

Review

A Concise Review of Catalytic Synthesis of Methanol from Synthesis Gas

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Abstract: Regenerative Robust Gasification promises to convert unsorted organic waste, including all plastic waste, into the fungible, primary feedstock chemical methanol. As the backbone of the C1 chemical industry, methanol has broad application in circular economy chemical synthesis. This paper summarizes traditional and newer approaches for producing methanol from synthesis gas. Approaches, methods, reaction mechanisms, catalyst systems, catalyst synthesis methods, reactor types, and many other aspects are summarized.

Keywords: syngas; methanol; catalyst; LPMEOH

1. Research Necessity

Methanol is a primary feedstock chemical for the subsequent synthesis of chemicals and products [1]. Some examples include formaldehyde, acetic acid, acetic anhydride, dimethyl ether (via Methanol-to-Dimethyl Ether, MTD) [2], olefins (via Methanol-to-Olefins, MTO) [3], gasoline (via Methanol-to-Gasoline, MTG) [4], aromatics (via Methanol-to-Aromatics, MTA) [5], and dimethyl carbonate (via Methanol-to-dimethyl carbonate, MTC) [6].

Methanol is a traditional value-added chemical product. Compared with traditional petroleum-based fuels, alcohol can burn more fully due to the presence of oxygen. Methanol is the simplest alcohol with a small molecular weight. Second, methanol has a high-octane value and good anti-knock properties and can be used as a clean gasoline additive. As a fuel, the effective thermal efficiency of pure methanol is nearly 30% higher than that of gasoline. Therefore, methanol is a clean and efficient liquid vehicle fuel and a high-power raw material for fuel cells [7].

In general, methanol is widely used in chemical, agricultural, medical, and other fields. Research on methanol synthesis is, therefore, of great significance to the development of many fields.

Recently, the Consortium for Waste Circularity has advocated the use of “Regenerative Robust Gasification” to simplify waste collection and boost recycling rates. Robust Gasification refers to a type of gasifier that can accept everything in municipal solid waste (MSW) without the need for sorting. While Robust Gasifiers melt down and recover inorganics (e.g., metals and glass), these materials do not add benefit to the process, so inorganics that can be removed from the waste stream would likely be removed and recycled traditionally. To the extent that regional markets demand specific organic materials, such as biomass and particular plastics, these materials may also be selectively removed to serve the demand of other material-specific recycling processes. However, all other materials, including multi-layer plastics, metallized flexible films, and many materials that are not conducive to traditional recycling can be gasified into syngas. “Regenerative robust gasification” refers to the use of syngas for the subsequent manufacture of new products, plastics, and packaging, as opposed to use for fuel and/or power. Since syngas is not easily transported,



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the conversion of syngas into a fungible, widely used chemical feedstock, such as methanol, is proposed. Therefore, a small-scale, distributed manufacture of methanol from waste-derived syngas is required. This work provides a concise review of current state-of-the-art methanol synthesis from syngas.

2. Research Background and Current Situation

The methanol synthesis process includes gas and liquid phase synthesis methods. Due to the differences between these methods, each one will be reviewed separately below.

2.1. Gas Phase Processes

2.1.1. Synthesis Methods and Catalysts

At present, commercial methanol synthesis is primarily a gas-phase process. According to different operating pressures, the gas-phase process can be characterized as high-pressure, medium-pressure, and low-pressure [8].

High-Pressure Gas-Phase Methanol Synthesis

In 1923, Mittash and Schneider of BASF (Germany) first synthesized methanol through a zinc oxide/chromium-based ($\text{ZnO}/\text{Cr}_2\text{O}_3$) catalyst with carbon monoxide (CO) and hydrogen (H_2) at 300–400 °C and 30 MPa. Then, they established the world's first commercial methanol plant capable of producing 300 tons of methanol annually [9].

Before the mid–1960s, almost all methanol synthesis factories used the high-pressure method with the $\text{ZnO}/\text{Cr}_2\text{O}_3$ catalyst. However, the high temperatures and pressures resulted in high costs. Additionally, the activity of the catalyst was poor, the purity of methanol was low, and large quantities of chromium posed pollution risks.

Low-Pressure Gas-Phase Methanol Synthesis

In 1966, ICI (Britain) successfully developed a copper/zinc oxide/alumina ($\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$) catalyst. Copper-based catalysts have been widely used in the industry because of their good activity and selectivity. The ICI method requires lower pressures and temperatures (5.0–8.0 MPa, 240–270 °C), which reduces the cost and consumption of raw materials. Additionally, side reactions, such as alkylation, are reduced, and the purity of crude methanol increases [10].

Five years later, Lurgi (Germany) introduced another low-pressure methanol synthesis process using a more active copper/zinc oxide/alumina/vanadium oxide ($\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3/\text{V}_2\text{O}_5$) catalyst system, which has the same excellent performance. This led to an upsurge in research on low-pressure methanol synthesis processes using copper-based catalysts [11].

Medium-Pressure Gas-Phase Methanol Synthesis

While the low-pressure method offered considerable advantages, one disadvantage is the requirement for large-volume reaction vessels. Therefore, the medium-pressure method was developed based on the low-pressure method.

The medium-pressure method has the same catalytic system as the low-pressure method, using a copper-based catalyst and the same reaction temperature, but the reaction pressure is increased to 10–20 MPa. Therefore, this method not only has similar advantages to the low-pressure method but also solves the shortcomings of the excessively large footprint required in the production of the low-pressure method.

Non-Copper Catalyst

It has been discovered that noble metals, such as Pd, Pt, Zr, and Rh, can also be active catalysts for methanol synthesis [12–15]. Although the mechanism of methanol formation on these catalysts has not yet been elucidated, it has been recognized that these metals offer good activity for methanol synthesis due to their strong hydrogenation properties, accompanied by the ability to activate adsorbed CO. Studies have shown that the activity and selectivity of Pd and Rh catalysts are largely affected by the composition

of the support and additives. It has been found that Pd supported on some types of materials, such as silica or cerium dioxide, has high activity and selectivity for methanol synthesis. Song et al. [16] used hollow silica as a carrier to prepare a new eggshell-type Pd/SiO₂ catalyst and Ca-Pd/SiO₂ catalyst with Ca as an additive by the “incipient wetness impregnation” (IWI) method and investigated methanol synthesis performance of two types of catalysts. It was found that the activities of Ca-Pd/SiO₂ and Pd/SiO₂ were 36.50 and 2.54 mmol CO/mol Pd/s at 250 °C and 2.5 MPa, respectively. The selectivity to methanol was 95.2% for both catalysts.

2.1.2. Types of Reactors

The synthesis of methanol generally involves synthesis gas (syngas) production, conversion, purification, crude methanol synthesis, and methanol refining (Figure 1). The reactor is central to the entire methanol synthesis process.

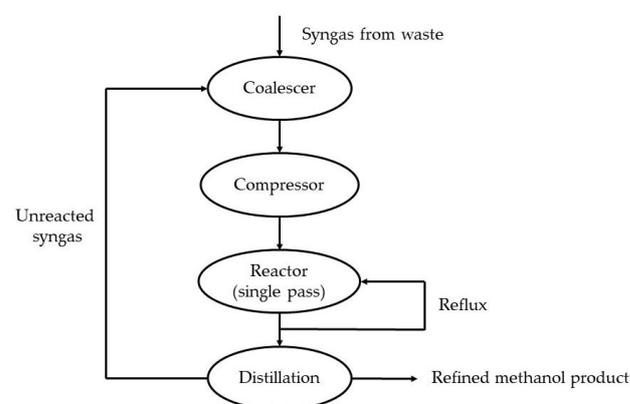


Figure 1. Process of synthesizing methanol [9].

Continuing research on methanol production focuses on the reduction of costs and upsizing scale. The high-pressure method cannot compete with low- and medium-pressure methods, so it is being phased out. Since the mid–1970s, almost all new or expanded methanol factories in the world have adopted low- or medium-pressure methods. The following are the representative methods among them:

ICI Method

The ICI process is most widely used in cold shock synthesis towers [17,18]. The tower divides the reaction bed into several adiabatic sections. Between the two sections, cold syngas is introduced through a lozenge sparger. The temperature of each section is maintained at distinct values. Advantages of the ICI cold shock synthesis tower are: the reactor structure is simple and can be operated in a single tower; the temperature is easy to control, and the operation is stable; the production capacity is high (up to 3000 tons per day); catalysts are not layered, simplifying loading and unloading; utilization of reactants is high; and the investment is relatively low. The disadvantages are as follows: catalyst loading is relatively high, and the recovered heat of the reaction is relatively low. Compared to the Lurgi process, the ICI process control system is more complex and more important for better controlling the temperature in each section.

Lurgi Method

The Lurgi method mainly uses shell-and-tube isothermal reactors [17]. Reactors are generally of two types: catalysts are packed in tubes, with water flowing between tubes to remove the heat of the reaction; catalysts are packed between the tubes, and water flows in the tubes. The reaction gas flow is axial in both types of reactors. Its advantages are: temperature distributions in the catalyst bed are uniform, temperature changes are small, few side reactions, and product quality is high; reaction temperatures can be accurately

controlled by adjusting the pressure of the by-product steam, and the catalyst has a long service life; yield is high; heat released during the methanol synthesis reaction can be recovered and utilized. Saturated medium-pressure steam, as a by-product, can also be used as a heat source of the distillation tower reboiler during the subsequent refining of the crude methanol product. The process becomes less sensitive to fluctuations as production capacity increases, and crude methanol is relatively pure. The disadvantage is that the reactor structure is complex, and cost is relatively high, thus limiting its production scale.

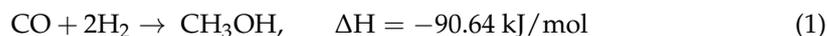
Other

In addition to the above two reactor types, there are other reactors that also perform well. For example, the Linde reactor is an isothermal coil heat exchanger [10]. Catalysts are placed outside the coil, and water inside the coil is used to remove heat, creating high-pressure steam as a by-product. Its principles and characteristics are very similar to those of the Lurgi method. The Linde process offers good performance but with complexity and cost. The Linde method may not scale as well for high production requirements.

The Topsoe reactor is similar to the ICI method [19]. The reactor is a multi-stage adiabatic synthesis reactor with a heat exchanger placed between catalysts to remove heat. Its advantages are: the pressure drop between beds is small, and the methanol synthesis reaction rate can be accelerated by increasing the gas velocity, also increasing methanol yield; the reactor is allowed to be filled with smaller catalyst particles, which improves reaction rate; and the production scale can be expanded by increasing the height of the reactor with the diameter unchanged. The disadvantages are as follows: the reaction gas flows axially, resulting in large pressure drops within the bed, which increases the difficulty of equipment manufacturing and investment costs; the gas distribution in the recycle loop is relatively uneven; and the recycled gas volume is large, so catalysts placed in the reactor cannot be fully utilized.

2.1.3. Reaction Mechanism

The primary methanol synthesis reaction stoichiometries are as follows:



The production of methanol from syngas is exothermic. Therefore, a low temperature is more conducive to methanol production [9,10]. However, traditional industrial methanol synthesis is carried out under relatively high temperatures and high pressures, so the theoretical conversion rate of CO is equilibrium limited. There have been many reports on traditional gas-phase methanol synthesis, and much effort has been made to avoid the accumulation of reaction heat. Usually, the single-pass conversion rate of CO for methanol synthesis is still less than 20%.

This fundamental thermodynamic equilibrium limitation is difficult to overcome. At the same time, various side reactions and water generated during the hydrogenation of CO₂ to produce methanol reduce the purity of crude methanol. The methanol concentration in the output is very limited. Therefore, work is needed to refine crude methanol, such as recycling and distillation, which increases capital and operating costs. In addition, the most popular copper-based catalysts in gas phase methanol production tend to be thermally unstable. Furthermore, they are easily poisoned by S, Cl, and other elements, requiring multi-step purification of the syngas feed. If the reaction temperature exceeds the catalyst tolerance, thermal sintering deactivates the catalyst. To control the temperature of the reaction bed within an acceptable range, the single-pass conversion rate is maintained at a low level.

2.1.4. The Role of CO₂ in Methanol Synthesis

In the industrial synthesis of methanol, a certain amount of CO₂ is usually required for raw synthesis gas. The conversion of syngas to methanol may involve several undesirable

side reactions. Additionally, Cu-based catalysts also have activity for some of these side reactions, so the specific reaction mechanism is still undetermined. A widely accepted route is the stepwise hydrogenation of chemically adsorbed CO to produce methanol without the dissociation of CO. It is generally believed that the presence of a certain amount of CO₂ promotes the production of methanol from syngas, but the role of CO₂ is still debated, as highlighted below.

Klier [20] believed that CO₂ does not participate in methanol synthesis, and its role was to regulate the surface structure, valence, and dispersion of copper in copper-based methanol synthesis catalysts.

Denis et al. [21] believed that CO₂ could alter CO hydrogenation by forming formate and then serving as a catalyst to increase the reaction rate of methanol synthesis.

Chinchen et al. [22] used tracer atom technology to show that when methanol is synthesized from CO/CO₂/H₂ on Cu/ZnO/Al₂O₃ catalyst, methanol is directly generated from CO₂ instead of first generating CO through reverse water gas shift and then producing methanol. CO₂ is the direct precursor of methanol synthesis, and CO can regenerate the active Cu surface by reducing CuO to Cu.

Zhang et al. [23] used three different gas compositions CO + H₂, CO₂ + H₂, and CO + CO₂ + H₂ to synthesize methanol and studied the role of CO₂ in methanol synthesis. It was shown that the conversion and efficiency of the three types of gas compositions to methanol follow this order: CO + CO₂ + H₂ > CO₂ + H₂ > CO + H₂. CO₂ significantly promoted the methanol synthesis reaction, and CO₂ was also the carbon source for methanol synthesis.

Daniel et al. [24] indicated that CO₂ content in syngas facilitates methanol synthesis by controlling the oxidation state of the interface sites. In the absence of CO₂, interface sites are obviously less active and more metallic.

2.1.5. Research on the Active Center of Copper-Based Catalysts

At present, there is no consensus on the active center of copper-based methanol synthesis catalysts, and sometimes even conflicting results are obtained [25]. There are mainly the following three points of view:

Cu⁰ Is the Active Center

Represented by ICI [26], it is believed that Cu⁰ is the only effective component in low-temperature and low-pressure methanol synthesis catalysts. Chinchen et al. [27] used copper-based catalysts with different supports to determine the relationship between the reaction activity and the surface area of copper metal. They found that the two were directly proportional. Robbins et al. [28] studied the relationship between reaction activity and the surface area of copper metal on different Cu/SiO₂ structures and reached the same conclusions as Chinchen. Therefore, they believe that the surface of copper metal is the active center for methanol synthesis. Since the activity per unit surface area of copper is not influenced by the carrier, they believe that the carrier only functions as a structural agent to maintain dispersion, and they did not find a strong interaction between Cu-ZnO. Another experimental result that supports the Cu⁰ active center theory is that no Cu⁺ and Cu²⁺ are found through in-situ detection of the catalyst in the reducing or reaction atmosphere. In-situ surface analysis by Fleisch et al. [29] showed that only Cu⁰ existed in the industrial Cu/ZnO/Al₂O₃ catalyst under synthesis conditions.

Cu⁺ Is the Active Center

As early as 1955, Nata believed that it was the Cu⁺ oxidation state copper, instead of metallic copper, that really played the role of an active center for methanol synthesis. Herman et al. [30] proposed that the active center of Cu-based catalysts should be Cu⁺ dissolved in ZnO. They found that the activity of the catalyst with more Cu⁺ sites was better, and the increase in activity came from the Cu⁺/ZnO solid solution structure. Duprez et al. [31] found Cu⁺ by XPS during the reaction and found a good correla-

tion between the Cu^+ content and methanol synthesis activity. Through NMR research, Chu et al. [32] found that the activity of synthesizing methanol on copper catalysts containing different alkali metal additives is only related to the amount of Cu^+ .

$\text{Cu}^0\text{-Cu}^+$ Is the Active Center

Duprez's [31] research results show that in low CuO content catalysts (<30%), the Cu^{2+} ions dissolved in the ZnO lattice are reduced to $\text{Cu}^0\text{-Cu}^+$. Due to the easy oxidation-reduction properties of CuO and the high stability of Cu^+ , they believe that the two-dimensional $\text{Cu}^0\text{-Cu}^+$ species are the active species in Cu/ZnO catalyst. Denise et al. [33] studied the relationship between copper surface area and the activity of $\text{Cu/ZnO/Al}_2\text{O}_3$ catalysts under normal pressure. The yield of methanol was shown to be proportional to the difference between the copper surface area before and after the reaction, and this difference is equal to the amount of copper oxidized during the reaction.

2.1.6. Summary

In summary, the Zn-Cr -based catalyst that was first invented for the high-pressure process has now been eliminated due to harsh operating conditions, low activity, and environmental pollution caused by heavy metals in the catalyst. Pd -based catalysts belong to noble metal catalysts, and the industrialization cost is relatively high. The low-temperature methanol synthesis technology on Cu -based catalysts is relatively mature, and its good activity and high methanol selectivity make it a representative catalyst for the middle- and low-pressure methanol synthesis processes. However, the commonly used copper-based catalysts are thermally unstable, and are sensitive to poisoning by S , Cl , and other elements. Moreover, the fundamental limitations of thermodynamics are difficult to overcome for the traditional gas-phase methanol synthesis process, and the reaction conditions are relatively harsh, resulting in a series of shortcomings, such as low synthesis efficiency, high energy consumption, and high cost. Under this circumstance, research has been devoted to low-temperature liquid-phase processes that can reach higher conversion.

2.2. Liquid Phase Processes

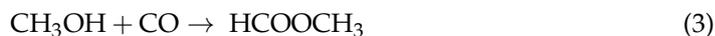
Danish scientist J. Christiansen first proposed the liquid phase methanol synthesis process in 1919, but it was not until 1975 that it finally attracted attention when it was proposed again by Chemical Systems Inc. (Fort Smith, AR, USA) [34]. Different from the gas-solid two-phase reaction of the industrial synthesis process, the liquid-phase synthesis method is a gas-liquid-solid three-phase system. Briefly, a liquid phase medium with a high heat capacity and high thermal conductivity is introduced as a solvent, which removes reaction heat rapidly, thereby keeping the reaction system at a lower temperature. At the same time, the catalyst is dispersed in the liquid phase medium, which increases the reaction surface area and accelerates the reaction process. Therefore, methanol synthesis can be carried out at a lower reaction temperature and pressure. According to the thermodynamic equilibrium, a lower temperature corresponds to a higher equilibrium conversion rate. Generally, the research on the low-temperature liquid-phase methanol synthesis process mainly uses CO/H_2 as the raw material and synthesizes methanol at $100\sim 150\text{ }^\circ\text{C}$ and $1\sim 3\text{ MPa}$. The single-pass conversion rate of CO can reach 90%. This process solves the problems of the traditional gas phase method and has the advantages of high single-pass conversion, low water content in product methanol, and low energy consumption, so it should offer commercial benefits.

2.2.1. Reaction Mechanism

CO/H_2 Reaction System

Unlike the one-step reaction of direct hydrogenation of CO to produce methanol in the gas phase method, current researchers generally believe that the mechanism of low-temperature liquid-phase methanol synthesis that uses CO/H_2 as a raw material follows a two-step reaction mechanism. Methanol already produced facilitates the reaction and is

first carbonylated to produce methyl formate, and then one molecule of methyl formate is hydrogenolyzed to produce two molecules of methanol. The net reaction result is the formation of one molecule of methanol.



The first carbonylation reaction step is the rate-controlling step [35].

CO/CO₂/H₂ Reaction System

Zeng et al. [36] used CO/CO₂/H₂ as the raw material to synthesize methanol in the low-temperature liquid phase, and believe that the reaction mechanism is mainly composed of three steps: CO in the raw material undergo a water-gas shift to generate additional CO₂, and then the CO₂ reacts with H₂ to produce formate; the formate reacts with the alcohol in the catalytic system to generate an ester; the ester is hydrogenated to generate methanol. Figure 2 shows the difference between the mechanisms of the traditional gas phase methanol synthesis (A) and the low-temperature methanol liquid phase synthesis of the alcohol system (B).

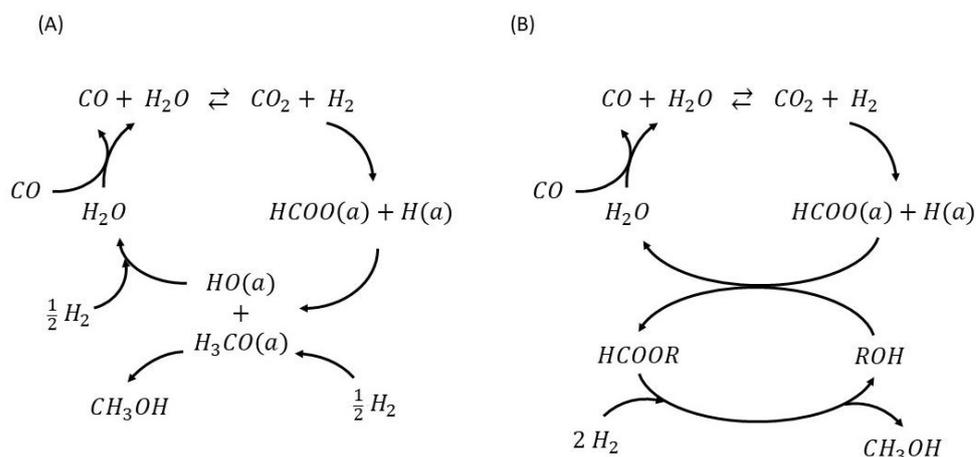


Figure 2. Illustration of two commonly accepted pathways for methanol synthesis. (A) The typical gas phase mechanism proceeds via a formate intermediate, which is hydrogenated into a methoxy group before methanol is released. (B) In the liquid phase mechanism, the formate reacts with an alcohol to form an ester before methanol is released [37].

Yang et al. [37–39] used Cu/ZnO and Cu/MgO as catalysts, respectively, and observed changes in the functional groups of adsorbed intermediates on the catalyst surface during low-temperature methanol synthesis by DRIFTS (Diffuse Reflectance infrared Fourier Transform Spectroscopy). Then, they inferred the corresponding reaction mechanism according to changes. For these two catalysts, the conclusions were roughly the same, except for the differences in the adsorption sites on the catalysts. The mechanism of methanol liquid phase synthesis in the ethanol system is shown in Figure 2B. In the process of mechanism research, ethanol is introduced into the reaction system in the form of ethanol vapor under atmospheric pressure, so the products measured in the experiment exist in gaseous form. The research results show that adsorbed formate is easily formed when the catalyst is exposed to synthesis gas. Formate can react with ethanol at low temperatures to produce adsorbed or gaseous ethyl formate. In the absence of ethanol, formate cannot be hydrogenated. As an intermediate product of the reaction, ethyl formate is easily reduced by hydrogen atoms on Cu to obtain gaseous methanol and ethanol. Moreover, the study found that the reaction of adsorbed formate species with ethanol in the gas phase to form ethyl formate is the key step in low-temperature methanol synthesis. This step changes the reaction process such that formate is the intermediate rather than the methoxy group as in

the traditional gas phase of methanol synthesis. Since the generation of methanol no longer goes through the formation of methoxy groups, the methanol synthesis can be achieved at low temperatures. Ethanol significantly reduces the temperature required for the reaction and can be recycled. It not only plays the role of heat carrier but also acts as a catalyst. At the same time, the carbonylation reaction was found to be a Rideal-type process, which was affected by electronic effects and steric hindrance [40].

These studies suggest that in the alcohol solvent system, the mechanism of methanol synthesis is changed by the solvent. Whether it is a single copper-based catalyst or a composite catalyst, the reaction produces the corresponding intermediate formic acid ester, and then further undergoes hydrogenolysis to obtain methanol. This is a common feature of the reaction mechanism and is the most obvious difference from the traditional gas-phase methanol synthesis mechanism.

2.2.2. Main Catalyst

At present, there have been many studies on the low-temperature liquid phase methanol synthesis process, and there are various types of catalysts. Generally, the catalyst for the liquid phase methanol process is an inseparable composite system composed of a carbonylation catalyst, hydrogenolysis catalyst, solvent, and additives. It can also be divided into homogeneous and heterogeneous catalytic systems. The homogeneous catalysis system uses alcohol as the solvent and a strong alkaline substance as the carbonylation catalyst. In heterogeneous catalytic systems, Cu catalysts are commonly used as the main active catalysts and alcohol solvents, or inert solvents are used as dispersion media.

Carbonylation Catalyst

Alkali metal methanolate are the most effective carbonylation catalysts at present. Considering factors such as activity and price, the most used are sodium methoxide or potassium methoxide. The outstanding advantages of sodium methoxide catalysts are high activity and good selectivity. However, sodium methoxide catalysts have some disadvantages, such as rapid deactivation and the production of unwanted products (HCOONa , Na_2CO_3), which may be problematic. Therefore, attempts have been made to find a carbonylation catalyst that can replace sodium methoxide.

The catalytic activity of carbonylation of alkali metal formate is slightly lower than that of sodium methoxide, but it is more stable. Sodium formate has the best catalytic activity [41]. Under reaction conditions of 170 °C, 5 MPa, with a H_2 to CO ratio of 2, the single-pass conversion rate of CO can be about 84%. After sodium formate is deactivated, it can be regenerated by the hydrogenation catalyst, so sodium formate is a promising catalyst for carbonylation.

Organic nitrogen-containing heterocyclic olefins are also catalysts for methanol carbonylation (Green and Kiyoshi) [42–46]. Under the reaction conditions of $T = 40\text{--}80$ °C and DBN (1,5-Diazabicyclo [4.3.0]non-5-ene) as a catalyst, the molar yield of methyl formate reached 50% to 80%. Due to the high synthesis cost of DBN, it has not been commercialized, which limits its development and application.

The commonly used carbonylation catalysts mentioned above (CH_3ONa or HCOOK) are sensitive to CO_2 and H_2O in feed gas. Trace amounts of either can quickly deactivate the catalysts. Reactions of sodium methoxide inactivation include:



However, industrial synthesis gas usually contains CO_2 and H_2O , and the purification cost is high. Therefore, the industrial application of the liquid-phase methanol process has been limited [47].

Hydrogenolysis Catalyst

Highly active hydrogenolysis catalysts can improve the hydrogenolysis rate of the intermediate product ester RCOOCH_3 , reduce the RCOOCH_3 concentration in the product, and increase the selectivity to methanol. Most researched among them are nickel-based hydrogenolysis catalysts and copper-based hydrogenolysis catalysts.

Nickel-Based Catalyst

In 1986, Brookhaven National Laboratory (BNL) [48] first reported the use of Ni-based catalysts to achieve 90% single-pass conversion of CO under reaction conditions of 373 K and 1–5 MPa. The catalyst composition is NaH-RONa-M(OAc)_2 ($M = \text{Ni, Pd, and Co}$), in which sodium alkoxide has CO carbonylation activity and acts on the esterification reaction, while the Ni-based catalyst has good hydrogenolysis reaction activity. Mahajan et al. [49,50] synthesized methanol using $\text{Ni(CO)}_4/\text{KOCH}_3$ /methanol/glyme catalyst system at 150 °C, 1–3 MPa. The selectivity to methanol can be greater than 95%, and the single-pass conversion rate of syngas exceeds 90%. An inert coolant that is not miscible with methanol was added into the liquid phase at 0–70 °C to overcome the problem of indirect heat exchange on a large number of surfaces required for the reaction mixing process. Ohyama [51–53] developed two catalysts, $\text{NaH/2-methyl-2-butanol/Ni(CH}_3\text{COO)}_2$ or Ni(CO)_4 . Under conditions of 423 K and 5 MPa, the single-pass conversion rate of CO over these catalysts reached 90%, with a methanol selectivity of 99%.

Although the nickel-based catalyst has high activity and selectivity, toxic, volatile, and flammable intermediates, such as Ni(CO)_4 and $[\text{HNi}_2(\text{CO})_6]^-$, are easily produced during the reaction, which reduces their research significance and practical value. Organic nickel/ CH_3OK catalyst has the same activity and selectivity as the first two catalysts. No toxic intermediates are generated during the reaction [54]. However, removal of residual water in the preparation process of organic nickel is complicated, which increases the catalyst preparation cost. At present, only Amoco and Brookhaven National Laboratory are still working on the exploration and development of nickel-based catalyst systems.

Copper-Based Catalyst

Cu-based catalysts are the most used catalysts in gas phase medium and low-pressure processes, and they are also the key point of methanol synthesis research. This type of catalyst has good activity, high methanol selectivity, low operating pressure, and temperature, so it is an excellent choice for hydrogenation catalysts in liquid-phase, low-temperature methanol processes.

Machionna et al. developed a copper-based catalyst with activity and selectivity comparable to those of nickel-based catalysts [55]. Kokubu et al. used Raney Cu, CH_3OK and solvent to synthesize methanol in a liquid phase at 120 °C and 5 MPa [56]. Researchers at the University of Pittsburgh used a slurry-bed reactor to synthesize methanol with $\text{Cu-Cr}_2\text{O}_3/\text{KOCH}_3$ catalyst under 373–453 K and 5 MPa conditions [57]. All of them obtained high synthesis gas conversion and selectivity.

2.2.3. Solvent

Solvents are also very important in liquid methanol synthesis systems. According to their characteristics, they can be roughly divided into three categories. (1) Inert solvents that do not participate in the reaction process and are purely used as heat carriers, such as paraffin and mineral oil. (2) A mixed solvent system that uses a heat carrier solution together with a solution participating in the catalytic process, such as the p-xylene (heat carrier) and sodium methoxide (carbonylation agent) systems. (3) An alcohol solvent that acts as a dual heat carrier and catalyst. Studies suggest that this type of system can be further divided into two sub-categories, depending on the additional catalyst used. One is early developed; strong alkaline substances, such as sodium methoxide or potassium methoxide, were added to methanol solution as homogeneous catalysts for methanol carbonylation. Methyl formate was hydrogenolyzed by a copper-based catalyst; the second

was developed later, without adding strong alkaline substances, such as sodium methoxide, and using only a copper-based catalyst in an alcohol solution (usually ethanol solution) to achieve low-temperature methanol liquid phase synthesis. These three types of solution systems are discussed separately as follows.

Inert Solvent

The principle of this reaction system is the same as that of the gas-phase methanol process. The essence is to disperse the catalyst in an inert solvent that does not participate in the reaction, so no carbonylation catalyst is needed. Paraffin oil, as an inert solvent heat carrier, is one of the more commonly used solutions for studying liquid-phase methanol synthesis. The use of paraffin oil is that, on the one hand, it can transfer the heat released by the reaction over time and control the temperature of the reaction bed within the working range of the catalyst; on the other hand, it facilitates uniform dispersion of the catalyst and reduces the accumulation of reaction heat on catalyst particles, which prevents sintering and promotes uniform mass transfer.

Aiming at the liquid phase methanol synthesis of a paraffin system, Xiaobing et al. studied the effect of co-precipitation conditions on catalytic activity [58]. They found that precipitation and aging processes are the main factors affecting the microstructure of the catalyst. With increased precipitation and aging, the crystallinity of each species in the precursor increases. With increased calcination temperature or time, the average particle size of the microcrystals in the catalyst increases. Thus, the activity and stability of the catalysts are affected.

Wei et al. [59] prepared Cu/ZnO/Al₂O₃ catalyst in situ in paraffin by a direct liquid phase method and tested its catalytic activity on syngas to lower alcohols at low temperature. The catalyst preparation and reaction were coupled to make the catalyst uniformly dispersed. The effect of carbon nanotubes and carbon microspheres on catalytic activity was also studied. The results showed that the addition of carbon nanospheres significantly reduced the Cu⁰ crystal size of Cu/ZnO/Al₂O₃ catalyst and increased the dispersion of Cu components due to the localized effect of the pores, thereby increasing methanol selectivity. Because the large Cu⁰ crystal size is beneficial to CO insertion and carbon chain growth, the smaller the grain size, the higher the methanol selectivity, and the larger the Cu⁰ grain size, the higher the ethanol selectivity.

Yuan et al. [60] developed Cu/MgO/ZnO catalyst for low-temperature methanol synthesis in paraffin medium. No carbonylation agent is required, and a CO conversion rate of 63% and methanol selectivity of 99% can be achieved at low temperatures. Studies have shown that the introduction of MgO can promote the formation of Cu⁺, which is conducive to the dispersion of Cu⁰ and Cu⁺ in the carrier and increases the catalytic activity. They also analyzed the deactivation of the catalyst and verified again that low temperatures are desired for methanol synthesis as the main reason for the catalyst deactivation was copper sintering.

Mixed Solvent

In this type of system, one of the solvents will participate in the reaction, so the principle follows the liquid phase methanol process. The representative solvent mixture of this approach is the p-xylene, sodium methoxide, and alcohol mixture system. The carbonylation reaction of methanol is an ionic reaction. When reacting in a non-polar solvent, the reaction rate will increase as the dielectric constant of the solution decreases. Therefore, adding a non-polar solvent with a lower dielectric constant than methanol may increase catalytic activity. It was found that when p-xylene was used as the solvent, the yield and selectivity of methanol were the highest among common solvents.

Wei et al. researched the p-xylene system [61,62]. Aiming at the low activity and poor stability of Cu/Cr₂O₃ catalyst, Cu/Cr₂O₃/SiO₂ catalyst prepared by the co-precipitation method and Cu/Cr₂O₃/Al₂O₃ catalyst prepared by a sol state co-precipitation were developed. For the Cu/Cr₂O₃/SiO₂ catalyst, it was found that the addition of silicon makes the

catalyst structure looser, the specific surface area larger, and the Cu reduction temperature lower, thereby improving the reactivity, selectivity, and stability of the Cu/Cr₂O₃/SiO₂ catalyst. The researchers believed that, on one hand, the addition of silica support may increase the hydrogenolysis activity of the catalyst, reduce the concentration of methyl formate in the catalyst system, and inhibit the deactivation of sodium methoxide; on the other hand, the silica support stabilizes the catalyst structure, enhancing the stability of the hydrogenolysis catalyst itself.

When investigating the effect of zirconium additives on the performance of Cu/Cr₂O₃/SiO₂ catalysts, the results showed that zirconium dioxide, as a structural and electronic promoter, had an effect on low-temperature liquid phase methanol synthesis [62]. This is because zirconium additives can increase the specific surface area of the catalyst and promote dispersion of the copper and chromium components in the catalyst. In addition, ZrO₂ enables Cu⁺, Zr⁴⁺, and Cr³⁺ generated on the catalytic surface to form a composite center, which can stabilize Cu⁺. Additionally, Cu⁺ plays an important role in the reaction steps, such as H₂ activation and CO bond breakage, to improve catalyst activity.

A study on the Cu/Cr₂O₃/Al₂O₃ catalyst prepared by the sol state co-precipitation method showed that there was an optimal value for the aluminum content [61]. The addition of aluminum also improved the catalyst activity and methanol selectivity and made the active components in the catalyst more dispersed, more reactive sites on the catalyst surface, increased specific surface area, and enhanced adsorption for raw gas, thereby improving the activity and stability of the catalyst.

Alcohol Solvent

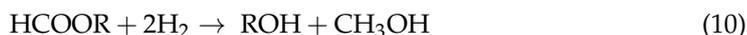
The alcohol solution system for liquid phase methanol synthesis can be subdivided into two types: homogeneous and heterogeneous.

Wender et al. [63] proposed a methanol solution system using sodium methoxide. A mixed catalyst composed of alkali metal alkoxide and copper-chromium catalysts was used to catalyze methanol carbonylation and methyl formate hydrogenolysis, respectively. It was found that when the concentration of alkali metal alkoxide was low, the amount of methanol produced increased with increasing concentrations of methyl formate, but when the concentration of alkali metal alkoxide was high, the rate of methanol synthesis decreased. The researchers believed that a high concentration of alkali metal alkoxides covers the hydrogenolysis active sites on the surface of the copper-chromium catalyst.

Tiansheng et al. [64,65] found that Cu/MgO catalyst could effectively catalyze the hydrogenolysis step. When combined with the esterification catalyst potassium formate, it showed high catalytic activity, reaching a total carbon conversion rate of 91% and 99% methanol selectivity under 150 °C and 5 MPa. The disadvantage is that the composition of the catalyst is complex. Hu et al. [41,66] found that Cu/MgO catalyst modified by alkali metal had better performance. Cu/MgO-Na and sodium formate worked together to increase the carbonylation activity of the catalyst. When the atomic ratio of Cu:Mg:Na was 1:2:1, the catalyst had the highest activity for methanol synthesis, and the single-pass conversion of CO reached 90%. However, CO₂ was formed during the reaction, and the stability needed to be improved.

As mentioned above, although sodium methoxide has relatively high catalytic activity for methanol carbonylation, it is easily deactivated due to the presence of trace amounts of CO₂ and H₂O in the synthesis gas. Tsubaki et al. [67] discovered and proposed that liquid phase methanol production from synthesis gas can be realized with merely copper-based catalysts in an alcohol solution, without strong alkaline substances such as sodium methoxide, as a catalyst for carbonylation. They prepared a Cu/ZnO catalyst at 150 °C and 5 MPa by the co-precipitation method in a slurry-bed reactor with C₁–C₄ alcohol as the liquid medium, without adding strong alkaline carbonylation reagents. It achieved a CO conversion over 50% and methanol selectivity over 90%. The alcohol solvent not only served as the liquid medium but also participated in the reaction process, but it was not consumed (just like the catalyst). It should be noted that, similar to the ICI process, CO₂

($\varphi = 2\text{--}5\%$) must be used as an inducer in this process. If there is no CO_2 in the raw gas, the product methanol cannot be obtained [68]. The inferred reaction process is as follows:



The overall main reaction of steps (7)–(11) is methanol synthesis from carbon monoxide, i.e., Equation (1).

After Tsubaki et al. proposed a pure alcohol catalyst system, Cu-ZnO catalysts have been researched more thoroughly. Reubroycharoen et al. [69,70] found that when the atomic ratio of Cu to Zn is one, the catalyst showed the highest activity. The single-pass conversion of total carbon reached 47%. Bao et al. [71] found that the addition of Zn could improve the pore size distribution of CuO, prevent Cu aggregation caused by reduction, and obtain highly dispersed Cu and Cu-ZnO_x particles.

The type of alcohol solvent also has an impact on catalytic activity [72]. Isopropanol has a strong nucleophilic attack ability, which can capture the adsorbed formic acid group and esterify it, and then generate two molecules of alcohol. Zeng et al. [68] prepared Cu/ZnO catalyst by the co-precipitation method and studied 13 kinds of common alcohols as liquid phase methanol synthesis solutions. The research results showed that the influence of the alcohol solution was mainly reflected in the formation rate of the intermediate ester, which also confirmed the reaction process inferred by Tsubaki et al., as mentioned above (solvent alcohol participates in the carbonylation reaction). In contrast to the hydrogenolysis of esters, the carbonylation reaction was considered to be the rate control step. Carbonylation reaction is a nucleophilic reaction [73], so high hydroxyl electronegativity and low steric hindrance facilitate the progress of the reaction. For example, 1-butanol has a lower steric hindrance, but the oxygen atom on the hydroxyl group has a lower electronegativity, making the activity not as high as 2-butanol. The oxygen atom on the hydroxyl group of isobutanol is highly electronegative, but the steric hindrance is large, which makes it less active than 2-butanol. Therefore, the oxygen of 2-butanol has good electronegativity and suitable steric hindrance, and thus exhibits the highest catalytic activity. According to the research of Reubroycharoen et al. [70], it can be found that, as a result of the balance between the electronic effect and the steric effect, when the carbon number of the alcohol is the same, secondary alcohol has the highest activity. For the six primary alcohols, from ethanol to hexanol to benzyl alcohol, the yield of methanol decreased as the carbon number of the alcohol increased.

In the pure alcohol system, since sodium methoxide is not used as a carbonylation catalyst, it can tolerate a certain amount of CO_2 and H_2O in syngas, which reduces feed-stock purification costs. From this point of view, when catalyst activity can be effectively improved, the pure alcohol system has more industrial application prospects.

2.2.4. Additives and Supports

The performance of catalysts largely depends on their composition. In the copper-based methanol synthesis catalyst, copper is considered the main active component, but the catalytic activity of copper alone is relatively poor and thermally unstable. The appropriate addition of other components can greatly improve the performance of the catalyst. Many additives and supports have been mentioned, such as ZnO, Al_2O_3 , ZrO_2 , MgO, SiO_2 , and carbon nanotubes. Most additives loosen structure, improve dispersion of Cu components, provide stability, and mitigate thermal sintering. At present, rare-earth and alkaline earth metals and their oxides are commonly used as additives for catalysts as attempts to solve problems by adjusting structure, surface acidity and alkalinity, electronic properties, etc.

Qi et al. [74] found that when TiO_2 was added as an additive, the Cu crystal size was reduced, the surface area increased, and catalytic activity was significantly improved. It was also found that TiO_2 moved the reduction peak to a lower temperature and promoted the reduction of copper as an electronic promoter.

Cabrera et al. [75] used palladium as an additive of a copper-based catalyst. They found that Pd could significantly improve the reduction properties of Cu and increase the rate of the methanol synthesis reaction due to its excellent ability to dissociate and overflow hydrogen.

Chen et al. [76] believed that Mn additives could improve the activity of $\text{CuO}/\text{ZnO}/\text{Al}_2\text{O}_3$ catalysts and adjust the ratio of Cu^+/Cu^0 , therefore increasing the number of active centers and making Cu^{2+} reduction harder. The addition of Mn additives could also increase the dispersion of Cu on catalyst surfaces and stabilize the active components, thereby improving the resistance to sintering.

Alkali metal salts can catalyze the carbonylation reaction of methanol and increase the conversion rate of feed gas. For example, the catalytic activity of Cu-MnO_x alone is low, but the addition of K_2CO_3 can improve the activity of the entire reaction system [64]. The conversion of total carbon reached 90.2%, and the methanol selectivity was about 99.1%.

Chen et al. [77] believed that Al, Sc, and Cr could cause cation defects on the ZnO surface and increase the concentration and stability of Cu^+ during catalyst activation and the reaction process. Especially after adding Sc, the Cu/ZnO catalyst had a larger specific surface area, which was conducive to the production of methanol.

Bell et al. [78] believed that adding Ce to Cu/ZrO_2 catalyst could improve the performance of the catalyst. At 473–523 K and 3 MPa, the methanol synthesis activity of $\text{Cu}/\text{Ce}_{0.3}\text{Zr}_{0.7}\text{O}_2$ is 2.7 times higher than that of $\text{Cu}/\text{m-ZrO}_2$.

2.2.5. Preparation Method for Catalyst

The preparation method of the catalyst can directly affect the physical and chemical properties of the catalysts, such as the crystal size, dispersion degree, and pore structure. The preparation of Cu-based catalysts for methanol synthesis includes precipitation, impregnation, ball milling, and sol-gel methods.

Co-Precipitation Method

The co-precipitation method is the most used method for preparing copper-based methanol synthesis catalysts. A common process of Cu/ZnO catalyst preparation by co-precipitation is shown in Figure 3. By adjusting the precipitation temperature and pH value, uniformly dispersed metal cations in solution can be converted into organometal/oxide precursors through rapid solidification. After calcination and reduction, highly dispersed and well-mixed solid metal/oxide catalyst are formed. The preparation process of the precipitation method includes precipitation, aging, filtration and washing, as well as drying, calcining, granulation, and reduction. The adjustment of each step affects the physical structure and chemical properties of the product catalyst.

In the process of co-precipitation, the control of pH and temperature is extremely important. Fujita et al. [79] believed that due to the exothermic reduction reaction of CuO in H_2 , the local temperature of the CuO particles would increase during the reduction process, leading to the aggregation and growth of CuO crystal particles. Therefore, keeping the reduction temperature lower can control the Cu crystal sizes to be smaller. Through sodium carbonate titration, Behrens et al. [80] found that when the pH value was low, Zn^{2+} would stay in the liquor and could not be precipitated. The optimal precipitation pH was the lowest pH for the complete precipitation of Zn^{2+} (pH = 7). When the precipitation temperature was 60 °C and pH = 7, after calcining and reduction, the catalyst components obtained were highly dispersed, which is conducive to high Cu-Zn catalyst activity. Jeong et al. [81] used the co-precipitation method to synthesize a series of Cu/ZnO catalysts for low-temperature methanol synthesis with a pH value of 6–10. They found that the catalyst produced at pH = 8 had the smallest copper crystals, the largest number

of strong acid sites on the surface, and the highest catalyst activity. The catalytic activity was positively correlated with the number of strong acid sites on the catalyst surface. The strong acid sites on the surface helped in the adsorption and activation of CO and increased the conversion rate of CO at low temperatures.

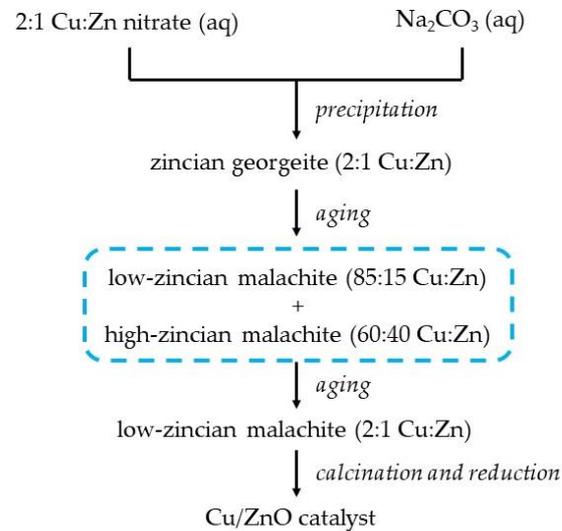


Figure 3. Flow Jdiagram for the precipitation preparation of Cu/ZnO catalysts [79].

Paul et al. [82] prepared zincian georgeite (an amorphous copper–zinc hydroxycarbonate), the precursor of their Cu/ZnO catalyst, by co-precipitation using acetate salts and ammonium carbonate. They attributed the superior performance of their catalysts to the exclusion of alkali metals from the synthesis procedure, which are known to act as catalyst poisons.

Precipitation methods include direct precipitation, co-precipitation, and complex precipitation [62,79]. Catalysts prepared by this method have high dispersion, small crystal grains, and strong interaction between the components, but the processes are complicated, and sometimes the strong interaction is not conducive to the reduction of the catalyst.

Sol-Gel Method

The sol-gel method is a common method for preparing nanocatalysts. Metal ions and organic ligands are uniformly dispersed in a solvent, and then hydrolyzed and condensed to form a sol. The colloidal particles in the sol polymerize during the aging process to form a gel with a three-dimensional network structure. After calcination, reduction, and passivation of the gel, a product catalyst can be obtained.

Wei et al. [61] used the impregnation method, co-precipitation method, and sol-gel method to prepare Cu/Cr₂O₃/SiO₂ catalysts and to evaluate their activity. The results showed that the catalyst prepared by the sol-gel method had the best catalytic activity and methanol selectivity. Ali et al. [83] added the surfactant sodium dodecyl sulfonate (SDS) to the gel-forming process to obtain MgO particles with an average particle size of 13.2 nm. However, the addition of the surfactant introduced sulfur, which was toxic to the catalyst.

Citric acid (C₆H₈O₇·H₂O) is a commonly used chelating agent, which contains three (-COOH) groups available for complexation. Citric acid can chelate with Cu²⁺ ions to form a sol, which can be transformed into a gel after heating, evaporation, dehydration, and condensation. Chelated citric acid in gel undergoes self-combustion at about 200 °C. Combustion consumes C, O, and H elements to generate a large amount of gas. Therefore, the prepared catalyst has a larger surface area and pore volume. Lei et al. [84] prepared Cu/ZnO catalyst by the citric acid sol-gel combustion method and found that the gel of citric acid during calcination in Ar atmosphere could generate a large amount of gas. The reducing gas, such as CH₄ and CO, could, in situ, reduce the calcination product CuO to

Cu, so the subsequent additional reduction treatment was no longer needed. The activity was highest when the stoichiometric ratio of citric acid to Cu was 0.8.

Because the gel has a three-dimensional network structure, it can maintain a certain structure and morphology after calcination, so the catalyst prepared by the sol-gel method has a high dispersion of active metals and a smaller particle size. However, the disadvantage is that the organic ligands are expensive and the preparation conditions are harsh.

Other Synthesis Methods

There are reports of other catalyst preparation methods, but the reports are also very limited, and each presents problems.

The physical pulverization method prepares nanoparticles by mechanical pulverization, electric sparks, or other methods. Ball mill, colloid mill, and other methods of size reduction are commonly used. Huang et al. [85] used a ball mill method to grind and mix the powders of copper and zinc oxide in air or vacuum. They found that mixing in air was better than mixing in a vacuum. Because the partial oxidation of copper in the air enhanced the interaction with zinc oxide, the resulting catalyst had a higher copper surface area. The preparation process of this method was simple and the cost was low, but high-strength mechanical mixing can destroy internal catalyst structures, introduce impurities, reduce the purity of the catalyst, and controlling the particle size distribution is difficult.

Impregnation involves the immersion of the solid carrier into a salt solution containing active components, followed by separation of the residual liquid after a certain period. In this way, active components are attached to the solid in the form of ions or compounds, and when the impregnation is balanced, the remaining liquid is removed, followed by similar drying, calcination, and other post-treatments. The active component salts can be left on the inner surface of the carrier. The salts of these metals or metal oxides are evenly distributed in the pores of the carrier. After being decomposed and activated by heating, a highly dispersed catalyst is obtained. Chappell et al. [86] prepared Cu/SiO₂ catalyst by the impregnation method using SiO₂ as a carrier and added Al, Zr, Ga, Zn, and other metal additives to improve its performance. The impregnation method has the advantages of simple operation, low preparation cost, and a high single batch yield. The prepared catalyst also has good dispersity, moderate inner interaction, and good catalytic performance, but it has high requirements for the specific surface, thermal stability, and electronic effects of the support.

The flame combustion synthesis method is a general method for the preparation of metal oxide catalysts with a high specific surface area. Burner design and combustion conditions determine the specific surface area, structure, and phase composition of the catalyst. Jensen et al. [87] mixed acetyl pyruvate of volatile Cu, Zn, Al precursors with fuel (H₂ and CH₄), and air for high temperature combustion and gasification, resulting in decomposition, condensation, rearrangement, and rapid cooling to obtain catalysts. Moreover, the metal particles could be more fully mixed in the gas phase, which increased the interaction between the components. The specific surface, morphology, and crystal phase structure of the particles can be changed by adjusting the flame temperature, the residence time in the high-temperature zone, and the solution concentration to improve the activity, selectivity, and stability of the catalyst. Methanol synthesis is a structure-sensitive reaction over copper-based material, and in the traditional precipitation method it is difficult to control the structure during the calcination process, which leads to losses of the active surface area. The flame combustion synthesis method offers better control of the structure and thus limits surface area losses.

2.2.6. Reactor Types

Unlike the gas-solid two-phase reaction of the gas-phase synthesis process, the liquid-phase synthesis method is a gas-liquid-solid three-phase reaction, so the reactor must be

adjusted accordingly. At present, the most used reactors in liquid phase methanol synthesis are slurry beds and trickle beds.

Slurry Bed Process

The three-phase slurry bed reactor is like a bubbler, with a heat exchanger placed in the bed. In the reactor, a paraffin-like long-chain hydrocarbon compound with a high heat capacity and large thermal conductivity is added as an inert medium, and the fine powder catalyst is dispersed in a liquid phase medium to form a slurry and placed in the reactor. At the beginning of the reaction, syngas must be dissolved and dispersed in an inert oil medium to reach the surface of the catalyst, and the product after the reaction must undergo a similar process before it can be collected. The reactor can be batch or continuous, and a single reactor or multiple reactors can be connected in series. The general process is that the purified and compressed synthesis gas flows through the reactor from bottom to top and forms a three-phase bubbling bed with the slurry, where mass transfer occurs between the phases and reacts on the surface of the catalyst. Output gas is discharged from the upper part of the reactor, where reaction heat is absorbed by circulating inert hot liquid, which is exchanged via heat exchanger, so as to maintain the bed temperature, while producing steam as a by-product.

Since the liquid inside the reactor is in a fully mixed flow state, the reaction temperature is uniform, and temperature control is simple and effective. At the same time, the average temperature of the slurry-bed reactor is much higher than that of the tubular fixed-bed reactor, so it has a higher reaction rate and product selectivity. The reaction pressure is reduced, which can reduce gas compression costs. Additionally, replacement and addition of catalysts during operation is possible, greatly improving the utilization of the equipment, which is a significant improvement over the tubular fixed-bed reactor, which must be shut down often to replace the catalyst. At the same time, it also has the advantages of simple operation and easy separation of solid and liquid.

The slurry-bed reactor has a simple structure, uniform dispersion, good heat transfer performance, and convenient operation. However, catalyst sedimentation and aggregation in the reactor may occur. Therefore, catalyst utilization efficiency may be low, and overall efficiency may not be high.

Trickle Bed Process

In 1990, Pass et al. proposed a trickle bed method to synthesize methanol [88]. The structure of the trickle bed reactor is similar to that of the traditional gas phase fixed bed reactor. The fixed layer is composed of catalysts with larger particles. Liquid flows from top to bottom in the form of droplets, and gas also flows from top to bottom. The gas and liquid are distributed among the catalyst particles.

The trickle bed has the advantages of both a slurry bed and a fixed bed. Similar to a fixed bed, it has a large catalyst loading and no abrasion. The reactor is equipped with heat exchangers, making material flow in the catalyst bed close to plug flow without back mixing. The trickle bed has a high conversion and isothermal reaction similar to the slurry bed and is more suitable for synthesis gas with a low hydrogen to carbon monoxide ratio. From an industrial point of view, the liquid phase fluid in the trickle bed contains very little catalyst powder, and the conveying equipment is easy to seal and has little abrasion. Therefore, it may be more reliable for long-term operations.

2.3. CO₂ and H₂ Methanol Synthesis

In addition to the mature industrialized gas phase method and the hot liquid phase method currently being studied, there is also a CO₂/H₂ synthesis process for methanol production. However, compared to the CO-synthesis process, CO₂ process is less reactive, requires a larger reactor, and is not yet mature, so only a brief introduction is given here [89].

In the early 1980s, Topsøe used CO₂ and H₂ contained in the exhaust gas of a refinery to obtain methanol successfully through the adiabatic reaction of the catalyst. Then, the Tokyo

Gas Company synthesized methanol with CO₂ and H₂ using the Cu/ZnO/Al₂O₃ catalyst. Lurgi and Southern Chemical Corporation used CO₂ and H₂ to synthesize methanol with a low-pressure catalytic system. Both showed that although CO₂/H₂ methanol synthesis process reduced the circulation of the system, the methanol synthesis rate was low. Although various highly active metal catalysts have been reported for CO₂ hydrogenation to methanol, the methanol selectivity of most of them is still below 60%. However, the CO byproduct can still be reused, so it still has industrial application prospects. In addition, the reaction mechanism of catalytic CO₂ hydrogenation to methanol is still controversial and needs to be studied further [90–92].

It has been reported that a new type of Ni-Ga bimetallic catalyst has good performance of CO₂ hydrogenation to methanol [93]. The catalyst can complete the CO₂ hydrogenation process under atmospheric pressure and has good stability. In₂O₃-based catalysts are also promising in the CO₂ hydrogenation to methanol and are currently receiving a lot of attention [94]. These catalysts are still in the optimization stage, and the catalytic technology is not yet mature. However, this process has great potential in terms of operating conditions and methanol synthesis performance. Therefore, the development of a suitable catalyst is the key to the industrialization of methanol synthesis from direct CO₂ hydrogenation in the future.

3. Summary and Prospect

The gas phase method for synthesizing methanol is commercially mature, and the high-pressure method has been eliminated due to high energy consumption, large investment in equipment, and poor product quality. Medium- and low-pressure methods are now widely used. However, the traditional gas phase methanol synthesis process requires a high reaction temperature and is limited by thermodynamics, resulting in a series of disadvantages such as low synthesis efficiency, high energy consumption, and high cost. In view of the many shortcomings of the gas-phase process, a low-temperature and high-conversion liquid-phase methanol synthesis process has emerged. In the low-temperature liquid phase methanol synthesis process, the catalyst is a composite system in which the main catalyst, solvent, carrier, and additive are all important. Currently, however, each has limitations. Therefore, finding a catalytic system that has high catalytic performance and high selectivity but is also stable and does not easily deactivate, and can be recycled and regenerated, is the focus of ongoing research. The synthesis method of the catalyst and the type of reactor will also affect methanol synthesis. Therefore, their optimization and development are also future research directions. The development of the liquid phase methanol synthesis process into commercial applications, thus, requires significant further research.

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