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Research Progress on the Effects of Cu-Based Catalysts on CO_2 Hydrogenation to Methanol

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Abstract. CO_2 hydrogenation to methanol is an important route for reducing carbon emissions and utilizing hydrogen energy, and multiple catalytic systems have been developed. Among them, Cu-based catalysts remain an important class because of their low cost and substantial research foundation. This review focuses on structural regulation of Cu-based catalysts and discusses the effects of Cu particle size, the Cu^0/Cu^+ ratio, metal–support interfaces, oxygen vacancies, spinel supports, and alloying on reaction performance. The function of Cu-based catalysts is attributed mainly to multisite cooperation. Cu^0 primarily supplies hydrogen species, whereas Cu^+ and oxide interfaces more readily stabilize oxygenated intermediates. Excessive pursuit of Cu dispersion or defect concentration is not advisable. A more rational direction is to maintain moderate CO_2 adsorption, stable adjacent Cu^0/Cu^+ structures, and low interfacial deactivation during the reaction.

Keywords: Cu-based catalysts, CO_2 hydrogenation, methanol synthesis, support defects, metal–support interface, selectivity regulation

1. Introduction

Conversion of CO_2 into methanol is an important route for carbon-emission reduction and for achieving carbon peaking and carbon neutrality. Methanol can be used as a liquid fuel and can also be further converted into important organic chemical feedstocks such as formaldehyde and dimethyl ether. The main difficulty of the reaction is that CO_2, as a linear molecule, is not readily bent and has a high carbonyl bond energy. The catalyst surface must provide suitable CO_2 adsorption sites and available hydrogen species. If the surface is only effective for H_2 activation, it is difficult for CO_2 to enter the reaction. If CO_2 adsorption is too strong, intermediates remain on the surface and subsequent hydrogenation slows down. The reaction also produces water, which changes hydroxyl coverage and may even promote Cu particle migration or interfacial reconstruction. Therefore, CO_2 hydrogenation to methanol cannot be solved by a single site; it is more accurately regarded as a sequential cooperation of surface processes [1].

Cu-based catalysts have attracted extensive attention because $Cu/ZnO/Al_2O_3$ has been widely used in syngas-to-methanol synthesis and Cu species are effective for H_2 activation and hydrogenation. However, metallic Cu alone usually shows insufficient CO_2 adsorption ability, so the support, Cu valence state, and interfacial structure become critical. In general, Cu^0 provides hydrogen species, Cu^+ stabilizes oxygenated intermediates such as HCOO* and CH_3O*, and oxide

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defects promote CO_2 adsorption and polarization. Based on this understanding, this review discusses Cu particle size, the Cu^0/Cu^+ ratio, oxygen vacancies, support acid–base properties, and alloying within a structure–intermediate–selectivity framework, focusing on how HCOO*, CO*, and CH_3O* affect methanol formation and side reactions [2].

2. Structural characteristics of Cu-based catalysts and their effects on performance

Cu particle size is often considered a basic structural factor. When the particles become smaller, the number of surface Cu sites increases and the contact area with the support also increases, which favors the formation of more interfacial sites. Thus, highly dispersed Cu is often associated with high activity. However, excessively small Cu species can migrate under H_2 atmosphere, high temperature, and the presence of water; moreover, after a certain reaction time,the resulting sintered Cu particles may lose their initial advantages. Evaluation of Cu particle size should not rely only on the average size from TEM; changes before and after reaction, the number of interfacial sites, and reduction behavior should also be considered together [3].

The Cu^0/Cu^+ ratio is a core factor in this reaction. In general, Cu^0 provides H_2 dissociation and hydrogen spillover, whereas Cu^+ functions by stabilizing oxygenated intermediates such as HCOO* and CH_3O*. Methanol formation is likely to occur in regions where Cu^0, Cu^+, and the oxide are adjacent rather than being carried out by a single valence state. When Cu^+ is insufficient, CO_2 activation and intermediate stabilization are inadequate; when Cu^+ is excessive, H_2 activation ability may decrease. Under characterization conditions, valence-state ratios obtained by XPS or Cu LMM Auger spectra mostly correspond to non-reaction states. Sample transfer, exposure to air, and pretreatment all affect the results; therefore, the Cu^+ fraction in a fresh sample cannot be directly equated with the real active structure.

The support not only supports Cu particle dispersion but also plays at least three other roles: providing CO_2 adsorption sites, regulating the electronic structure of Cu species, and influencing the residence of water and oxygenated intermediates on the surface. Differences among supports are ultimately reflected in the reaction pathway. If a support only enhances CO_2 adsorption but does not assist subsequent hydrogenation, formate or carbonate species may accumulate. If the contact between the support and Cu is insufficient, hydrogen species and activated CO_2 species are difficult to connect in sequence. A suitable support should polarize CO_2 moderately without completely immobilizing intermediates [4, 5]. Oxygen vacancies are a common way to boost CO_2 activation.A proper amount of oxygen vacancies can enhance CO_2 adsorption and make linear CO_2 more readily polarized. Oxygen vacancies also change the electronic environment around nearby Cu species, which in turn affects the Cu^0/Cu^+ balance. When defects are excessive, overly strong adsorption sites may form on the surface. If carbonate or formate species are difficult to convert further, the reaction rate decreases. Oxygen vacancies that appear abundant in initial characterization may be occupied or modified by water under real reaction conditions. Therefore, defect engineering should control effective defects rather than simply increasing the number of vacancies [4].

Spinel oxides are also important in this reaction.Taking $ZnGa_2O_4$ as an example, spinel supports have relatively stable crystal frameworks and adjustable cation coordination and oxygen-vacancy distributions. Compared to some single oxides, spinels tend to keep their interfacial morphology better under high temperatures and in the presence of water. Their value lies not only in stability but also in structural tunability. Oxygen vacancies, cation vacancies, and local lattice distortion jointly affect the CO_2 adsorption mode and may also change the anchoring positions of Cu species. If Cu gets stabilized near defects, the distance between CO_2 activation sites and H_2 activation sites

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becomes shorter, so the methanol pathway can run more smoothly. If defects mainly stabilize carbonate species that are difficult to convert, the advantages of these supports are also weakened.

Alloying and bimetallic regulation, as current frontier research areas, provide more options for Cu-based systems. Adding elements like Zn, Ga, Zr, Pd, or Ni can lead to alloys, oxide-interface species, or dispersion promoters. If a second metal alters the electronic structure of Cu, the adsorption strength of CO* may change. If it improves Cu dispersion, the activity increase may mainly originate from the number of sites. If it boosts interfacial stability, the long-term performance will probably benefit. By combining XRD, TEM, XPS, H_2-TPR, CO_2-TPD, and in situ IR, it is possible to determine which step is changed by the second component [4, 5].

3. Reaction mechanism of CO_2 hydrogenation to methanol

CO_2 hydrogenation to methanol involves multiple steps. CO_2 is first adsorbed and polarized on the surface, while H_2 must dissociate into reactive hydrogen species. Carbon-containing intermediates then undergo multiple hydrogenation steps, and methanol finally desorbs from the surface. Common pathways include the formate pathway, the carboxyl pathway, and the CO pathway. In the formate pathway, CO_2 forms HCOO* on support or interfacial sites and then proceeds to methanol through species such as H_2COO*, H_2CO*, or CH_3O*. The CO pathway is more closely related to the reverse water–gas shift reaction. CO_2 is first reduced to CO*, and CO* may undergo further hydrogenation or desorb directly as CO. In real catalytic systems, these pathways are usually not completely separated; one pathway may dominate, while another competes as a side route [1, 3].

HCOO* is a widely discussed intermediate. The appearance of formate signals in in situ IR indicates that CO_2 has undergone initial activation. This evidence is valuable, but it should not be overinterpreted. An increase in HCOO* peak intensity does not necessarily mean faster methanol formation; sometimes it only indicates accumulation of surface species. If subsequent hydrogenation of HCOO* is slow, it is closer to a spectator species. Whether HCOO* participates in the main pathway should be judged by whether its formation and consumption change synchronously with methanol yield. Cu^+ sites, oxygen vacancies, and basic sites on the support help form HCOO*, whereas Cu^0 sites provide hydrogen for subsequent hydrogenation. When the two types of sites are too far apart, the pathway is interrupted; when binding is too strong, the intermediate is difficult to convert further [2].

The CO pathway is an important source of methanol selectivity loss. As temperature increases, the reverse water–gas shift reaction occurs more readily and CO selectivity often increases. CO is not completely inert. Adsorbed CO* may still enter the methanol pathway if it undergoes further hydrogenation. However, Cu surfaces adsorb CO only weakly, so CO* readily desorbs as gaseous CO, diverting carbon species away from the methanol formation pathway. Support acid–base properties, oxygen-vacancy concentration, and interfacial electronic structure all affect the residence time of CO*. If a catalyst converts CO_2 to CO without further hydrogenation of CO, high CO_2 conversion may be achieved, but methanol yield remains low [1].

CH_3O* is a precursor that lies closer to methanol in the reaction pathway. Its formation indicates that carbon–oxygen intermediates have undergone relatively deep hydrogenation. If CH_3O* is too unstable, the methanol pathway lacks an effective precursor. Conversely, if CH_3O* is too stable, it occupies surface sites. For Cu-based catalysts, the conversion of CH_3O* depends on the balance among Cu^+ sites, interfacial oxygen species, and hydrogen supply. In situ IR, isotope labeling, and DFT calculations can be used to evaluate this step, but a single spectral peak cannot independently support a mechanistic conclusion; reaction rate, product selectivity, and time-dependent changes in intermediates need to be considered together.

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The C_{2+} alcohol pathway represents a competing pathway. Compared with methanol formation, C_{2+} alcohol formation requires not only CO_2 activation and hydrogenation but also C–C coupling. Under thermocatalytic conditions, this step is usually more difficult to control. If the surface CO* concentration is high and suitable coupling sites are present, part of the carbon flux may enter longer-chain oxygenated products. If hydrogen coverage is too high, hydrogenation readily suppresses coupling. For systems targeting methanol, C_{2+} alcohols should not be overemphasized. This pathway indicates that methanol selectivity is determined by competition among multiple branch reactions rather than by a single step.

4. Structure–intermediate–selectivity correlation framework

As shown in Figure 1, the purpose of the structure–intermediate–selectivity framework is to convert characterization results into reaction interpretation. The structure layer includes Cu particle size, the Cu^0/Cu^+ ratio, support crystal phase, oxygen vacancies, cation vacancies, metal–support interfaces, and alloy structures. The intermediate layer focuses on the formation, accumulation, and consumption of species such as HCOO*, CO*, and CH_3O*. The selectivity layer corresponds to products such as methanol, CO, methane, and C_{2+} alcohols. The three layers do not exhibit a strict one-to-one correspondence. A structure that enhances CO_2 adsorption does not necessarily improve methanol selectivity, and a stronger intermediate peak does not necessarily indicate acceleration of the main reaction pathway. The key issue is whether the evidence is coherent: the structural change must be real, the intermediate change must explain the pathway, and the product distribution must change accordingly.

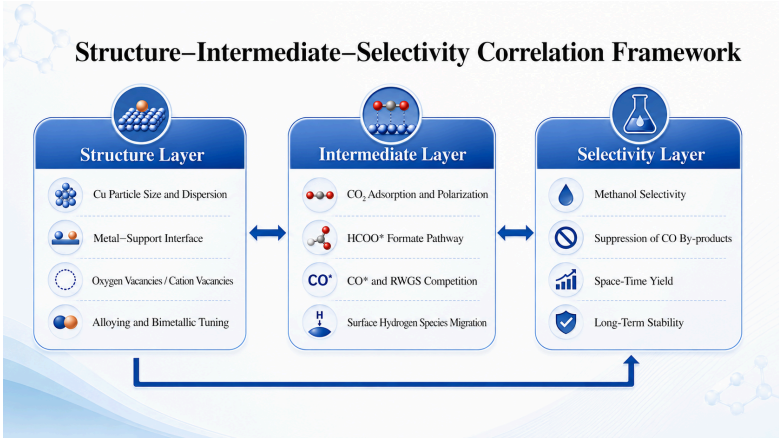

Figure 1. Schematic illustration of the structure–intermediate–selectivity correlation framework

The Cu/ZnO system provides a typical example. ZnO can change the electronic environment around Cu and can also participate in CO_2 adsorption and stabilization of oxygenated intermediates. Cu^0 provides hydrogen species, while Cu^+ or ZnO-related sites stabilize formate and methoxy species. If the Cu–ZnO contact is insufficient, activated CO_2 and surface hydrogen cannot be effectively coupled. If the interface is over-reduced or sintered, the original cooperative sites decrease. The study by Kattel et al. on the Cu/ZnO system demonstrates that methanol formation cannot be attributed only to the metallic Cu surface area; the interfacial structure is also a source of activity [2].

Defective oxide supports provide a test case for this framework.Oxygen vacancies belong to the structure layer and alter CO_2 adsorption configurations and surface electronic distribution. HCOO*,

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CO*, and CH_3O* belong to the intermediate layer and affect the direction of carbon flux. Methanol selectivity and CO selectivity are reaction outcomes. When an appropriate amount of oxygen vacancies promotes HCOO* formation, the methanol pathway may benefit. When oxygen vacancies are excessive, surface adsorbates bind too strongly, and water may occupy defect sites; the reaction does not necessarily improve as expected. Defect signals must be judged under reaction conditions. Without supporting intermediate and product data, discussion of the number of oxygen vacancies alone easily becomes a superficial argument [5].

Defect structures in spinel supports make the analysis more detailed. In materials such as $ZnGa_2O_4$, local coordination of Zn, Ga, and O affects acid–base properties and electronic structure. Oxygen vacancies may shorten the distance between CO_2 activation sites and Cu hydrogenation sites, cation vacancies may change the activity of neighboring oxygen species, and lattice distortion may increase the anchoring strength of Cu. If these structural changes promote the conversion of HCOO* to CH_3O*, methanol selectivity is more likely to improve. If defects mainly stabilize carbonates, surface carbon species may block the pathway. Spinel supports are not necessarily superior to other oxides; instead, they offer more flexibility in tuning the relationships among defects, interfaces, and intermediates.

This framework also helps identify misinterpretation of characterization results. A decrease in the H_2-TPR peak temperature may indicate that Cu is more readily reduced, but it may also indicate weaker Cu–support interaction. Enhancement of strong adsorption peaks in CO_2-TPD may represent improved CO_2 adsorption capacity, but it may also indicate an increase in carbonates that are difficult to convert. An increased Cu^+ fraction in XPS may be favorable for intermediate stabilization, but it may also originate from surface oxidation in air. If these signals are directly interpreted as the reasons for high methanol selectivity, the logic is insufficiently robust. A more appropriate approach is to place them into the same evidence chain and judge them jointly through in situ spectra, reaction rates, and stability tests.

5. Design strategies for Cu-based catalysts

Synergistic regulation of Cu^0/Cu^+ serve as a design starting point. An ideal Cu-based catalyst should retain the H_2 activation ability of metallic Cu and also provide Cu^+ or interfacial sites to stabilize oxygenated intermediates. Reduction temperature, reduction atmosphere, precursor type, promoters, and support defects all affect this ratio. The Cu valence state is not static; H_2, CO_2, water, and oxygen migration in the support continuously change the surface state during reaction. Comparing only the Cu^+ content of fresh samples is of limited value. A more relevant question is whether Cu^0/Cu^+ maintains an appropriate balance during the reaction and whether this balance correlates with the methanol formation rate.

Interface engineering should address the problem of spatial relay. CO_2 can be polarized on support or defect sites, H_2 can dissociate on Cu sites, and intermediates must transform between the two types of sites. If the interfacial distance is too large, activated species cannot encounter hydrogen; if binding is too strong, sites may be covered. If the interface is unstable, even good short-term performance is difficult to maintain. An effective interface is not simply one with the largest area; it must maintain a balance among adsorption, hydrogenation, and desorption. Regulation of Cu loading, calcination–reduction procedures, and support defect concentration can change the number and strength of interfacial sites. Performance evaluation should ultimately be based on methanol space-time yield and long-term stability.

CO_2 hydrogenation to methanol necessarily produces water. Water affects surface hydroxyl concentration and may also change the state of oxygen vacancies. Some supports exhibit strong CO_2

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adsorption capacity in dry characterization, but under water-containing reaction conditions, the number of effective defects may decrease. Structurally stable composite oxides and spinel oxides are therefore attractive. They may not necessarily exhibit higher initial activity, but they may be more suitable for maintaining long-term interfacial structures. For practical catalysts, stable moderate activity is sometimes more meaningful than short-term high activity.

Alloying design should not pursue new elements alone. Before introducing a second metal, the reaction bottleneck should be identified. The problem may be weak CO_2 adsorption, slow subsequent hydrogenation of HCOO*, excessive CO by-products, or easy sintering of Cu particles. Different bottlenecks require different promoters. If the CO pathway is too strong, CO* adsorption and further hydrogenation need to be regulated. If the problem is Cu deactivation, support anchoring and interfacial stability are more important. Summarizing all promoter effects as electronic effects or synergistic effects makes the analysis superficial. Catalyst design requires a narrower and clearer causal chain.

Stability evaluation should not be mentioned only briefly at the end of an article. Under CO_2 hydrogenation to methanol conditions, Cu particle sintering, changes in Cu valence state, support hydroxylation, modification of oxygen vacancies by water, and reconstruction of metal–support interfaces can all lead to deactivation. Some catalysts show relatively high conversion in the short term, but methanol selectivity decreases after operation for a period of time. Such results have limited value for practical application. Performance evaluation should at least consider CO_2 conversion, methanol selectivity, methanol space-time yield, and stability simultaneously. If structural comparison before and after reaction can be included, the conclusions are more reliable than those based only on initial data.

6. Conclusions

Using the structure–intermediate–selectivity framework, this review summarizes how multiple structural layers affect the performance of Cu-based catalysts for CO_2 hydrogenation to methanol and derives design strategies for Cu-based catalysts with high CO_2 conversion, methanol selectivity, methanol space-time yield, and stability. Placing Cu particle size, the Cu^0/Cu^+ ratio, oxygen vacancies, spinel supports, and alloying in the same analytical chain facilitates the interpretation of performance differences. This review proposes that systems with higher methanol selectivity are usually not those in which a single characterization parameter reaches an extreme value, but those in which structural factors maintain a reactive balance. This conclusion addresses the limitation of long-standing discussions that only classify and compare catalyst types and provides a deeper structural analysis of Cu-based catalytic systems. However, this review remains at the theoretical level and is based on the organization of previous studies; it lacks first-hand experimental data and evidence under real reaction conditions, and its analytical scope and approach are still insufficient. Future experimental research should focus on how to synthesize Cu-based catalysts with multiple optimized structures in the laboratory and how to effectively select and balance structural components. Overall, this review emphasizes the need for future Cu-based catalysts to focus on precise control of interfaces and reaction pathways rather than separately optimizing a single component, offering guidance for future research in this field.

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