Performance comparison of mainstream catalysts in the CO_2 hydrogenation of CH_3OH

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Abstract. Carbon dioxide capture, utilisation and storage (CCUS) has been a hot topic in recent years and among the products derived from carbon dioxide conversion, methanol is favoured by many scientists for its wide range of applications. Scientists are also looking for different types of catalysts to complete this conversion process more efficiently. This paper compares the selectivity, yield and stability of oxide supported metal catalysts, oxide supported oxide catalysts and other typical catalysts to identify the most favourable catalysts that could be used for industrial production in the future. Through this comparison, In-Co/Ce catalysts are one of the most beneficial options.

Keywords: Catalyst for CO_2 utilization, Copper-based catalyst, In_2O_3-based catalyst, Transitional metal carbides.

1. Introduction

Methanol is not only a basic raw material for the chemical industry, but also a clean liquid fuel. The crisis on energy and environment such as the increasing depletion of fossil energy and global warming, has become a major problem people facing today, so CO_2 hydrogenation is an important reaction in low carbon chemistry; on the one hand, it can directly reduce CO_2 emissions and mitigate the greenhouse effect; on the other hand, we can synthesize fuels and chemicals to achieve an artificial carbon cycle and alleviate the shortage of fossil energy. Due to the strong thermodynamic stability of CO_2, how to make the reaction proceed efficiently under mild conditions has become an urgent problem to be solved. In recent years, researchers at home and abroad have improved the economics of converting CO_2 to methanol by means of homogeneous catalysis, multiphase catalysis and the construction of novel catalytic systems. a summary of the CO_2 catalytic conversion process can lay the foundation for a more efficient use of CO_2 resources.

2. Oxide supported metal catalysts

The current study shows that copper-based catalysts and noble metal catalysts are the two main types of catalysts with high activity, while Co, Fe_3C, Mo_2C, WC, and $SnCl_4$ catalysts are also active, but with limited performance [1].

2.1. Copper-based catalysts

Copper-based catalysts are one of the most useful systems for the catalytic hydrogenation of CO_2 to methanol. Copper-based catalysts have been focused on because of their high efficiency and cheapness, but current production rates and other unmet criteria limit the large-scale industrial use of copper-based catalysts [2].

Most of the catalysts used for CO_2 hydrogenation contain copper and zinc as main components and with different carriers, among which the main active systems are Cu-ZnO, Cu-ZnO/ Al_2O_3, Cu-ZnO/ZrO_2, Cu-ZnO/SiO_2, etc [2].

   The main focus of the debate about copper-based catalysts is the active center of copper-based catalysts. Copper-based catalysts are usually composed of Cu and ZnO co-loaded on a carrier and the active center is established by the synergistic interaction of Cu and ZnO. Moreover, As Fig. 1 shows, ZnO is used to separate Cu particles from sintering as spacers in the Cu/ZnO system.
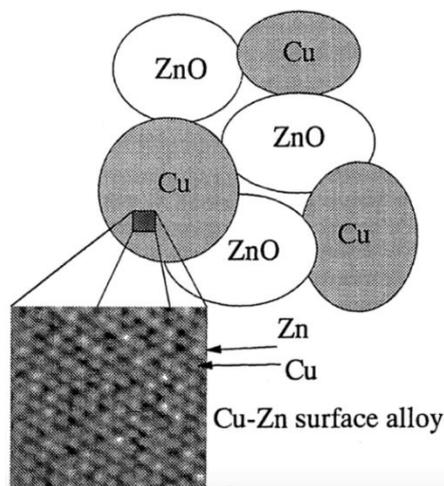

Figure 1. Cu-Zn alloy model [2]

   It is generally believed that among them Cu's play a major role - providing active sites for the catalyst, while ZnO's another role is to increase the copper dispersion on the catalyst surface [3]. Many studies show that there are two active sites for CO_2 hydrogenation to synthesize methanol on copper-based catalysts, and it is found that the CO_2 conversion rate is closely related to the copper surface area, one of the mainstream explanations is that the increase of copper surface area will result in more atomic hydrogen of carbon-containing substances adsorbed on the surface of Cu [2].

   This explains the necessity of ZnO, since the specific surface area of Cu has a positive correlation with catalytic activity and the addition of ZnO increases the specific surface area (dispersion) of Cu [4].
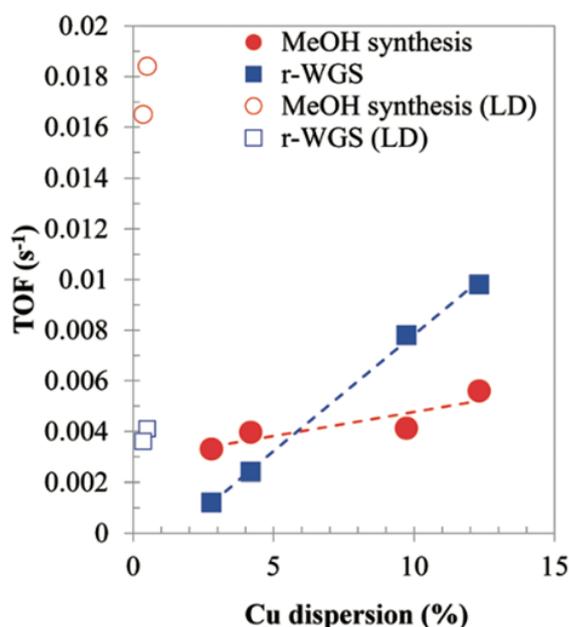

Figure 2. Turnover frequencies relationship with Cu dispersion [5]

   Turnover frequencies (TOF) defined as number of reactant molecules transformed per unit amount of surface copper atoms in a given time. TOF is an evaluation value of catalytic activity, and a higher TOF value represents higher catalytic activity. According to Fig. 2, there is no relationship between TOF and Cu dispersion in the case of very low dispersion. (The hollow circles and squares in the

figure). However, at a higher Cu dispersion, the turnover frequency for methanol increases with the increase of Cu dispersion.

The figure proves that copper dispersion has a significant positive effect in reaction for the synthesis of methanol from carbon dioxide. Karelovic et al. showed that with the increase of Cu loading, the specific surface area of the catalyst decreased, and Cu dispersion decreased [5]. In the meantime, the Cu surface area increased and then decreased, with the maximum at 5%. The copper nanoparticles formed on the catalyst surface were significantly more active for the inverse water-gas conversion reaction when the copper loading was lower than 5%, resulting in a lower methanol selectivity of about 40%. In contrast, for copper loading above 5%, the formation of large size copper clusters resulted in a high (80%) methanol selectivity.

The study focused on the relationship between Cu-ZnO mass fraction in the catalyst on CO_2 conversion, methanol selectivity and yield pointed out a positive linear relationship between CO_2 conversion and copper loading with increasing Cu-ZnO content, and a gradual increase in CO_2 conversion and methanol yield with increasing Cu and ZnO mass percentages [3].

2.1.1. Single metal oxide carriers

Currently, Al_2O_3 is a raditional catalyst carriers, which have been used in CO_2 hydrogenation catalytic reactions since the late 20th century. Al_2O_3 acts as a skeleton and also disperses the active components of the catalyst. It has been shown that using Cu-ZnO/ Al_2O_3 catalysts can improve the CO_2 conversion and methanol selectivity to a certain extent compared to Cu-ZnO [3]. In addition to its ability to form zinc aluminate with ZnO to prevent agglomeration of active sites, its disorderly nature and surface characteristics contribute to CO_2 adsorption and activation. However, Al_2O_3 is not flawless in practice, and it has been shown that the Al_2O_3 carrier can also reduce the catalyst activity during use due to the hydrophilic nature of Al_2O_3, water can cause a decrease in the methanol production rate [3]. In contrast to ZnO is ZrO_2. ZrO_2 also harvests a lot of attention due to its high stability in reducing or oxidizing atmosphere. Similar to ZnO, ZrO_2 increases the copper dispersion on the catalyst surface and is applied to methanol synthesis reactions because of its special properties of the surface that can provide adsorption sites for CO_2. Unlike Cu-ZnO, the catalytic activity in the Cu-ZrO_2 system does not show any correlation with the specific surface area of Cu, and the enhancement of its catalytic activity is positively correlated with the increase in the strength of the Cu-ZrO_2 interfacial interaction and the increase in the interfacial area [3]. However, there is still a great controversy in the study of the effect of ZrO_2 crystalline phase in Cu/ZrO_2. Another single metal oxide carrier of interest is SiO_2, which has a larger specific surface area and stronger dispersion activity than Al_2O_3. However, CuOZnO/SiO_2 catalysts have been criticized for their low CO_2 conversion and SiO_2 thermal stability. Although the conversion of CO_2 and H_2 is low, it is undeniable that it is highly selective for methanol production.

2.1.2. Composite metal oxide carriers

In recent years, new research directions have been made to study the reaction process of CO_2 methanol synthesis using various metal oxides or metal complex oxides with relatively low hydrogenation energy as catalysts. The combination of multiple metal oxides into composite carriers has received more and more research and attention. The representative one is the $AlCeO_x$ composite carrier with a mesoporous structure, which can substantially increase the specific surface area of the catalyst due to its good mesoporous structure characteristics. With the optimum $Al2O_3$/CeO_2 mass ratio, the CO_2 conversion was increased to 22.5 % at 280ºC, the methanol selectivity reached 94% at 200 ºC, and the methanol space-time yield reached 0.23 g/(gcat-h) at 220ºC [3]. The was a study pointed out $CeTiO_x$ composite carriers possess a larger specific surface area of the loaded catalyst (5 times that of CeO_2 and 9 times that of TiO_2), and thus the activity of $CeTiO_x$-loaded copper-based catalysts was significantly enhanced with 7- and 12-times higher CO_2 conversions, respectively [3]. This shows that the composite metal oxide carriers possess great potential to enhance the catalyst performance in the synthesis of methanol from CO_2. In a study by Jin et al., it was found that Cu/CeO_2

can achieve 89.9% methanol selectivity by isovolumetric impregnation at 240 degrees and 2 MPa, which is the highest among copper-based catalysts [6].

2.2. Noble metal catalysts

In addition to the common copper-based catalysts, noble metal catalysts have also been extensively studied in the field of CO_2 to methanol synthesis, and their future applications are being explored because of the strong H_2 dissociation and activation ability of noble metals such as Pd and Au. The ability to form alloys with metals or metal-oxide interfaces with oxides is also highly reactive in the preparation of methanol by CO_2 hydrogenation [7].

2.2.1. Palladium-based catalysts

The supported Pd catalysts are the most commonly used Noble catalysts in CO_2 to methanol synthesis process, which show considerable activity and selectivity for CO_2 hydrogenation to methanol, and the Pd carriers include various oxides: Ga_2O_3, Al_2O_3, Cr_2O_3, SiO_2, TiO_2, ZnO, ZrO_2. Pd/ZnO catalysts and copper-based catalysts have very similar activities in the steam reforming of synthetic methanol [2]. Moreover, Pd/ZnO catalysts exhibit higher carbon dioxide selectivity and stability than copper-based catalysts. The PdZn alloy formed during high temperature pre-reduction is the active site for methanol synthesis and inhibits the RWGS reaction to produce CO. Reducing the particle size of PdZn alloy and increasing the surface area of PdZn alloy particles are beneficial to improve the methanol selectivity. However, the performance of Pd/ZnO catalysts is strongly influenced by the loading of Pd, and only in the optimum range of Pd loading (around 5%-10%), Pd/ZnO catalysts have a desirable performance. In addition, the combination of Pd/Ga_2O_3 also has a particularly good performance, with significant results on both CO_2 conversion and methanol selectivity [7].

2.2.2. Au catalysts

As with Pd, some other Nobel metals such as Au also have a strong H_2 dissociation and activation ability. However, the performance of Au and its carriers is sometimes a dilemma, Au/Al_2O_3, Au/TiO_2, Au/ZnO and Au/ZrO_2 are the four catalysts with Au as the active component. At 0.5 MPa and 220~240ºC, Au/ZnO had the best methanol selectivity of more than 50%, but the CO_2 conversion was below 1% [8]. Further study revealed that the Au particle size played a key role, the larger the Au particle size the higher the methanol selectivity, but the lower the CO_2 conversion [8].

3. Oxide supported oxide catalysts

3.1. In₂O₃-based catalysts

In_2O_3-based catalysts have shown good activity, the high selectivity of methanol and good stability during the reaction.

The Bulk-In_2O_3 itself shows catalytic properties, the calculation carried by Pérez-Ramírez et al. shows that the apparent activation energy for methanol synthesis on the In_2O_3 (111) surface is lower than that of reverse water gas shift reaction (RWGS), so the selectivity of methanol is greatly improved. The study illustrates the mechanistic and kinetic fingerprints of the reaction that converts CO_2 into methanol. The oxygen atom surrounded by three in atoms acts as the active center for the reaction. If the In_2O_3 catalysts can be used under high pressure, high space velocities and low temperatures, the RWGS reaction competing with methanol synthesis may be completely avoided, and the conclusion is consistent with the calculation resort mentioned above. The model was designed based on the data of temperature and concentration-dependent parameters calculated by DFT, with CH_2OOH and $CH_2(OH)_2$ as the intermediate being considered during calculation. The results are expected to bring the development of In_2O_3-based materials and have the potential for large-scale application of bulk-In_2O_3 in converting CO_2 into methanol [9].

Muller et al. designed a model and monitored hydrogenation reaction which used In_2O_3 catalysts to convert carbon dioxide into methanol at 300 ºC and 2 MPa by in-situ XAS. After having probed the evolution of the structure of In_2O_3 catalysts, the whole reaction process can be divided into three stages: activation, stable catalytic performance and deactivation. In the first stage, the rate of methanol production rises constantly, followed by a stable performance that maintains a high activity. At last, deactivation comes with a remarkable symbol: a gradual decrease in space-time. Under the reaction conditions, the oxygen has vacancies, and the reduction of the coordination number around In_2O_3 leads to the formation of the In_2O_{3-x}, which is the active center in the reaction. The three stages also influence the evolution of the crystalline In_2O_3 structure. Loaded In_2O_3 catalysts show higher catalytic activity than Bulk-In_2O_3 due to their better dispersion and larger specific surface area. Loading In_2O_3 onto other oxide carriers increases the dispersion of In_2O_3 and the number of oxygen vacancies in the catalysts, which can enhance the ability of adsorbing CO_2 [10].

The team of Pérez-Ramírez tested In_2O_3 loaded of various common carriers (ZrO_2, TiO_2, ZnO, SiO_2, Al_2O_3, C, SnO_2, MgO), among which In_2O_3 loaded of ZrO_2 shows the best result which can effectively increase the number of oxygen vacancies. The introduction of ZrO_2 carriers also confirmed that it has good effects on the catalytic performance of In_2O_3. Both In_2O_3/ZrO_2 and In_2O_3 have good selectivity for methanol in 473-573 K. The stability of the catalysts is also good after testing.

As shown in Fig. 3, both In_2O_3/ZrO_2 and bulk-In_2O_3 have high selectivity for methanol in temperatures ranging from 473K to 573K, with the $Cu/ZnO/Al_2O_3$ catalysts having lower selectivity for methanol. As can be seen from the graph is that the In_2O_3/ZrO_2 catalyst has the best selectivity among the three catalysts. The stability of the catalysts is tested, as illustrated in Figure 3B. The In_2O_3/ZrO_2 catalyst still maintains a high performance after a 1000-hours test, so the picture illustrates that the In_2O_3/ZrO_2 catalyst also has high stability. In Fig. 3C, the effect of different metal oxide carriers on the catalytic performance is tested. The In_2O_3/ZrO_2 catalyst has an obvious advantage over other metal oxide carriers [11].

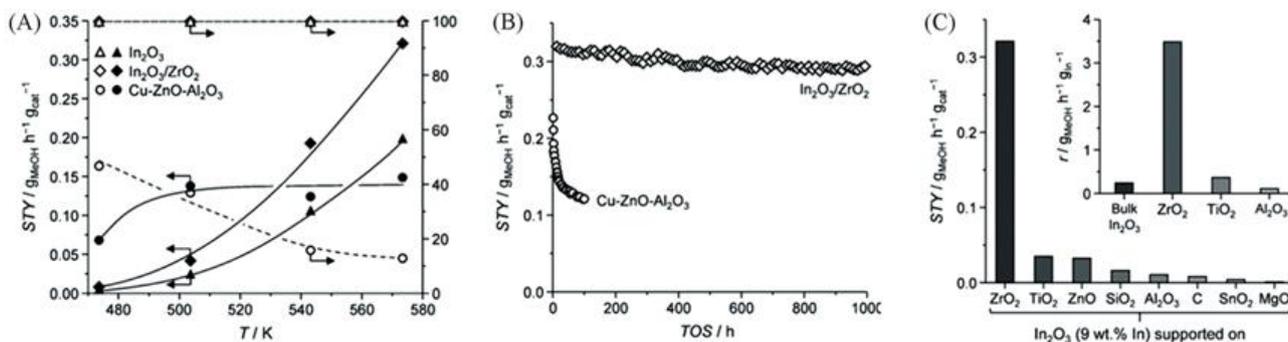**Figure 3.** (A) Methanol STY and selectivity for CO_2 hydrogenation over bulk-In_2O_3, In_2O_3/ZrO_2 and $Cu/ZnO/Al_2O_3$ catalyst at various temperatures, (B) the evolution of the methanol STY with time on stream (TOS) over In_2O_3/ZrO_2 and $Cu/ZnO/Al_2O_3$, and (C) methanol STY for different In_2O_3-supported catalysts after 4 h on stream

Zhang Kewen et al. used DFT theory to analyze the HCOO pathway for the synthesis of methanol and calculate the activation and reaction energies of each radical in the HCOO pathway. CO_2 is first hydrogenated to HCOO, which reacts with H atoms to become H_2COO and H_3CO, and finally, H_3CO becomes methanol by protonation. The NiO-supported In_2O_3 has a flat structure consisting of three In_2O_3 layers and a Ni layer, and the surface contains two In-O chains with four in atoms and six O atoms. The oxygen vacancies on the surface are created by the removal of oxygen atoms. H_2 on the surface of $In_2O_3(110)$ can dissociate into H atoms, and the CO_2 occupies the oxygen vacancy in the multi-dentate conformation. CO_2 has higher adsorption energy on the surface of NiO-supported $In_2O_3(110)$ than that on the $In_2O_3(110)$ surface. And the conclusion can be made that the NiO-supported $In_2O_3(110)$ has a more stable surface than before because the support of NiO enhances the CO_2 adsorption properties of the In_2O_3 catalyst. The analysis of Muliken charge pattern shows that

the transfer of electric charge helps activate CO_2, thus increasing the efficiency of CO_2 hydrogenation for methanol synthesis [12].

3.2. ZrO_2-based oxide solid solutions

Recently, ZrO_2-based binary oxide solid solutions have received much attention. The ZnO-ZrO_2 solid solution prepared by Li et al. showed a high methanol selectivity at 87.0% in the synthesis of methanol under industrial conditions. It also shows good stability despite some interfering substances such as SO_2 and H_2S. In addition, the results show that the key to enhancing the catalytic performance is the synergy of Zn and Zr sites which is rather than independent sites, and the Zn-Zr interface is the active center of the reaction which enables the hydrogen cracking and the activation of CO_2 adsorption. The group also reported that $MaZrO_x$ (Ma=Cd, Ga) solid solution-catalyzed hydrogenation from CO_2 to methanol has good performance, with up to 80% selectivity to methanol and up to 12.4% CO_2 one-way conversion.

When having comparable activity, the oxide catalysts always have higher selectivity to methanol than the Cu-based catalysts. Besides, both the In_2O_3-based catalysts and ZnO-ZrO_2 solid solutions can be resistant to water and sulfur-containing substances. However, oxide-based catalysts may generally require higher reaction temperatures, which is connected to the higher energy consumption [13].
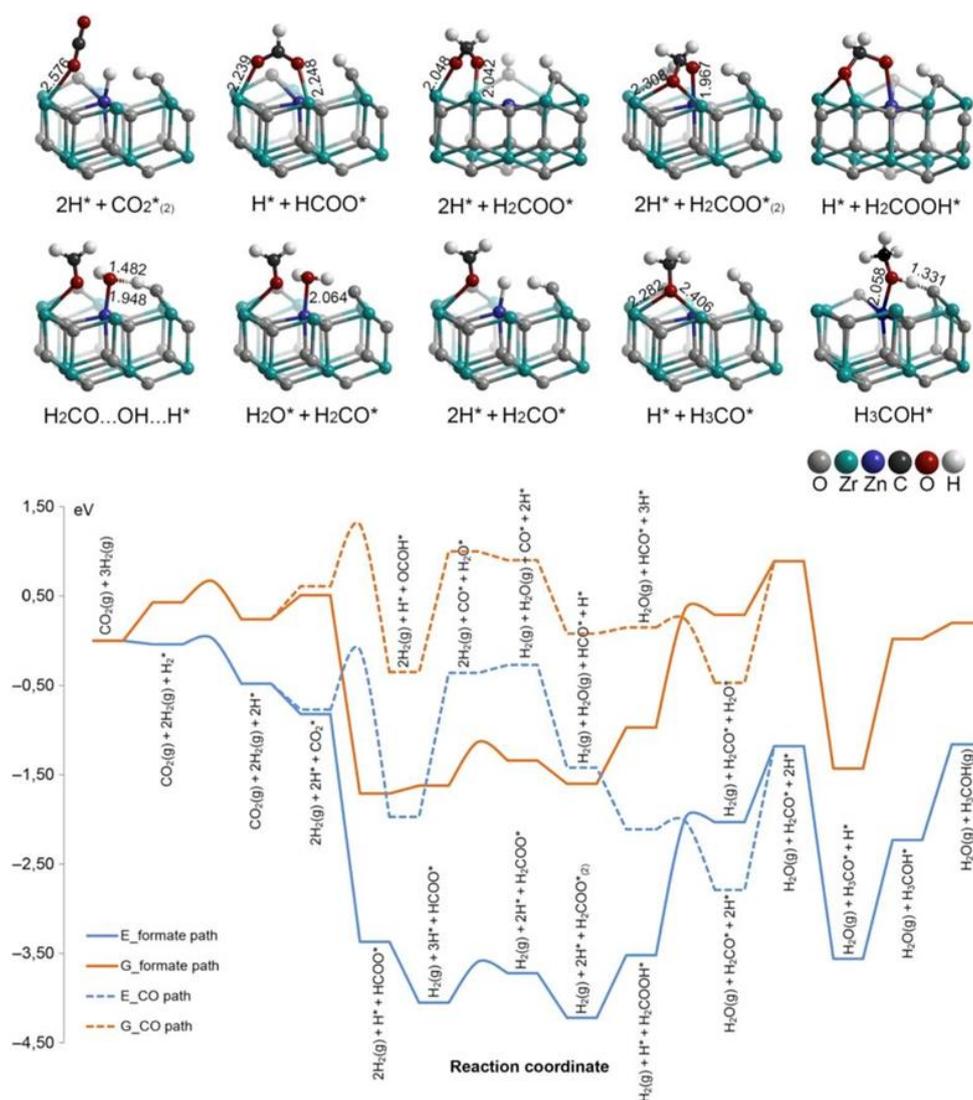

Figure 4. DFT calculations. Reaction diagram [energy (E) and Gibbs free energy (G) at a typical reaction temperature of 593 K] of CO_2 hydrogenation to methanol on the (101) surface of the tetragonal ZnO-ZrO_2 model

4. Other catalysts

4.1. Transitional metal carbides

Transition metal carbides are metal derived compounds expected to be used in many catalytic processes. Their high melting point, high hardness and excellent hydrogenation catalytic properties make them stand out in photocatalysis. Similar to Pt, Rh and other precious metals, they also have the characteristics of high thermal stability and mechanical stability.

In the three decades of research on metal carbides, many of their hidden properties have been found. Metal carbides can not only become an effective carrier for metal dispersion, but also affect the reactivity of supporting metals by changing chemical bonds.

Metal carbides also play a special role in the research of carbon dioxide hydrogenation. As long as the proportion of a in metal carbides is changed, the degree of carbon dioxide adsorption and other properties can be affected. For example, in the currently known transitional metal carbides, molybdenum carbide not only has the ability of H_2 dissociation, but also can cut the C=O bond. Molybdenum carbide generally has a Polycrystalline structure, in terms of catalysis, the most usual type is β-Mo_2C and α- MoC_x ($0.5 < x < 1$), all of them can provide higher selectivity and efficiency for carbon dioxide hydrogenation. In order to find out the advantages and disadvantages of various catalysts β-Mo_2C, CO Mo_2C catalysts and $PtcO/CeO_2$ (6.6%) and $PdNi/CeO_2$ Catalysts were tested under the same conditions. The performances of these catalysts are as follows (Table 1). Compared with the traditional catalyst, the catalyst shows better selectivity in the conversion of CO_2 and CO selectivity. The main reason for this result is that Mo_2C has the ability to destroy the C=O bond and remove oxygen from Mo_2C-O. More importantly, it can dissociate hydrogen to help carry out the operation of carbon dioxide hydrogenation. Then the catalytic performance of Mo_2C was further improved by increasing the content of Co. It can be seen from table 1 that when 7.5 wt% CO was added to Mo_2C, the conversion of carbon dioxide increased by 0.8%, and the ratio of CO:CH_4 increased significantly [14].

Table 1. Comparison of carbon dioxide conversion, turnover frequency (TOF) and CO: CH_4 ratio of four catalysts

Catalyst	CO_2 Conversion (%)	TOF (min^{-1})	CO:CH_4 Ratio
$PtCo/CeO_2$	6.6	14.6	4.5
$PdNi/CeO_2$	2.5	5.6	0.6
Mo_2C	8.7	25.7	14.5
$Co-Mo_2C$	9.5	16.1	51.3

Although the excellent catalytic performance of TMC is indeed an ideal material, its inherent characteristics still hinder the exertion of catalytic performance. For instance, when participating in oxidation reaction, many TMC catalysts have intense expression, and the passivation treatment in order to avoid oxidation also needs strict control conditions.

Generally speaking, iron carbide is rarely used in the research of CO_2 hydrogenation. Because of its high chemical stability, it is often used as raw material for ironmaking. However, it has recently been incorporated into the research process of carbon dioxide utilization process.

Liu et al. Studied the activation mechanism of carbon dioxide by χ-Fe_5C_2 and θ-Fe_3C through the combination of theory and calculation, and detected the possibility of their promoting carbon dioxide activity. The final results show that χ-Fe_5C_2 and θ-Fe_3C are both active for the direct dissociation of carbon dioxide, so iron carbide will become a more effective catalyst than pure iron. Moreover, iron carbide also plays a role in the methanation of carbon dioxide, so methane production will be high in the future [15].

4.2. Binary and Ternary oxides catalysts

4.2.1. Binary oxides

In the research of carbon dioxide hydrogenation, catalyst In2O3 has a good prospect. The newly developed bimetallic catalyst Inx-Coy has optimized quite a lot of performance on the basis of pure In2O3. Because the surface of Inx-Coy is reconstructed and covered with a core-shell structure with In2O3 as the main element, its adsorption capacity for carbon dioxide and carbonaceous substances is significantly increased. The difference in selectivity between Co3O4 and Inx-Coy catalysts was due to the different CO_2 adsorption capacity and the stabilization of carbon-containing intermediates such as *HCOO. CO_2 and carbon-containing intermediates adsorbed much stronger on In-Coy than on Co3O4 caused a feasible C/H ratio, thus allowing the *CH3O to desorb CH3OH instead of being over-hydrogenated to CH4 [16].

Co-Cu oxide catalyst can be prepared by coprecipitation method and applied to the reduction of carbon dioxide to methanol. It can be seen from the results that the metallic element of $Co_x Cu_y$ is deeply related to its structure and the performance of the catalyst. $Co_9Cu_1O_X$ catalyst showed high activity and selectivity in the formation of C channel. At the reaction temperature of 200ºC, the activity of C^{2+} channel could reach 18.6 mmol·g_{cat}^{-1} h^{-1} and the selectivity could reach 60%.

4.2.2. Ternary oxides

Ternary oxide catalysts can be prepared by impregnation and coprecipitation. It has more excellent structural properties and can provide more possibilities for the research of carbon dioxide hydrogenation to methanol.

In trimetallic oxide catalysts, the metal composition of the catalyst and the reduction temperature affect the catalytic performance. The catalyst $Co_7Cu_1Mn_1O_x$ (200) reacts in H_2 at a temperature of 200ºC for 2 hours, demonstrating an excellent catalyst performance. The construction of this catalyst provides the possibility to reduce the reaction temperature of conventional thermal catalysis [17].

Cu-Ce-Zr ternary metal oxide catalyst can be prepared by coprecipitation. Because CeO_2 and ZrO_2 can reduce the decomposition temperature of H_2 and enhance the adsorption capacity of carbon dioxide, they are very effective in the research of carbon dioxide hydrogenation. Especially when the mixed catalyst is synthesized in the ratio of $CeO_2/ZrO_2=1$, the highest peak of CO_2 conversion is reached. After studying the performance and activity of three-way catalysts with different components, the experimental results are listed in Table 2. It can be seen from the table that although $Cu_{30}Zr_{70}O$ has the highest methanol selectivity, up to 65%, its CO_2 conversion and CH3OH space-time yield (STY) are quite low. In contrast, $Cu_{30}Ce_{35}Zr_{35}O$ has a relatively balanced performance and can play a greater role in carbon dioxide hydrogenation [18].

Table 2. Properties of catalysts with different metal compositions

Sample	CO_2 conversion (%)	CH3OH selectivity (%)	CO selectivity (%)	CH3OH STY (mmol$_{CH3OH}$·h^{-1}·g_{cat}^{-1})
$Cu_{30}Zr_{70}O$	2.0	65.0	35.0	0.87
$Cu_{30}Ce_{15}Zr_{55}O$	5.5	61.8	38.2	2.28
$Cu_{30}Ce_{25}Zr_{45}O$	9.6	58.3	41.7	3.75
$Cu_{30}Ce_{35}Zr_{35}O$	14.3	53.8	46.2	5.15
$Cu_{30}Ce_{45}Zr_{25}O$	12.8	47.7	52.3	4.09
$Cu_{30}Ce_{55}Zr_{15}O$	8.3	42.2	57.8	2.35
$Cu_{30}Ce_{70}O$	3.1	35.5	64.5	0.74

5. Analysis

From the above catalysts, three of the most typical examples have been selected as examples. The Cu-based catalyst is by far the most widely used of the methanol synthesis catalysts. The Cu-Zn catalyst has excellent performance for the synthesis of methanol, and although the conversion of CO_2

and H_2 is low, it has good selectivity for methanol production. Increases in both temperature and pressure lead to increased conversion of CO_2 and H_2 and higher methanol selectivity. Recent studies have shown that the interaction between Cu and the carrier improves the catalytic effect, and this has been demonstrated with Cu/ZrO_2 and Cu/CeO_2. In_2O_3-based catalysts have high stability and selectivity for methanol, and they are investigated by lots of scientists. The In_2O_3 catalysts loaded with ZrO_2 have excellent performance, with a selectivity of >99.5% for methanol and very high yields under certain conditions. The In-Co catalysts loaded on CeO_2 carriers are characterized by good stability, high selectivity for methanol and high yields, with moderate to high-performance indicators and essentially no shortcomings [19]. As is shown in Fig. 5, the three kinds of catalysts have their own advantages, so they all have the possibility to be applied in industrial production.
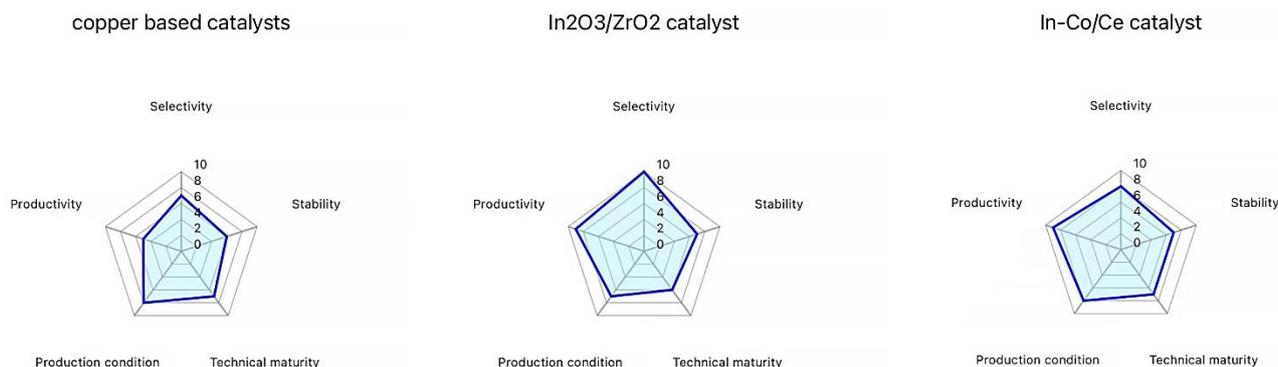

Figure 5. The performance of copper-based catalysts, In_2O_3/ZrO_2 catalyst and In-Co/Ce catalyst.

After taking them together, they can show that copper-based catalysts are characterized by their relaxed influence on the reaction environment and have a reasonably good level of technological maturity.

The recent emergence of In_2O_3/ZrO_2 catalysts demonstrates the advantages of very high yields and selectivity, which shows the great potential of these catalysts for the future, but the reaction conditions are relatively demanding, and more investment is needed to increase the technological maturity of these catalysts.

In-Co/Ce catalysts are a more comprehensive option, firstly they have more relaxed reaction requirements and very high yields, but further improvements are needed in terms of stability.

6. Conclusions

This paper reviews the main catalysts currently used for the synthesis of methanol from CO_2, including metal-based catalysts (represented by copper), non-metallic catalysts (represented by In_2O_3) and other emerging composite catalysts. A performance visualization of a representative catalyst from each category is presented to analyze the characteristics of the different catalysts for local adaptation. The copper-based catalysts were found to be characterized by a wide range of applications and relaxed reaction conditions, while the In_2O_3 catalysts were characterized by very high yields and selectivity but harsh reaction conditions. The composite metal-based In-Co/Ce catalysts were found to have excellent yields and reaction conditions.

Copper-based catalysts are currently the most widely used and have a relatively high level of technological maturity, but the high yields and selectivity showed by the emerging non-metallic and composite metal catalysts are pointing the way to future catalyst development, and more investment is urgently needed in these emerging catalyst areas to improve their technological maturity and stability and to provide more possibilities for future CO_2 utilization.

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