper surface area of 11.5 m² g⁻¹ and pore volume of 0.20 ml g⁻¹. This resulted in a higher activity of methanol synthesis from hydrogenation of CO₂. Ma and co-workers [61] also investigated the effects of the oxalate-gel precipitation method for methanol synthesis from CO₂ hydrogenation. Their experiment used four Cu/ZnO/ZrO₂ catalysts with their nitrate solutions dissolved in deionized water, DMF, ethanol and diethylene glycol. The experiment indicated that the physical properties of the solvents had great influence on structure and catalytic performance. The higher viscosities of ethanol and diethylene enabled slower nucleus growth rate and created finer particles [61]. However, the high surface tension of diethylene glycol caused shrinkage upon drying, agglomeration of precipitate and a structural collapse. Thus, the low surface tension, higher viscosity solvent ethanol proved to induce the highest catalytic activity.

5.3 Solid-state reaction

The solid-state reaction method provides an effective alternative of precipitation methods. The procedure process is simple, quick and does not require a solvent. The process includes the mixture of hydrated metal salts and a specified chemical reagent, which are then ground, dried and calcined [43,62]. Guo and co-workers [62] utilized the solid-state reaction method in the formation of a Cu/ZnO/ZrO₂ catalyst. Catalysts prepared by mixing copper, zinc and zirconium hydrated metal salts and then adding citric acid grounded in an agate mortar. The precursor was then dried and further calcined in air at various temperatures (400-800 °C). They claimed that the solid-state reaction under the same reaction conditions and compositions as their experiment, exhibited higher activity than carbonate co-precipitation and oxalate co-precipitation methods. The most active sample,

labeled CZZ-400 (CZZ was derived from the catalyst being composed of Copper, Zinc, and Zirconium while the 400 designated the calcinations temperature in Celsius), saw no visible decline in CO₂ conversion or methanol selectivity over a 96 h period. This signifies a highly stable performance by solid-state reaction as well. The Cu compositions were also very close to their theoretical value. It shows that solid-state reaction can control composition catalyst.

5.4 Combustion method

The combustion method provides a source of fine, homogenous metal oxide powders, however in this process used a solvent and precursor in which is expensive. This is causing uneconomical process. The combustion method is a very quick preparation due to its short reaction time [64,65]. This method introduces a thermally induced redox reaction between an oxidant (metal nitrates) and a fuel source (urea, glycine, citric acid). Guo and co-workers [64,65] investigated the effects of urea and glycine as the fuel source in combustion synthesis of a CuO/ZnO/ZrO₂ catalyst. It observed that the fuel / oxidant ratio was of great importance to the activity of the catalyst. 40% to 150% of the stoichiometric amount of urea and 50% to 150% of the stoichiometric amount of glycine examined during the experiments. It concluded that fuel-deficiencies exhibited higher activity due to the formation of small grain size, low reduction temperature and larger catalyst surface area. The optimal stoichiometric amount occurs in 50% for both urea and glycine.

6. Process parameters

Previously mentioned that preparation catalyst method, a certain process parameters optimized to result in high activity catalyst. Calcination and the pH level have shown to have great influence on the morphology of the catalysts studied.

6.1 Effect of calcination

Temperature and conditions of the calcination process have a direct impact on the structure and properties of the catalyst surface. Changes to the high temperature and changes flow rate of heat to raise the temperature can increase the size of the agglomeration of particles and catalyst [62,63]. Ma and co-workers [63] studied the effects of the calcinations process on the oxalate gel-precipitation method on Cu/ZnO/Al₂O₃ as previously mentioned. Ethanol solvent used to produce the dried precursor in the preparation step. The precursor divided into catalyst Cu/ZnO/Al₂O₃ 1, Cu/ZnO/Al₂O₃ 2,

Cu/ZnO/Al₂O₃ 3, Cu/ZnO/Al₂O₃ 4. Cu/ZnO/Al₂O₃ 1, Cu/ZnO/Al₂O₃ 2, Cu/ZnO/Al₂O₃ 3 (Table 4) were calcined under mild temperature changes under nitrogen, air and oxygen atmospheres respectively. Cu/ZnO/Al₂O₃ 4 calcined under rapid temperature changes under an air atmosphere. Rapid temperature changes can increase the amount of carbon monoxide produced from oxalate decomposition. CO reacts with CuO-based catalyst to release large amounts of heat and this causes sintering on the surface of a catalyst. Therefore, mild temperature changes are preferred. The oxygen atmosphere of C₃ showed the highest catalytic activity due to the oxygen oxidizing the CO from the oxalate into CO₂. This prevents further reduction of CuO particles and enhances the formation of methanol.

The study by Guo and co-workers [62] mentioned in the solid-state reaction section, highlighted the effect of calcination temperature on the preparation of the Cu/ZnO/ZrO₂ catalyst. The catalysts named CZZ-400, CZZ-500, CZZ-600, CZZ-700, and CZZ-800. The CZZ refers to the catalyst composition of copper, zinc and zirconium and the attached number designated the calcination temperature in Celsius. Lower calcination temperatures resulted in finer particles and the higher BET surface area. Particle size and agglomeration grew linearly with calcination temperature. The methanol yield and CO₂ conversion increased with decreasing calcination temperature. The most active catalyst was CZZ-400 with a CO₂ conversion of 15.7% and methanol yield of 9.1%. These trends indicated that with higher dispersion increased the catalytic activity of cu-based catalyst.

6.2 Effect of pH

The dispersion of CuO and ZnO particles is of great importance in catalytic activity of Cu/ZnO based catalysts. During the preparation, the pH controls the formation of copper and zinc precipitates [32,66]. Jeong and co-workers [56] has conducted a series of experiments on CuO/ZnO catalysts which prepared by co-precipitation method by controlling a pH range of 4-11. They found that CuO crystalline was formed at a pH of 4 and ZnO crystalline at a pH of 7. Samei and co-workers [32] also noticed that the precipitation of CuO formed at acidic pH of 5 while ZnO formed at alkali pH of 9.5. Both concluded that the Cu and Zn were dispersed at high pH (9-9.5) can lead to the occurrence of a high catalytic activity. [32,66] It is recommended to use the Cu and Zn species as active site for hydrogenation of CO₂.

7. Deactivation

Lose the surface area of copper associated with decreased the activity of a catalyst. It is associated with a sintering. Toxicity of sulfur, chlorine and other components are not removed prior to entering the reactor. It occurs during the production of synthetic gas [33]. Stabilizers useful for minimize the amount of sintering. These stabilizers include metal components such as ZnO, which dilute in the active site of catalyst. Silica can reduce the amount of sintering during the synthesis process. As mentioned before, then silica should be inserting into the catalytic surface to prevent the occurrence of agglomeration and crystallization. This leads to a reduction in the process of sintering and deactivation of the catalyst [31].

8. Discussion

Synthesis of methanol has been the answer to scenario in the face of conditions where the depletion of fossil fuels. Industrial process has proven to be an effective way to produce methanol. Reducing carbon dioxide emissions also attracted researchers because of the hydrogenation of carbon dioxide as a key reaction for the synthesis of methanol. This will be very good for industrial processes in order to reduce the impact of environmental problems.

The conversion of carbon monoxide has been optimal for an industrial process. However, synthesis of methanol has created a controversy. There is uncertainty in main reaction and still disputed. The main reaction should be investigated further in order for hydrogenation of carbon dioxide could be a viable source of methanol synthesis. This has created many theories for the optimal approach in order to develop a catalyst for methanol synthesis. However, in addition, through carbon dioxide hydrogenation then increased the activity of catalyst in methanol synthesis has experienced progress

Agglomeration and sintering greatly contributed to the deactivation of the catalyst. To develop the optimal catalyst, the catalyst must exhibit high dispersion of the active site and has a large surface area. To prevent the agglomeration of the catalyst, it has conducted an investigation into the stages of precipitation catalyst as well as the composition of the catalyst.

Oxalate gel-precipitation method has proved ultrafine quasi-spherical particles, show resulting in higher surface area for the synthesis of methanol. Calcination temperature change may inhibit oxidation and resulting in a sintering on the surface of copper so that fine particles are not going fine particles as desired.

Solid-State reaction method is specially designed catalyst preparation, because it does not re-

quire an expensive solvent. Since the particles surface reaction results with a good structure, so that it can interact with both the support of the activity of the catalyst.

The important key is present on the interaction between copper, zinc, silica, zirconia and palladium. The nature and role of each component is still unclear. However, the observable effects of the promotion of a wide range of metal on the composition of the catalyst on the reaction results in methanol synthesis. Effect of zirconia on the promotion of copper can change the role of copper from the active site to become a reservoir of hydrogen as suggested by Arena and co-workers [50].

A catalyst that is capable of producing CO₂ conversion and high conversion of methanol, based on various references observed almost in all temperatures. This shows that the reaction at low temperature can produce methanol conversion and selectivity of methanol is high, so that it can reduce the consumption of energy on the reactor and reduce production costs.

9. Conclusions

Methanol synthesis has become a viable option to mitigate the current fossil fuel depletion and carbon dioxide emissions. This desired process would offer an ecologically friendly option to the environmental crises. Prominent issues continue to determine the development of an optimal catalyst for carbon dioxide conversion into methanol. Due to the lack of carbon dioxide conversion during industrial processes, alternative catalysts it has been investigate.

The higher dispersion of active site species seems to be unanimous among modified catalysts investigated in this paper. Therefore, it seems variations in catalytic activity related to other properties of the surface.

The addition of a SiO₂-TiO₂ promoter led to promising results with the highest yield and CO₂ conversion. The addition of the SiO₂-TiO₂ promoter to copper-based catalyst (Cu/ZnO) may enhance the hydrogen adsorption/dissociation capability to the remodeled copper hydrogen reservoir.

The addition of zirconium has also proved to be a high activity catalyst for methanol synthesis. Zirconium's interparticle effect on copper seems to change its role into a hydrogen reservoir rather than an active site. This role of a hydrogen reservoir may play an important part in catalyst activity and needs to be investigated further. Therefore, a possible zirconia-silica-titanium oxide influenced catalyst need to be investigating as well.

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