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Research progress of catalysts for synthesis of low-carbon alcohols from synthesis gas

 Xiaoxiao Xue,^{ID} ^{ab} Yujing Weng,^{*ab} Shicheng Yang,^{ab} Shihang Meng,^{ab} Qi Sun^{*ab} and Yulong Zhang^{*ab}

In recent years, the application value of low-carbon alcohols (C1–C6 alcohols) in the fuel, chemical, environmental protection and other fields has become increasingly prominent. Catalytic conversion of synthesis gas to low-carbon alcohol is one of the important ways to realize the industrial production of low-carbon alcohol. Lack of high-performance catalysts is the main reason that restricts the industrial development of producing low-carbon alcohols from synthesis gas. The construction of a dual active-center catalyst with high activity and stability, and the study of its function and catalytic mechanism have become significantly important. In this paper, the characteristics of the reaction process of syngas to low-carbon alcohols, and the catalytic mechanism and preparation methods of different catalyst systems were reviewed, which provide the basis for further research on high performance catalysts.

1. Introduction

Since entering the 21st century, global energy consumption still mainly depends on primary energy sources such as coal, oil and natural gas. A shift from fossil to renewable carbon resources can decouple chemical production from fossil resources and

alleviate CO₂ emissions. However, to be cost-effective and environmentally competitive with fossil-based processes, it is imperative to maximize feedstock utilization efficiency. With the continuous consumption of fossil energy and the increasingly serious environmental problems, the development and utilization of new and environmentally friendly energy has become urgent.^{1,2}

As a type of renewable clean energy, low-carbon alcohol has gradually been used in the field of fuels and the chemical industry, and related research has become increasingly popular.³ Low-carbon mixed alcohols (alcohol mixtures of C1~C6) can firstly be used as high-quality power fuels. Although their calorific value is lower than that of gasoline and diesel, due

^aCollege of Chemistry and Chemical Engineering, Henan Polytechnic University, Jiaozuo, Henan 454003, P. R.China. E-mail: wengyj@hpu.edu.cn; qisun_l@hotmail.com; zhangyulong@hpu.edu.cn; Tel: +86-18239181096; +86-18910395509; +86-13311269796

^bHenan Key Laboratory of Coal Green Conversion, Henan Polytechnic University, Jiaozuo, Henan 454003, P. R.China



Xiaoxiao Xue joined the research group of Professor Zhang Yulong at the College of Chemistry and Chemical Engineering, Henan Polytechnic University in 2017 as a doctoral student. His research centres on the development of heterogeneous catalysts for the direct conversion of CO-containing syngas into higher alcohols.



Yujing Weng completed his Bachelor's degree in Chemical Engineering at the Taiyuan University of Technology. He earned his PhD in Chemical Engineering from the Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences. He is currently an associate professor at the College of Chemistry and Chemical Engineering, Henan Polytechnic University and

joined Zhang Yulong's research group. His main research direction is industrial catalysis, using coal chemical synthesis gas as a raw material, exploring the clean and efficient chemical conversion path for the utilization of synthetic gas resources.



to the presence of oxygen atoms in alcohols, their combustion is more complete than that of gasoline and diesel. Meanwhile, there are fewer harmful substances in the released gas, which is an environmentally friendly fuel; secondly, low-carbon alcohol has a higher octane number, better explosion-proof and shock-resistant performance, and can replace the carcinogenic methyl *tert*-butyl ether as a fuel additive; finally, low-carbon alcohols can be used directly as bulk/fine chemical products, which can also be separated to obtain individual alcohols with high economic value such as ethanol, propanol, butanol, and pentanol.^{4–6} The current methods for preparing low-carbon alcohols have major drawbacks. Take ethanol as an example. The industrial production of ethanol mainly includes two methods: fermentation and chemical synthesis. Fermentation not only brings serious environmental pollution but also consumes a lot of food crops. The calculation shows that 1 ton C₂H₅OH consumes about 4 to 7 tons of crops. Fermentation of food crops to ethanol seriously violate China's development strategy; chemical synthesis requires a large amount of sulfuric acid, and the equipment is corroded seriously, which leads to high production costs. It is a method worth considering to prepare low-carbon alcohols through catalytic conversion of synthesis gas (CO and H₂ mixed gas) with abundant sources and low prices. Synthesis gas can be obtained by coal gasification, natural gas steam reforming and biomass gasification.^{7,8} If the

production of low-carbon alcohols through the catalytic conversion of synthesis gas achieves industrial production, it will, to a certain extent, alleviate the oil shortage and serious environmental pollution problems.

After decades of research, low-carbon alcohol synthesis technology is still in the laboratory stage, although companies or research institutions, such as Dow, IFP and the Shanxi Institute of Coal and Chemical Industry, Chinese Academy of Sciences, have conducted pilot tests. On the recent reported catalysts, C₂+ alcohols (alcohols with 2 or more carbon atoms) are not high enough, while the price of C₂+ alcohols is often higher. Among them, the price of propanol and butanol is about twice that of ethanol. Therefore, the main reason for the synthesis process of low-carbon alcohols failed to achieve industrialization is that the performance of the catalyst cannot meet the needs of industrialization.^{9,10} In other words, after decades of research, the design and development of catalysts with higher activity and selectivity is still the focus and difficulty of research in the field of low-carbon alcohol synthesis. Based on recent research, this article summarizes the reaction characteristics and synthesis process of synthesis gas to low-carbon alcohols, and focuses on the analysis of the catalytic reaction mechanism, design ideas and preparation methods of promising catalysts.



Shicheng Yang joined the research group of Professor Zhang Yulong at the College of Chemistry and Chemical Engineering, Henan Polytechnic University in 2017 as a doctoral student. His research mainly focuses on the conversion of CO-containing syngas into aromatics.



Sun Qi is currently a professor and doctoral supervisor at the School of Chemistry and Chemical Engineering, Henan Polytechnic University. He is the director of Henan Provincial Key Laboratory of Coal Green Conversion. He has long been engaged in basic and applied research in the coal chemical, petrochemical and environmental chemical fields and has made outstanding contributions

in the field of industrial catalysis.



Shihang Meng completed his Bachelor's degree in Applied Chemistry at the College of Chemistry and Chemical Engineering, Henan Polytechnic University. He joined the research group of Professor Zhang Yulong at same school in 2019 as a graduate student. Currently, his research mainly focuses on the development of heterogeneous catalysts for the direct conversion of CO-

containing syngas into higher alcohols.



Yulong Zhang is currently a professor and doctoral supervisor at the School of College of Chemistry and Chemical Engineering, Henan Polytechnic University. He is Deputy Director of Henan Provincial Key Laboratory of Coal Green Conversion. He is engaged in the research and development of coal conversion catalytic materials and process technologies, and mastering many key technologies of the coal conversion process.

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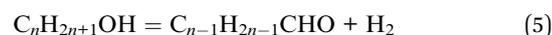
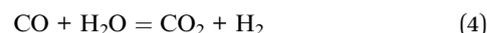
2. Reaction mechanisms of low-carbon alcohol synthesis reactions

In the process of catalyst research and development, strengthening the exploration of the synthesis mechanism of low-carbon alcohols is conducive to the targeted improvement of the catalytic structure and performance, and provides a solid theoretical basis for improving the activity, alcohol selectivity and long-term stability of the catalyst.

The synthesis of low-carbon mixed alcohols is similar to Fischer-Tropsch (F-T) synthesis and methanol synthesis, with some of the same surface reactions, but the reaction process or catalytic nature of the three is different. The F-T catalyst requires surface dissociative adsorption where the C-O bond is broken, while the methanol catalyst requires non-dissociative adsorption on the surface where the C-O bond remains. Due to the different electronic and physicochemical characteristics of the active sites of the catalyst, the former leads to the growth of hydrocarbon chains and the latter leads to the formation of oxygenated compounds. The design idea of the low-carbon alcohol catalyst is to optimize the combination of these two types of active components. The catalytic conversion of synthesis gas into low-carbon alcohol technology (some literature refer to higher alcohol synthesis, HAS) requires the catalyst to have dual functions, that is, the active sites of dissociative adsorption and non-dissociative adsorption.^{10,11} The CO insertion mechanism of syngas synthesis of low-carbon alcohols is shown in Fig. 1.¹² Part of CO dissociates and adsorbs to form adsorbed C* and adsorbed O*. The adsorbed C* is hydrogenated to form adsorbed *CH_x; the adsorbed *CH_x reacts with the adsorbed *CH_x to achieve carbon chain growth, forming an alkyl species *C_nH_{2n}. Undissociated CO* is inserted into the *C_nH_{2n} alkyl species to form an acyl species C_{n+1}H_{2n+3}CO*, and

the acyl species undergoes further hydrogenation to form a lower alcohol.

The reactions involved in the production of low-carbon alcohols from synthesis gas as follows. Reaction eqn (1) and (2) are the basic reactions for preparing low-carbon alcohols from synthesis gas. The reaction is an exothermic and reversible reaction with reduced volume. Increasing pressure or reducing the reaction temperature is beneficial to the synthesis of low-carbon alcohols. In the synthesis process of low-carbon alcohols, there are many types of parallel side reactions at the same time, such as the reaction to generate various alkanes and alkenes, and the water gas shift reaction, such as reaction eqn (3) and (4). In addition, there are secondary reactions to produce aldehydes and esters (5) and (6).



The reaction mechanism of synthesis gas to low-carbon alcohols shows that the formation of C₂₊ alcohols competes with the formation of C₂₊ hydrocarbons. Only on a catalyst that has strong chain growth ability and high non-dissociative adsorption CO* insertion activity, can it be possible to improve the selectivity of low-carbon alcohols. Therefore, to improve catalyst activity and lower alcohol selectivity, the key is to increase the number of dual active centers on the catalyst, and to achieve a certain balance between the content of the two types of active centers. The dissociation of the dual active centers, or the imbalance in the number of the two types of active centers will cause the catalyst performance to decrease. How to construct dual active centers with high activity and stability at the nanometer or even atomic scale, and to study its function and transient mechanism, has become a research hotspot that attracts many scientific researchers.

3. Synthesis gas to low-carbon alcohol technology

After decades of research, there are currently four main categories of processes for producing low-carbon alcohols from syngas: MAS process, IFP process, Sygmol process and Octamix process.¹³⁻¹⁷

3.1. MAS process.

Italy's SNAM Company and Danish Topsoe Company have modified methanol-based catalysts and corresponding process conditions, which can produce other alcohol products while producing methanol.¹⁸ In the alcohol products of this process,

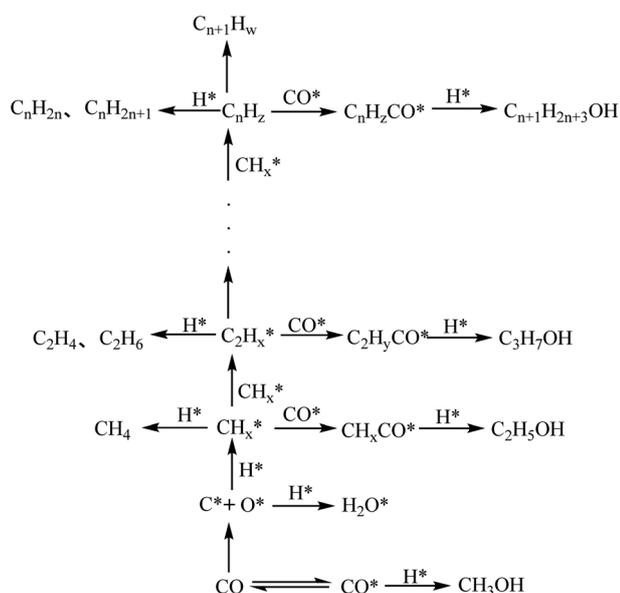


Fig. 1 The reaction process of CO hydrogenation catalyzed synthesis of lower alcohols.¹²



mechanism well explains the reason for there are more methanol and isobutanol in the reaction products on the Cu–Zn catalyst. According to the above chain growth mechanism, the insertion of CO is necessary during the formation of low-carbon alcohols, and the insertion center of CO must meet the following conditions: non-dissociatively adsorbed carbon monoxide, and dissociatively adsorbed hydrogen. At the same time, it has a mild hydrogenation activity to prevent the formation of hydrocarbons by over hydrogenation. The insertion of CO and hydrogenation to produce alcohols are completed in the same active center. In order to make CO and hydrocarbon groups better for bonding, the distance to the center of the chain extension should be as short as possible. Adding additives to Cu–Zn-based catalysts can significantly promote the performance of lower-carbon alcohols synthesis. It is found that the promoter Cs can obviously promote the performance of the catalyst Cu/ZnO/Al₂O₃ to synthesize low-carbon alcohols. Adding a small amount of Cr can significantly increase the surface area of the catalyst, thereby inhibiting the agglomeration of active metals, which in turn makes the catalyst have better activity and stability.^{22,23}

4.2. Modified F–T catalyst

In the F–T synthesis reaction, there are usually other side reactions to obtain oxygen-containing compounds such as alcohols. The production of oxygen-containing compounds such as alcohols, acids, ketones, vinegars, *etc.*, is varied with the F–T synthesis catalyst. Therefore, the modification of F–T synthesis catalysts to synthesize low-carbon alcohols has received extensive attention for research, among which Cu–Co and Cu–Fe are the two types of catalysts widely studied.^{24–27} The modified Fischer–Tropsch Cu–Co catalyst was developed by the French Petroleum Institute, and the synthesis products are mainly C1–C6 linear primary alcohols, whose product distribution is in line with the Anderson–Schulz–Flory (ASF) distribution of F–T. As to the catalytic mechanism, it is generally believed that Cu–Co catalysts for the synthesis of low-carbon alcohols have two types of active centers. Among them, Co is used for dissociative adsorption of CO to generate alkyl chains, and Cu is used for non-dissociative adsorption of CO to oxidize alkyl chains. To produce alcohol, the two type of active centers work together to form a dual-active center required for the synthesis of low-carbon alcohols.² In recent years, most research on the catalyst development mainly includes two aspects: (1) the ratio of active components Cu and Co; (2) the distribution of the two active centers. To make the active components Cu and Co close to the atomic scale, and distribute them as evenly as possible to increase the number of interfaces will significantly improve the synergistic effect of Cu and Co, leading to increase the selectivity of low-carbon alcohols. The reaction mechanism of Cu–Fe-based catalysts is shown in Fig. 3. The active center Cu of the catalyst can improve the non-dissociative adsorption of CO, thereby improving the ability of the catalyst to synthesize alcohols. The addition of Fe can improve the dissociative adsorption of CO. The ability to generate CH_x and promote the growth of carbon chain is conducive to the synthesis of low-

carbon alcohols.^{28,29} In addition, additives such as alkali metal promoters and supports have a great influence on the activity and selectivity of such catalysts.³⁰ Cu–Co catalysts must have alkali metals, otherwise the selectivity of alcohols will be very low. The role of the carrier is also obvious. The catalysts with the active phase supported on different carriers often get different products distribution. For example, catalyst supported on MgO mainly produces methanol, supported on TiO₂, CeO₂ or La₂O₃ mainly produce hydrocarbons, while supported on ZrO₂, SiO₂ and Al₂O₃ has higher C₂+ alcohol selectivity. It is reported that low-carbon alcohols could be synthesized with a cobalt metal-carbide (Co–Co₂C) catalyst.³¹ Density functional theory calculations show that Co₂C is highly effective for non-dissociative adsorption of CO for CO insertion, while Co metal is highly active for CO dissociative adsorption for chain growth. The interface between the Co and Co₂C worked as the dual sites for formation of low-carbon alcohols.

4.3. Molybdenum-based catalyst

The Dow Chemical Company in the United States first proposed molybdenum-based catalysts with high sulfur resistance and low carbon deposition, so it can be used under the conditions of higher sulfur content and lower H₂/CO molar ratio (0.7–1),^{32,33} respectively, including molybdenum sulfide, molybdenum oxide and molybdenum carbide based catalysts.

The catalytic mechanism of the molybdenum carbide-based catalyst is shown in Fig. 4. The low-valence molybdenum species and the high-valence molybdenum species constitute dual active centers. While, the low-valence molybdenum species is the chain growth center, where CO dissociatively adsorbs and forms surface alkyl groups. To be specific, high-valence molybdenum species undergo non-dissociative adsorption of CO, which is the active center for alcohol formation. The selectivity of low-carbon alcohols is related to the relative content of the two active centers.¹

The synthesis mechanism of low-carbon alcohols on K/MoS₂ catalysts is shown in Fig. 5. The catalysts of this series also have dual active centers, and the chain growth process is basically the same as that of molybdenum carbide-based catalysts.³⁴ Zhao Lu *et al.*³⁵ reported that high-performance nano-MoS₂-based catalysts for low-carbon alcohols through CO hydrogenation were synthesized using non-thermal plasma under ambient conditions. This flexible and facile approach can give the thinner and shorter MoS₂ slabs, expose more coordinatively unsaturated sites, and increase the number of active centers for alcohols formation. This kind of catalyst shows good catalytic performance. Wang Na *et al.*³⁶ reported a series of catalysts prepared by using molybdenum sulfide clusters as precursors, which provided good dispersion of MoS₂ particles with many coordination unsaturated Mo sites, which was conducive to the formation of intermediate active phase and improve the catalytic performance.

Catalytic mechanism of molybdenum oxide-based catalysts: studies have shown that there are both oxidized molybdenum (MoO_{2–x}) and metallic molybdenum (Mo) on the surface of such catalysts. Among them, MoO_{2–x} is conducive to the formation



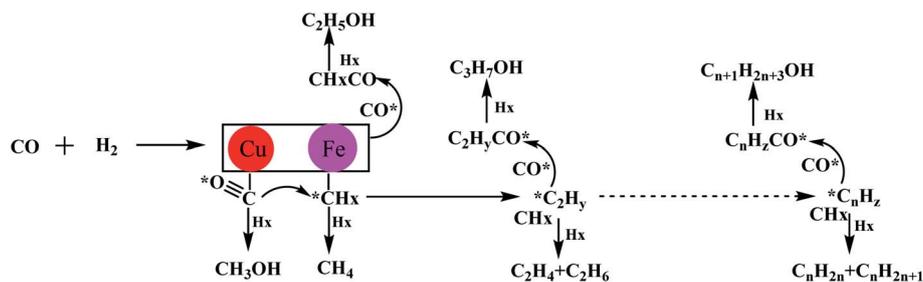


Fig. 3 Cu–Fe-based catalyst for the catalytic synthesis of low-carbon alcohols.³⁰

of alcohols. The reaction mechanism is shown in Fig. 6.³⁷ The synthesis gas undergoes dissociative adsorption on the Mo surface to form metal carbene, which is inserted into the metal-alkyl bond to achieve chain growth. On the MoO_{2-x} phase, CO undergoes non-dissociative adsorption, and the alkyl group migrates to the oxidized molybdenum. It reacts with the non-dissociatively adsorbed CO to form acyl groups. Finally, the hydrogenation reaction of alkyl and acyl groups forms hydrocarbons and mixed alcohols on molybdenum sites of different valences. Li *et al.*³⁸ prepared new MoO_2 by RF induced thermal plasma method. The core-shell catalyst has small particle sizes, an amorphous shell, and a crystalline core with strong core-shell interaction and abundant surface species in the shell, so as to improve its catalytic performance.

Although this type of catalyst has the advantages of sulfur and carbon deposition resistance, it still has the disadvantages of low activity and selectivity. Researchers have found that the total alcohol yield and C2+ alcohol selectivity of molybdenum sulfide-based catalysts can be improved by adding additives and changing the support.^{39,40} Alkali metals and alkaline earth metals, such as Na, K, Cs, Sr, Ba, *etc.*, are widely used as promoters for the synthesis of alcohol catalysts, which have a significant impact on the activity, selectivity and life of the catalyst. The most obvious effect of alkali metal additives is to inhibit the formation of hydrocarbons and improve the selectivity of alcohols. In terms of reaction mechanism in the CO hydrogenation reaction, the synthesis of methanol only requires the adsorption of CO in the molecular state; the synthesis of liquid hydrocarbons requires the dissociative adsorption of CO, which is conducive to the growth of the C–C chain, and the progress of the hydrogenation reaction; in the process of low-carbon alcohol synthesis, the molecular state adsorption and dissociative adsorption of CO work together. Only when the two reach an appropriate ratio, can the growth reaction of the C–C

chain and the insertion reaction of CO be facilitated to obtain the final higher alcohol product. Alkali metals can prevent the dissociative adsorption of CO at the active site, and facilitate its non-dissociative adsorption to produce alcohols. Some alkaline earth metals such as Sr and Ba also have the above effects. The addition of a small amount of alkali metal promoter can generally increase the reaction rate, while excessive alkali metal will block the active sites on the catalysts surface to reduce the effective surface area and deactivate the catalyst. Most studies have shown that after adding alkali metal compounds to molybdenum-based catalysts, the total activity of the catalyst is reduced, but the selectivity and the space-time yield of alcohols are significantly improved.⁴¹ Transition metal promoters of Fe, Co and Ni are studied on catalytic performance. Fig. 7 shows the reaction process of CO hydrogenation on molybdenum sulfide catalysts with transition metals as promoters.⁴⁶ The CO^* adsorbed on the surface of MS_x ($M = \text{Fe}, \text{Co}$ or Ni) is partially dissociated into CH_x^* , and CH_x^* is further hydrogenated to form CH_4 ; on the M-KMoS_2 surface, the non-dissociatively adsorbed CO^* is inserted into the metal-methyl group to form the precursor of an alcohol. The precursor can be further hydrogenated to form an alcohol, or dehydrated to form a hydrocarbon. In this process, the concentration of C1 intermediate compound on the catalyst surface has an important influence on the formation of methanol and branched alcohols (Table 1). For example, Wang *et al.*⁴² studied the mechanism of potassium and nickel in MoS based catalysts. In addition, noble metals (Rh, Pd), Mn, rare earth elements La, *etc.* can also be added to the molybdenum-based catalyst as additives, and their addition can increase the output of higher alcohols in the product.

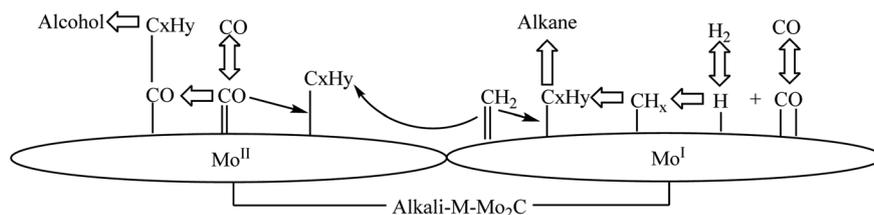


Fig. 4 Molybdenum carbide-based catalyst for the catalytic synthesis of low-carbon alcohols.¹



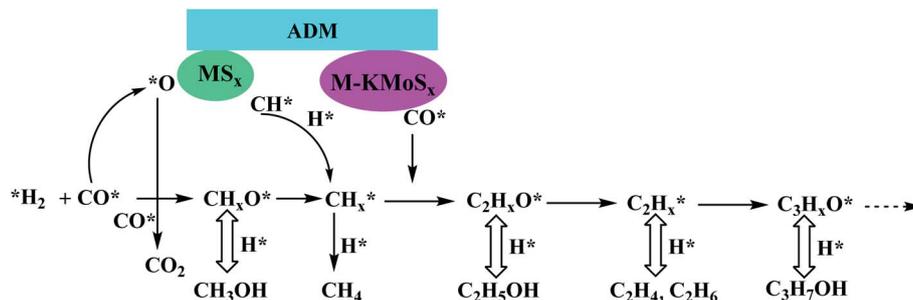


Fig. 5 Catalytic synthesis of lower carbon alcohols by molybdenum sulfide based catalyst.³⁴

4.4. Precious metal catalyst

Noble metal catalysts are represented by rhodium-based (Rh) catalysts, with ethanol as the main target product.⁴⁶ Rhodium-based catalysts are one of the most promising catalyst systems for syngas conversion to synthesize ethanol. However, considering the high price of noble metal rhodium, reducing the amount of rhodium loading and improving the utilization efficiency of metal rhodium have become the research focus. There are many opinions on the synthesis mechanism of low-carbon alcohols and active center structure of rhodium-based catalysts, among which CO insertion has been recognized by many researchers.⁴⁷ The mechanism is as follows: the first step is the adsorption of CO, in which C is adsorbed on rhodium, and O is adsorbed on the metal promoter; the second step is the hydrogenation of adsorbed CO to form an intermediate species -CH_x due to the interaction between the metal rhodium and the promoter. In the third step, CO is inserted into the intermediate species -CH_x to form -CH_xCO; in the fourth step, hydrogen is added to form alcohol. The preparation of rhodium-based catalysts with high dispersion has a positive effect on the hydrogenation of CO, and rhodium-based catalysts with different supports or with different additives will also have a profound impact on the catalytic effect during the reaction. Jiang *et al.*⁴⁸ used a template synthesis method to prepare two-dimensional ordered mesoporous carbon nanomaterials (MCNs) as the carrier of rhodium-based catalysts for synthesis of low-carbon alcohols. The catalytic activity test was carried out on a fixed bed reactor, and the results showed that the nano-sized MCNs supported catalyst has higher alcohol selectivity and C₂+ alcohol selectivity than the micron-sized ordered mesoporous carbon supported catalyst. The total alcohol yield

of the Rh/CMK-5-MCNs catalyst with a hollow framework structure is quite high, which indicates that there is an interaction between Rh metal particles and the support MCNs, which promotes the catalytic activity.

Based on the above analysis, it can be found that the current synthesis of low-carbon alcohol catalysts mainly has the following problems: (1) the activity is low with the CO conversion rate is relatively low, which is not conducive to the production of alcohols. (2) The reaction conditions are harsh, and the existing catalysts generally require high reaction temperatures and pressures, which undoubtedly increases the cost of industrial production. (3) The selectivity of C₂+ alcohol is low, which is the common deficiencies of the existing catalyst. Since the value of methanol in the low-carbon alcohol system is far behind the C₂+ alcohol, it will lead to low product economy. Therefore, how to further increase the proportion of C₂+ alcohols in low-carbon alcohols and prepare catalysts with high activity and stability is the direction of catalyst development in the future.

5. Catalyst preparation method

The preparation method of catalysts⁴⁹ influences the catalytic performance of low carbon alcohol synthesis catalysts. The preparation process of a catalyst is influenced by the temperature, the mixing method of active ingredients, drying conditions, calcination conditions, *etc.*, which directly affect the active metal components of the crystal structure of catalyst, the dispersion degree, and the REDOX performance, *etc.* Therefore, the preparation method of a catalyst directly affects the catalytic performance. The preparation methods of synthesis gas to

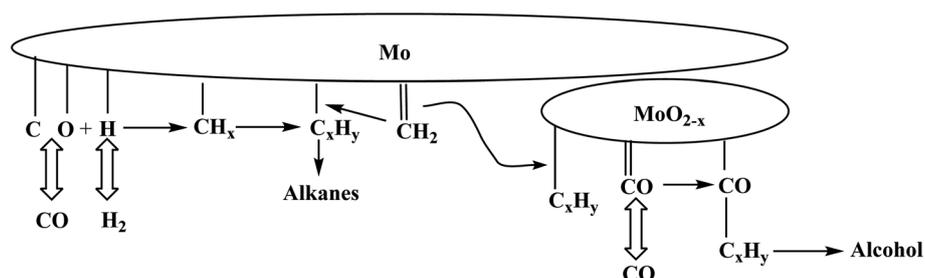


Fig. 6 Catalytic synthesis of low-carbon alcohols by alkali metal modified molybdenum oxide-based catalysts.³⁷



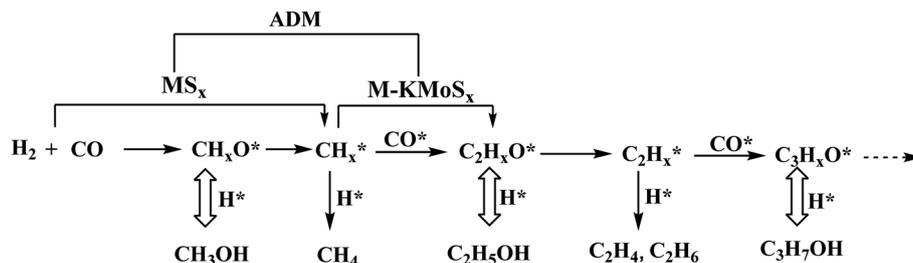


Fig. 7 CO hydrogenation reaction mechanism on K–MoS₂ catalyst modified by transition metal (M is Fe, Co or Ni).⁴⁶

Table 1 Performance of CO hydrogenation over catalysts

Catalyst	CO con. V(%)	Selectivity (wt%)		ROH distribution (we%)		Ref.
		CH _x	ROH	MeOH	C ₂ + OH	
K _{0.5} -(Ni ₁ Mo _{0.25})Si-PS	6.6	25.2	43.7	34.6	65.4	43
Mn–O–Rh ^{δ+}	42.4	59.7	40.3	11.7	88.3	44
Fe/K/β-Mo ₂ C	86.92	58.53	41.47	20.96	79.04	45
MoS ₂ -DN	27.3	31.4	68.6	40.7	59.3	35
K–Mo ₃ S _x -NiL	46.14	34.07	65.93	23.99	76.01	42
K–NiMo ₃ S _x	41.41	16.76	83.24	40.29	59.71	36

lower alcohol catalysts are different in many literature reports, mainly including co-precipitation method and impregnation method.^{50–52}

The co-precipitation method involves the interaction of salt solutions of two or more metal ions with the precipitation agent to form a precipitate containing several active metal components.⁵³ The co-precipitation method has the advantages of simple process, short preparation period, low calcination temperature, and stable catalyst performance. However, the addition of precipitating agent may cause excessive local concentration of the solution during the preparation process, resulting in agglomeration or uneven dispersion of metal components, reducing the catalytic performance of the catalyst.

The impregnation method loads one or several metal components on the carrier in the form of a salt solution. It has the advantages of simple operation and high metal utilization. The disadvantage is that the metal is not easy to disperse uniformly and is prone to agglomeration.⁵⁴ The traditional impregnation method can generally be divided into the excessive impregnation method and the equal volume impregnation method (also called incipient wetness impregnation). Excessive impregnation method can disperse the active metal better, and can maximize the adsorption capacity, but it is hard to exactly control the loading of the active component. To get higher activity, generally speaking, the larger the loading, the better. However, too much active metal loading will lead to agglomeration. The equal volume impregnation method can better control the loading of active components, but it will produce a nonuniform dispersion of active components with uneven metal particle sizes. In order to overcome the shortcomings of the traditional impregnation method, numerous studies have

been conducted to promote the full contact of the active metal with the surface of the carrier. One example is through the ultrasonic cavitation effect of ultrasound, in which the active metal can be dispersed evenly on the surface of the catalyst, thereby affecting the dispersion of the active metal, the crystal structure, and the pore diameter of the catalyst distribution and so on.

6. Conclusions

In the reaction process of synthesis gas to lower alcohol, the dissociative adsorption and non-dissociative adsorption of CO are the key to the synthesis of lower alcohol. Too much dissociative adsorption will result in the production of more alkanes in the product, while too much non-dissociative adsorption will result in less C₂+ alcohols (with higher economic value) in the synthesized low-carbon alcohols. Only when the catalyst has both strong chain growth ability and high non-dissociative adsorption CO* insertion activity, can it be possible to improve the selectivity of low-carbon alcohols. At present, the most researched catalysts are Cu–M (M is Zn, Co and Fe), Zn–Cr and other bimetallic catalysts, molybdenum-based catalysts and rhodium-based catalysts, *etc.* These catalysts have the synergistic effects of additives and supports to show higher activity and selectivity for the synthesis of low-carbon alcohols. Therefore, in order to improve the activity and the selectivity of the catalyst for low-carbon alcohols, the key is to research and design a catalyst with a large number of dual active centers and the ratio of the two types of active centers reaches a certain balance.

Author contributions

This manuscript was contributed by all authors. All the authors have ratified the manuscript.

Conflicts of interest

The authors confirm no competitive economic interest.

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