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A Brief Review of Carbon Dioxide Hydrogenation to Methanol over Copper and Iron Based Catalysts

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Abstract — *Climate change and global warming have become a challenging issue affecting not only humanity but also flora and fauna due to an intense increase of* CO_2 *emission in the atmosphere which has gradually led to amplification in the average global temperature. Hence, a number of mechanisms have been promoted to diminish the atmospheric commutation of carbon dioxide. One of the well-known techniques is Carbon Capture and Storage (CCS) which mechanism is based on capture and storage vast quantities of* CO_2*, as well as Carbon Capture and Utilization (CCU) which mechanism is based on* CO_2 *conversion to liquid fuels* (e.g. *methanol, hydrocarbons, carbonate, propylene, dimethyl ether, ethylene, etc.). Particularly, methanol* (CH_3OH) *is a key feedstock for industrial chemicals, which further can be converted into high molecular alternative liquid fuels. In this regard, hydrogenation of* CO_2 *is one of the promising, effectual and economic techniques for utilization of* CO_2 *emission. Nevertheless, the reduction/activation of* CO_2 *into useful liquid products is a scientifically challenging issue due to the complexities associated with its high stability. Thus, various catalysts have been applied to reduce the activation energy of the hydrogenation process and transform* CO_2 *into value-added products. Thereby, this review article highlights the progress and the recent advances of research investigation in Cu and Fe-based catalytic conversion of* CO_2*, reaction mechanisms, catalytic reactivity, and influence of operating parameters on product efficiency.*

INTRODUCTION

Worldwide energy consumption is rapidly amplifying due to the growth of economy and population. The dominant percentage of the energy is extracted via the incineration of non-renewable fossil fuels and resources, which definitely causes the production of greenhouse gases and extensive accumulation of carbon dioxide (CO_2) in the atmosphere which is one of the crucial reasons for global warming and climate change. First of all, the scholars from similar fields recognize the immensely high contribution of CO_2 as a greenhouse gas to global warming and this was endorsed by the leaders of not only developed but also developing countries during the previous world summit for climate change.

Figure 1 presents the evolution of annual emissions of CO_2 for the period between 1990 and 2014, as well as estimated carbon dioxide emissions to 2019. From the figure it can be observed that CO_2 emissions are slowly expanding or quite stable until approximately 2002. Since 2003, there has been a sharp increasing trend which in particular overlaps with the increasing global temperatures and attenuating between the temperatures and the sunspot numbers. Friedlingstein *et al.* [1] report that the global greenhouse gas would continuously grow in 2014 to a level of approximately 65% above emissions in 1990. The rapid growth the level of carbon dioxide in ambient air might cause to uninhabitable and irreversible planet for our future generations. At the same time we need to undoubtedly

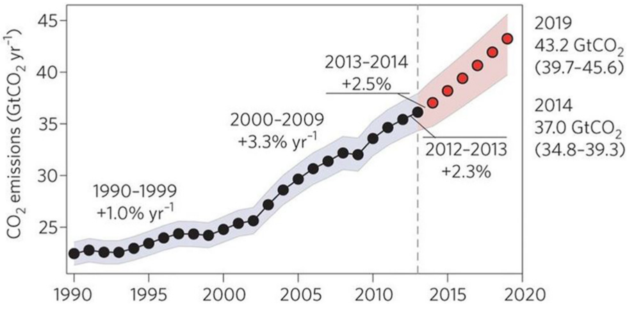

Figure 1

Global carbon dioxide emissions from fossil fuel combustion and cement production by 2014 (black dotes) and estimates to 2019 (red dots) [1].

increase our energy supply while reducing CO_2 emissions is one of the essential challenges encountering our global society today. The worldwide CO_2 emission should have to be diminished by 50–80% by 2050 in order to control the global mean temperature increase by 2–2.4 °C [2]. Hu *et al.* [3] state the global CO_2 emission from the use of fossil fuels and cement production was 36 billion tones in 2013. Consequently, the robust and clean technologies for CO_2 capture, storage and utilization are required at a large scale [4, 5]. Among the technologies, effective strategies in chemical (*e.g.* hydrogenation) conversion could play a considerable role in reduction CO_2 emission [6–8].

Catalytic conversion of CO_2 to methanol (CH_3OH) is considered as a promising way that might offer a comprehensive solution to the issues of greenhouse gas control and depletion of fossil fuels respectively. Methanol is a significant starting product for a number of valuable chemicals and can be applied as a clean fuel and fuel additive. Additionally, it can also be converted into aromatics, ethylene, and propylene as well as to other value-added petrochemicals that are nowadays mainly derived extracted from crude oil [9]. Moreover, methanol was mainly applied as a starting feedstock in the chemical industries and it could also be an efficient sustainable and alternative synthetic fuel if anthropogenic CO_2 and regenerative hydrogen are used as reagent for its synthesis. One of the most effective ways of accomplishing this goal is to explore high selective and active catalysts for methanol synthesis due to its thermodynamic stability of CO_2.

Thus, this review paper discusses the process, namely methanol synthesis via hydrogenation of CO_2. The review starts with accurate highlights regarding to CO_2 hydrogenation to methanol, reaction mechanism, and continues with the effect of selected catalysts and the effect of operating parameters on H_2/CO_2 to methanol, as well as recent technological and industrial advances in this field.

1 CO_2 HYDROGENATION TO METHANOL

Currently, comprehensive efforts and attentions are being paid on conversion of CO_2 to methanol. Olah *et al.* [10] reported that CO_2 hydrogenation to methanol, a new concept of "methanol economy" which relies on combination of Carbon Capture and Storage (CCS) with chemical recycling. Whereas renewable feedstock such as CO_2 and water are abundantly available, the energy required for the synthetic carbon cycle can come from any source of alternative energy like wind, solar, nuclear, and geothermal energy. This alternative cycle offers a robust mechanism ensuring sustainable future for human beings when fossil fuels become deficient.

The major reactions for hydrogenation of CO_2 to methanol are methanol synthesis (Eq. (1)) and water–gas-shift reaction (Eq. (2)). There is a possibility that CO formed from reaction (Eq. (2)) that incurs further hydrogenation to generate methanol (Eq. (3)) [11]. The methanol formation is an exothermal reaction with reduction of reaction molecule. Hence, the rise of pressure and the decrease of temperature should favor for the reaction from thermodynamical analysis. Nevertheless, taking into account the chemically inert nature of CO_2 and the reaction rate, the amplification of reaction temperature (*e.g.* >240 °C) promotes activation of CO_2 and then formation of methanol. The reverse water–gas-shift reaction leads to a reduction of methanol formation and causes extra consumption of hydrogen. Inui and Takeguchi [12] report that the large amount of water from by-product, from both the reverse water–gas-shift side reaction and synthesis of methanol, also had an inhibitory effect on the active metal during the reaction, thus leading to the catalyst deactivation. Consequently, synthesis of methanol from CO_2 hydrogenation needs more selective catalysts in order to avoid the formation of unnecessary and undesired by-products.

$$\mathrm{CO_2 + 3H_2 = CH_3OH + H_2O}, \quad \Delta H_{298\,\mathrm{K},5\,\mathrm{MPa}} = -40.9\,\mathrm{kJ/mol} \quad [\text{methnol formation}] \tag{1}$$

$$\mathrm{CO_2 + H_2 = CO + H_2O}, \quad \Delta H_{298\,\mathrm{K},5\,\mathrm{MPa}} = -49.8\,\mathrm{kJ/mol} \quad [\text{reverse water-gas-shift}] \tag{2}$$

$$\mathrm{CO + 2H_2 = CH_3OH}, \quad \Delta H_{298\,\mathrm{K},5\,\mathrm{MPa}} = -90.7\,\mathrm{kJ/mol} \quad [\text{methanol formation}] \tag{3}$$

Li *et al.* [13] proclaim that catalysts applied in hydrogenation of CO_2 are those used for synthesis of methanol from CO hydrogenation. Several research investigations [14–17] have emphasized on the effects of catalyst type (*e.g.* surface area, morphology, supports and promoters), operating conditions, reactor type, etc. Indeed, catalysts with high efficiency are key factor for synthesis of methanol through CO_2 hydrogenation. So far, the sustainable development of the catalyst is still not fully satisfactory in order to be applied for industrial applications due to the insufficient knowledge in catalytic design, properties and rational understanding of the CO_2 hydrogenation mechanism. However, more large-scale research on catalytic activities, efficiency and practical upgrade of Cu- and Fe-based catalysts could break the above-mentioned gap in industrial application of CO_2 hydrogenation to methanol.

1.1 Reaction mechanism

Due to significant complexity of methanol synthesis from hydrogenation of CO_2, atomic level perception regarding to the reaction mechanism has been a lingering challenge. Liu *et al.* [18] state that so far, the key issues in the field, such as where and how CO_2 is activated over the surface of the selected catalysts, remain infirm. The reaction mechanism has been initially discussed over Cu and oxides based catalysts [19, 20], which is still debatable. CO_2 can adsorb on bare oxides and hydrogen can disassociate on copper species [21]. The active Cu species is principally present as Cu^0 over Cu/ZrO_2 based on X-ray diffraction measurements [22]. However, research group headed by Jansen *et al.* [23] proposed that Cu+ is the active component for Cu/ZnO/SiO_2 catalyst employing static low energy ion scatter experiments. Liu *et al.* [24, 25] suggested that copper metal and low valence of Cu (Cu^+ and $Cu^{\delta+}$) may affect the catalytic activity of Cu-based oxide catalysts. Most recent studies [26–30] declare that resolution of the geometrical and electronic structures of the active site is the first step toward an efficient catalyst design with high selectivity and activity.

The redox mechanism involves the formation of CO via the Reverse-Water–Gas-Shift (RWGS) reaction and conventional synthesis gas to methanol conversion (Eq. (3)) [31]. As well as, the redox mechanism for the RWGS reaction can be easily modeled through the following scheme:

$$CO_2 + 2Cu^0 \rightarrow Cu_2O + CO \tag{4}$$

$$H_2 + Cu_2O \rightarrow 2Cu^0 + H_2O \tag{5}$$

Cu^0 atoms are certainly active to disassociate CO_2, while the reduction of oxidized Cu catalyst has to be quicker than the process of oxidation [32, 33]. Hence, hydrogen is suggested to be a reducing reagent without direct involvement in the intermediates formation in the reverse-water–gas-shift reaction. The other reaction mechanism is the format decomposition/pathway, where the formation of HCOO intermediate is generally considered to be the rate-determining step [34, 35]. According to Tabatabaei *et al.* [36] the intermediate is a bidentate format on Cu, the most stable absorbed species. Chen *et al.* [36–40] suggest that CO is formed from decomposition of format intermediate, deduced from unification of hydrogen (H_2) with CO_2. As well as, Sloczynski *et al.* [41] indicate that CO may be formed from decomposition of methanol, whereas the reverse-water–gas-shift mechanism can explain directly the CO formation as the major by product.

However, a few (critical amount) literatures were revealed on mechanisms for the reaction over Fe-based and oxides catalysts for methanol synthesis from hydrogenation of CO_2. Most recent and current research investigations [42–49] on reaction mechanism for Fe-based catalysts have been conducted for hydrocarbon, olefin and methane synthesis from CO_2 hydrogenation process.

1.2 Effect of catalysts on CO_2 hydrogenation to methanol

Since past few decades, many types of catalysts have been examined and investigated for the synthesis of methanol from CO_2 hydrogenation. The majority of catalyst for hydrogenation of CO_2 contains Cu as the main component along with different promoters or modifiers (Zn, Zr, Si, Al, Ti, Cr, Ga, Ce, etc.) [50–52] and literatures on catalytic CO_2 hydrogenation process containing Fe [53] for methanol synthesis have been found a very few. A proper support not only affects the stabilization and formation of the active phase of the catalyst but it is also able to control the interaction between the promoter and major component. Additionally, acidity and basicity characteristics of the catalyst are also determined by the selected support [18].

According to the research conducted by Deerattrakul *et al.* [54], 10 wt% CuZn/rGO catalyst performed the highest activity for the CO_2 hydrogenation with a 26% CO_2 conversion, 51% CH_3OH selectivity, and $424 \pm 18\ mg_{MeOH}$ at 250 °C and 15 bar after 5 h on stream of CO_2 and H_2. When the reaction was completed, the spent catalyst was re-evaluated its structure using XRD in order to examine the stability of rGO. The obtained pattern of XRD indicated that the catalyst still had the same structure as that of the initially used catalyst (see Fig. 2). When the loading was increased beyond 10 wt%, the conversion of CO_2 and space–time yield of methanol (STY_{MeOH}) decreased due to the agglomeration of active metals led to reduce copper oxides to metallic Cu^0, which is a crucial active metal for synthesis of methanol [54]. As well as, Deerattrakul *et al.* [54] have mentioned that his results have given the highest STY_{MeOH} under the lowest operating pressure comparing to previously published works [55–58]. The rGO reduced by hydrazine played very significant role in the enhanced performance of the CuZn/rGO catalyst [54].

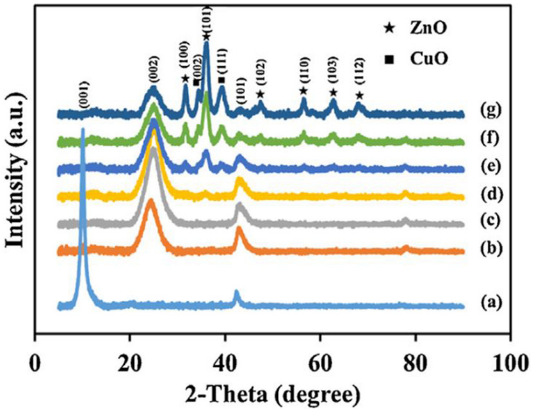

Figure 2

XRD patterns of (a) GO, (b) rGO, (c) calcined rGO, (d) 5% CuZn/rGO, (e) 10% CuZn/rGO, (f) 20% CuZn/rGO and (g) 30% CuZn/rGO [54].

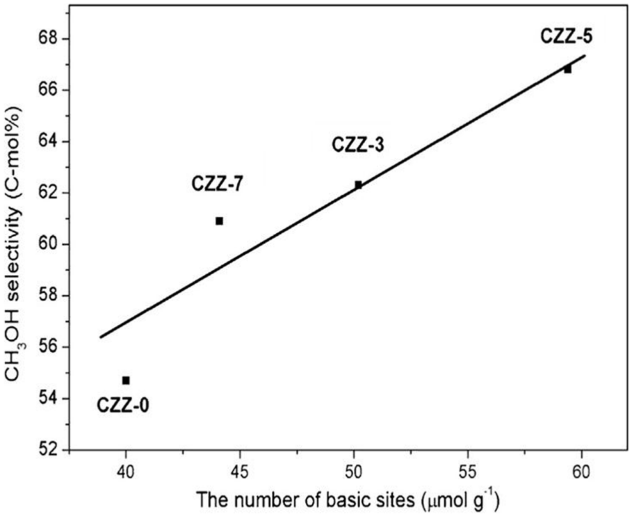

Figure 3

The relationship between CH_3OH selectivity and the number of basic sites over $Cu/ZnO/ZrO_2$ catalysts [28].

Liu *et al.* [58] tested the serials of Cu catalysts supported on TiO_2 modified with different amount of MgO which were prepared through an impregnation method for synthesis of methanol from CO_2 hydrogenation. During experimental investigation, the selectivity of methanol increased first and then decreased with amplifying the amount of MgO. A value of 55% was obtained over the Cu/5% supported MgO modified TiO_2 catalyst, which enhanced by 86% compared with unmodified Cu/TiO_2 catalyst sample. Regarding to CH_3OH yield, it took on a volcanic variation trend with the addition of MgO, a maximum value of 1.97% was obtained over the Cu/1% supported MgO modified TiO_2 catalyst, and the value increased by 54% comparing to the unmodified Cu/TiO_2 catalyst [58]. This assures that the modification of TiO_2 with an accurate amount of MgO is favorable for the improvement of the Cu/TiO_2 catalytic feature.

Dong *et al.* [28] applied $Cu/ZnO/ZrO_2$ catalyst for CO_2 hydrogenation to methanol prepared by precipitation–reduction method and reduced by different $NaBH_4$, and the report emphasized that methanol and CO are the only carbon containing products under the reaction condition. As the catalytic activities for conversion of CO_2 increased while CH_3OH decreased with increasing temperature of reaction from 230 °C to 270 °C. Basically, increasing temperature promotes the conversion and activation of CO_2, however, the CO production is more conducive than methanol because of the higher activation energy of RWGS reaction and endothermic character [59]. The catalysts prepared by precipitation–reduction method have shown an obvious advantage in methanol selectivity over the conventional $Cu/ZnO/ZrO_2$ catalyst, especially at 230 °C. The CH_3OH selectivity was 66.8% over $Cu/ZnO/ZrO_2$-5 (5–the $NaBH_4$/Cu molar ratio) sample at 230 °C, which is 12.7% higher than $Cu/ZnO/ZrO_2$-0 (0–the $NaBH_4$/Cu molar ratio) sample (see Fig. 3). A maximum STY of CH_3OH of 0.21 $g\,ml^{-1}\,h^{-1}$ with CO_2 conversion of 23% and methanol selectivity of 56.8% was obtained over $Cu/ZnO/ZrO_2$-5 at 270 °C.

Another example of catalytic CO_2 hydrogenation to methanol using $CuO/ZnO/Al_2O_3$ catalysts prepared via a solvent-free routine was investigated by Lei *et al.* [27]. Six CZA (all with the same Cu/Zn/Al atomic ratio of 60/25/15) prepared using citric acid, oxalic acid or urea as fuel by combustion and mechanical milling method [27]. This research group has also indicated that methanol and CO were the only carbon containing products under the reaction conditions. With the same fuel/salts molar ratio, CZA-citric acid-1.00 (molar ratio) catalyst performed the highest activity for hydrogenation of CO_2 with 14.6% conversion of CO_2, perhaps because of the larger exposed Cu surface area and smaller particle size. The calculated STY of methanol reached 0.12 $g_{MeOH}/(g_{cat}\,h)$, while the conversion of CO_2 and STY of methanol decreased to 12.1% and 0.1 $g_{MeOH}/(g_{cat}\,h)$ over CZA-oxalic acid-1.00. CZA-urea-1.00 has shown the lowest activity for hydrogenation of CO_2 with 3.2% CO_2 conversion and 0.022 $g_{MeOH}/(g_{cat}\,h)$ STY_{MeOH}, which could be resulted to the smaller exposed Cu surface area and larger particle size of CuO, and the formation of $ZnAl_2O_4$ [27]. Consequently, it was revealed that the CO_2 conversion and STY of methanol increased with the added amount of citric acid during catalyst preparation and the maximum conversion of CO_2 reached 16.2% over CZA-citric acid-1.25. Additionally, from above mentioned results, it can be inferred that Cu surface area is also one of the essential parameter for Cu/Zn/Al2O3 catalysts since it is related tightly to the catalytic activity of catalysts (see Fig. 4).

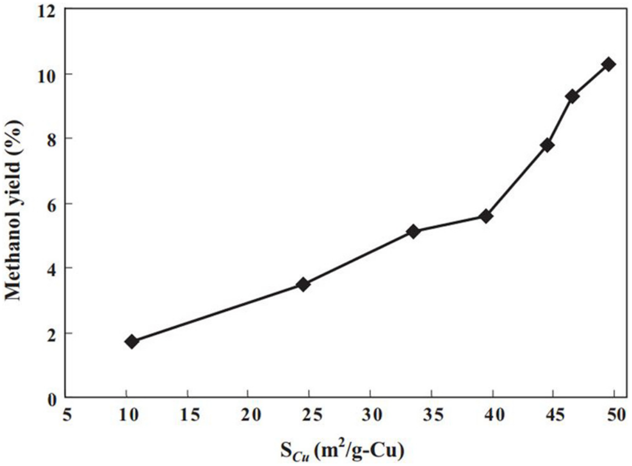

Figure 4

The relationship between methanol yield and the exposed Cu surface area (reaction conditions: $H_2/CO_2 = 3$, $T = 240$ °C, $P = 3.0$ MPa, GHSV = 3600 h^{-1}) [27].

Regarding to Fe-based catalysts, Dorner *et al.* [60] report that low loading of ceria to a Fe–Mn/Al_2O_3 catalyst leads to a marginal improvement in conversion of CO_2 and products selectivity, a decrease in reactivity was observed when the doping amount was increased to 10 wt%. Other additives such as Zn, Mg, Ru, Zr, and La have also been researched but promoting effect is nearly inappreciable [53, 61–63]. Iron based catalysts dispersed on various supports have also been tested extensively and the product distributions are highly dependent on supporting materials [53]. The support tends to act completely as a stabilizer to avoid sintering of active particles during the reaction process. Usually, alumina executes efficiently, since it could prevent sintering as a result of the stable interaction or metal support, followed by titania and silica [53, 64, 65]. Dorner *et al.* [60] reported that the addition of ceria to a Fe/Mn-Al_2O_3 catalyst leaded to a marginal improvement in conversion of CO_2 and product selectivity at low Ce-levels (2 wt%). During heavier doping, the effect of Ce on the overall conversion of CO_2 is decreased, with 14% loss in the yield. Ceria forms on top of the Fe particles, leaded to the blocking of the chain-growth sites during hydrogenation of CO_2, in the result, CO_2 is instead converted to CO, that desorbs without being converted to valued-added products as a the chain-growth active site concentration has been decreased by the heavier doping of ceria. This is due to the fact that the chain-growth probability is not affected between the ceria-free and ceria containing catalyst [60]. According to Dubois *et al.* [66] investigation, hydrogenation of CO_2 using transitional metal carbides, such as Fe_3C and Mo_2C indicated high conversion of CO_2 and methanol selectivity at 220 °C. Nevertheless, more particular literature on comprehensive application of iron based catalyst for methanol synthesis from CO_2 hydrogenation is still not sufficient and hence more profound scientific research is suggested to discover the hidden potential catalytic features Fe-based catalyst for methanol synthesis from hydrogenation of CO_2.

The catalysts with high efficiency are the key for synthesis of methanol through hydrogenation of CO_2. So far, comprehensive application of catalysts on industrial scale is still not fully satisfying due to the insufficient of the necessary knowledge in designing of catalysts for the mechanistic perception of CO_2 hydrogenation and control of relevant catalytic properties.

1.3 Effect of operating parameters on H_2/CO_2 to methanol

In this section the effect of operating parameters on H_2/CO_2 to methanol has been evaluated based on the previous experimental investigations with the results as shown in Table 1. The table summarizes the effect type of catalysts, temperature, pressure and type of reactor on CO_2 conversion (%), MeOH selectivity (%), MeOH yield (%) and STY of MeOH (g_{MeOH}/g_{cat} h).

2 RECENT TECHNOLOGICAL AND INDUSTRIAL ADVANCES

The first pilot plant capacity of 50 kg/h for methanol production from CO_2 and H_2 was constructed in 1996 in Japan with application of SiO_2-modified CuO/ZnO catalyst. Recycling the feed extracted a STY of methanol yield approximately 600 g/(L h), with selectivity of 99.9% over 8000 h under operating conditions $T = 250$ °C and 5 MPa [71]. According to Tremblay [72], another pilot plant for production of methanol from CO_2 and H_2 with yearly capacity of 100 tones is partially built by *Mitsui Chemicals*, Japan. In order to completely accomplish the construction and meet the target, H_2 will be generated via photochemical water splitting using solar energy [72]. Since 2010, this particular pilot plant of *Mitsui Chemicals* is under use at the R&D sites (Osaka Works) and currently synthesizes methanol, later used in the production of olefins, ethylene oxide, ethylene glycol and aromatics, using the CO_2 emitted from factories and hydrogen obtained from water photolysis. One of the main millstones was achieved by *Sud-Chemie* and *Lurgi AG institutions*, they together developed a highly selective and active catalyst for methanol production from CO_2 and H_2 at temperature 260 °C [73]. *Air Products Liquid Phase Conversion Company* for the US DOE National Energy Technology Laboratory reported that for the first time, a liquid-phase synthesis of methanol was also developed, which is able to convert CO_2 and H_2 into methanol of nearby 95% with immensely high selectivity in a single pass. As stated by

Table 1

Summary of the effect of operating parameters on H_2/CO_2 to methanol.

Type of catalyst	Type of reactor	T (°C)/ P (MPa)	CO_2 conversion (%)	MeOH selectivity (%)	MeOH yield (%)	STY of MeOH ($g_{MeOH}/g_{cat}\,h$)	Ref
$CuO–Fe_2O_3–3\%CeO_2$/HZSM-5	Fixed-bed	260/3	20.9	5.2	N/A	N/A	[8]
$CuO–Fe_2O_3–4\%CeO_2$/HZSM-5	Fixed-bed	260/3	17.1	4.6	N/A	N/A	[8]
$CuO/ZnO/Al_2O_3$-C-1	Fixed-bed	240/3	14.6	63.6	9.3	0.12	[27]
$CuO/ZnO/Al_2O_3$-C-1.25	Fixed-bed	240/3	16.2	63.8	10.3	0.13	[27]
$CuO/ZnO/Al_2O_3$-O-1	Fixed-bed	240/3	12.1	62.6	7.8	0.10	[27]
$CuO/ZnO/Al_2O_3$-U-1	Fixed-bed	240/3	3.2	53.9	1.7	0.022	[27]
$Cu/ZnO/ZrO_2$-0	Fixed-bed	230/5	16.7	54.7	N/A	0.14	[28]
$Cu/ZnO/ZrO_2$-5	Fixed-bed	230/5	15.4	66.8	N/A	0.16	[28]
$Cu/ZnO/ZrO_2$-0	Fixed-bed	270/5	22.5	51.8	N/A	0.18	[28]
$Cu/ZnO/ZrO_2$-5	Fixed-bed	270/5	23.0	56.8	N/A	0.21	[28]
5%CuZn/rGO	Fixed-bed	250/1.5	14	2.8	N/A	0.22	[54]
10%CuZn/rGO	Fixed-bed	250/1.5	26	5.1	N/A	0.424	[54]
20%CuZn/rGO	Fixed-bed	250/1.5	19	8.5	N/A	0.244	[54]
CuZnGa	Fixed-bed	270/3	15.8	N/A	29.3	0.135	[55]
$Cu/0.5\%MgO/TiO_2$	Fixed-bed	220/3	5.0	33.9	1.70	N/A	[58]
$Cu/1\%MgO/TiO_2$	Fixed-bed	220/3	5.2	37.9	1.97	N/A	[58]
$Cu/5\%MgO/TiO_2$	Fixed-bed	220/3	2.6	55.5	1.44	N/A	[58]
Cu/TiO_2	Fixed-bed	220/3	4.3	29.8	1.28	N/A	[58]
$Cu-Zn/SiO_2$	Fixed-bed	250/2	2.0	65.7	N/A	0.065	[67]
10Cu60Zn30	Fixed-bed	250/1.5	21	83	N/A	0.274	[68]
Fe–Cu/MCM-41	Fixed-bed	200/1	2	80	N/A	N/A	[69]
$Cu–ZnO/TiO_2–ZrO_2$	Fixed-bed	240/3	17.4	43.8	7.6	0.053	[70]

Shulenberger *et al.* [74], the first commercial CO_2 into methanol recycling plant by using indigenously available inexpensive geothermal energy is currently under construction after felicitous pilot plant operation by the *Carbon Recycling International Company* in Iceland. This particular plant called "Emissions-to-Liquids" is based on CO_2 conversion to vital by-products via integrated applications of indigenous industrial or geothermal energy sources, and hydrogen is produced via electrolysis of water [74]. Currently, the emissions-to-liquids methanol plant with nominal 50 000 ton/yr methanol production capacity is under operation and is designed to utilize existing sources of clean CO_2 or to process carbon dioxide from an emission sources, and is also constructed to produce its own H_2 feedstock from electrolysis or to utilize by-product hydrogen from another industrial process. The technological practicability of methanol production from CO_2 has also been highlighted in pilot plant applying two-step mechanistic approach, process reverse water–gas-shift separate from synthesis of methanol or single-step mechanistic approach (the two stages combined in a single reactor) [16]. However, Centi and Perathoner [16] allege that the first mechanistic approach is preferential due to greater catalyst productivity, lower reactor size and gas recycles.

Since 2015, research scientists at the Laboratory of Nanochemisty and Ecology, National University of Science and Technology (MIS&S) in Moscow (Russia), have been donating massive efforts in development of novel nano-sized, hetero and homogeneous catalysts to activate CO_2 [75, 76] in a reasonable, economically and ecologically efficient process for methanol production. Undoubtedly, all these extensive developments are immensely stimulating factors for sustainable development and for improvement of our environment.

CONCLUSION

Present work comprehensively highlighted recent advances in catalytic hydrogenation of CO_2 to methanol. From the research survey, it is inferred that a great number of catalytic studies on methanol synthesis from CO_2 hydrogenation have been focused on catalytic activities of Cu-based catalysts, while Fe-based catalysts indicated a contrary tendency. Cu-based catalysts along with various efficient promoters (*e.g.* Al, Ga, Si, Zr, etc.) are considerably useful. Accurately selected promoters and supports enhance the activity, stability and selectivity of the catalyst. Except promoters and support, higher surface area and smaller particle size of catalyst are considered as one of the most crucial factors for higher methanol yield production from hydrogenation of CO_2.

Although several efforts have been made to upgrade and modify the technological progress of methanol synthesis from hydrogenation of CO_2, the greatly effective process to enhance the conversion of CO_2 is still pursued because of the thermodynamically stable nature of carbon dioxide molecule. Detailed research investigations on the catalyst sensitivities to admixtures, catalysts reaction performance under complex conditions are required. Moreover, the robust mechanism for synthesis of methanol from CO_2 hydrogenation is not yet completely understood. As well as, as conversion of CO_2 into value-added products or chemicals requires energy in the form of hydrogen or heat, alternative energy like biomass, wind, solar, geothermal and nuclear energy, is recommended to be applied instead of fossil fuel during conversion process. Besides, the future scientific undertaking have to focus to develop more highly efficient and “smart” catalysts, mechanisms and integrated process technology to encounter not only economic but also environmental challenges and to promote bio-based “green” economy.

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