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A short review of heterogeneous catalytic process for mixed alcohols synthesis via syngas

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ABSTRACT

Mixed alcohol synthesis is an important process for the production of oxygenates fuels, fuel additives and other intermediates for chemical feedstocks via CO hydrogenation. The process is a highly exothermal reaction, which essentially needs the combination of carbon-chain growth and CO insertion functions over the catalysts. The key to the development of mixed alcohol synthesis is the selective control of alcohols and efficient removal of reaction heat via both catalyst and reactor innovation. ICC-CAS (Institute of Coal Chemistry, Chinese Academy of Sciences) has been worked on mixed alcohol synthesis over heterogeneous catalysts and gained some interesting results in the catalyst preparation and process engineering. This paper thus briefly introduced the recent research progresses at ICC-CAS.

1. Introduction

The catalytic process of mixed alcohol synthesis (MAS) from coal or natural gas derived from syngas is one of the challenging and attractive subjects in the field of C_1 chemistry. The resultant mixed alcohols obtained from this process can be used as fuels, fuel additives for octane or cetane enhancement, and intermediates for value-added chemicals such as medicine, cosmetic and polyester [1,2]. Recently, the huge consumption of crude oil and more stringent environmental regulations require more clean fuels and fuel additives, which brought the new interest to this technology [3]. Under this background, the mixed alcohol technology is expected to become one of the attracting routes for lowering the petroleum dependence, realizing the efficient conversion of natural gas and clean utilization of coal resources.

MAS is similar to methanol synthesis, Fischer–Tropsch (F–T) synthesis and ammonia synthesis in that both reaction stoichiometry and exothermic nature of the reaction dictate that the catalyst should be operated at high pressures and low temperatures [4]. In this process, the major reaction is the alcohol formation, while hydrocarbon formation and water–gas-shift reaction compose of the side reactions:

Alcohol formation

$$n\mathrm{CO} + 2n\mathrm{H_2} = \mathrm{C}_n\mathrm{H}_{2n+1}\mathrm{OH} + (n-1)\mathrm{H_2O}$$

Hydrocarbon formation

$$n\mathrm{CO} + (2n+1)\mathrm{H_2} = \mathrm{C}_n\mathrm{H}_{2n+2} + n\mathrm{H_2O}$$

Water–gas-shift reaction equilibrium

$$\mathrm{CO} + \mathrm{H_2O} = \mathrm{CO_2} + \mathrm{H_2}$$

Usually, the above MAS reactions take place over the catalysts with the function of hydrogenation, C–O bond breaking and CO insertion. The formation of alcohols involves the insertion of CO into a metal-alkyl bond to give an acyl intermediate that can form an alcohol molecule by hydrogenation [5]. The intermediates mainly depend on the type of catalyst in the composition, structure and reaction conditions. The active metals, preparation formula and process conditions determine the formation of the intermediate and its further transformation, which achieve the selective control of the low carbon mixed alcohols. Besides, the design of the process engineering is also important for the efficient removal of the react heat and enhancement of alcohol productivity. Thus, focusing on the development of the catalysts and reactor innovation, this paper gives a brief review on the heterogeneous catalytic process for mixed alcohol synthesis via syngas.

2. Catalyst design for mixed alcohol synthesis

The heterogeneous catalysts used for mixed alcohol synthesis can be broadly divided into noble metal-based and non-noble metal-based categories. The reported noble metal-based catalysts mainly serve for the conversion of syngas to ethanol and other C_{2+}-oxygenates, which usually contain Rh, Ru and Re supported on various oxides, such as SiO_2, Al_2O_3, CeO_2, ZrO_2, MgO, etc. [6,7]. The

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noble metal-based catalysts like Ru-based catalyst exhibit high ethanol selectivity in syngas conversion. However, these catalysts seem unattractive for commercial application due to the limited availability and high cost of noble metals [6]. The major non-noble metal-based catalysts available for mixed alcohols production from syngas are modified methanol catalysts, modified Fischer–Tropsch catalysts, and alkali-doped molybdenum (ADM) catalysts. The representative catalyst systems that have prospects for industrial applications are the following four classes [8]:

(1) MoS_2 catalyst system (Sygmol process) developed by DOW chemical.
(2) Cu–Co catalyst system developed by French Petroleum Institute (IFP).
(3) Cu–Zn–Al catalyst system (Octamix process) developed by Lurgi.
(4) Zn–Cr–K catalyst system (MAS technology) developed by Snam.

The above four catalyst systems have their respective features. IFP and Sygmol process have higher C_2^+ alcohol selectivity and better chemical prospect, while MAS and Octamix have high total alcohol productivity. In the past decades, the mixed alcohol synthesis catalysts have undergone a number of improvements related to better characterization for different catalyst compositions and to enhance per-pass conversion, alcohol yield, and product selectivity. But there is no catalyst that is best suited for every mixed alcohol process design. Generally speaking, the developed catalyst systems still have low catalytic activity, rigorous reaction conditions, poor product distribution and difficult post-separation, which restrict the commercialization of mixed alcohol synthesis. Although the researchers have made great efforts on the development of these catalyst systems, there still has large space to enhance the catalytic activity and selectivity toward higher alcohols.

At ICC-CAS, the exploitation of MAS catalysts has been carried out since 1990s. Till now, three series of catalyst systems are being developed: (1) F–T elements (Fe, Co, Ni, etc.) modified copper catalyst, (2) alkali-doped molybdenum sulfide catalyst, and (3) metal carbides catalyst.

2.1. Modified copper-based catalyst

Cu-based catalyst containing metal active toward Fischer–Tropsch synthesis (Fe, Co or Ni), such as Cu–Co-based catalyst, was considered as one of the most promising catalysts. However, the report associated with Cu–Co-based catalyst for large-scale industrial application, to our best knowledge, is not available due to the poor stabilization with long-term run and the low total alcohol selectivity from the practical point of view although the related catalysts have also been published by some authors more recently [2,9–12]. The catalysts systems promoted by other F–T synthesis elements (such as Fe, Ni) were also investigated by some researchers. Sibillia et al. [13] found the addition of Fe to Cu/ZnO methanol synthesis catalysts led to a significant improvement of hydrocarbons. Uchiyama et al. [14] reported a copper and sodium added $NiO–TiO_2$ catalyst, producing about 50 wt% C_2^+OH in total alcohols. Razzaghi et al. [15] investigated CO hydrogenation performance over $FeCu/SiO_2$ catalyst and found lower catalytic activity and alcohol selectivity of about 22%. Rotting [16] also reported that the alcohol formation over FeCu-based catalyst, but the products are mainly the mixture of alcohol and hydrocarbons. Kiennemann et al. [17] prepared the FeCuMoV catalyst using co-precipitation method and obtained the total alcohol yield of 0.1 g/ml(cat)-h with alcohol selectivity of 60%, which is closely to that of CuCo-based IFP catalyst. Unfortunately, the serious methanation over these catalysts was also observed. Thus, both activity and selectivity have been still the major obstacles for the further development. Recently, an efficient Fe-modified $CuMnZrO_2$ catalyst has been developed at ICC-CAS [18]. The introduction of Fe into $CuMnZrO_2$ catalyst led to a rise of the interaction between copper and iron and then promoted chain growth to form higher alcohols. However, Fe-modified $CuMnZrO_2$ catalyst still suffered from the poor selectivity to C_2^+OH and severe operation conditions due to the strong interaction of iron oxide with support. After adding zinc as the promoter, the modified catalyst showed a relatively higher activity and selectivity to alcohols under the similar mild reaction conditions to methanol synthesis. The main products were methanol, higher alcohols (C_2–C_5) and a certain amount of by-products including hydrocarbons, aldehydes, esters, acids, CO_2 and water. Excluding water products, the expected level of the carbon-containing by-products was below 40%. Besides, the catalyst showed a good stability during the run of 2400 h (see Fig. 1).

For our FeCu-based catalyst, Cu was known to be the major element for methanol synthesis, serving as the dissociative chemisorption of hydrogen and the associative adsorption of CO [5]. Iron elements, including FeCx, Fe_3O_4 and α-Fe were the active sites of F–T function of dissociative CO adsorption (C–C chain growth) and hydrogenation [19–22]. It appeared that the production of higher alcohols required the synergetic functioning of Fe and Cu. The reaction pathway for CO hydrogenation over the FeCu-based catalyst can be outlined in Scheme 1. The active iron species act as sites for CO dissociation, C–C chain growth and for hydrogenation, while copper sites adsorb CO molecularly. CO* molecule moves to an adsorbed *CHx group and inserts between metal site and the alky group via surface migration over a short distance between Fe and Cu sites, which is further hydrogenated to form ethanol. The carbon-chain growth of the alkyl group ($^*C_nH_z$) is propagated via *CHx addition. Then the direct hydrogenation of $^*C_nH_z$ species leads to the paraffin products. On the other hand, the CO insertion of $^*C_nH_z$ species and further hydrogenation result in the production of C_{n+1} higher alcohols. The general consensus is that a metallic copper atom should be within the atomic distance of an iron atom in order to create a catalytic site for higher alcohol synthesis from syngas. Thus, a homogeneous distribution of the active sites and atomic distances between these sites would be necessary for obtaining Fe–Cu-based catalyst with a high MAS performance, and any agglomeration of one type of sites, or separation of different types of sites from each other, would lead to a worse selectivity as reported for CuCo-based catalysts [5]. The precise conditions of co-precipitation, drying, calcinations and reduction were extremely critical and all these factors determined

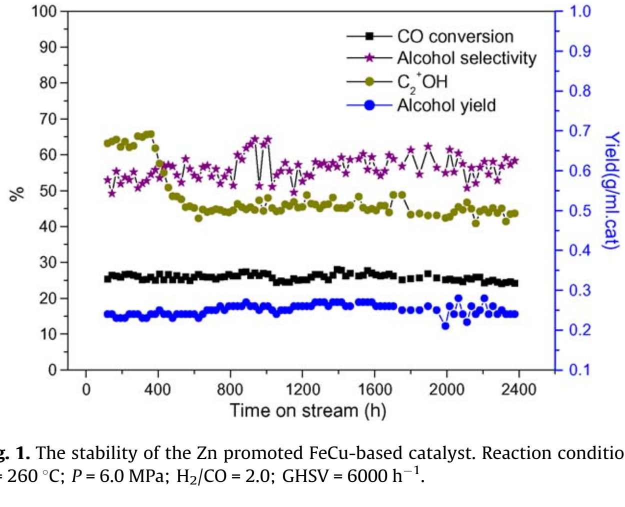
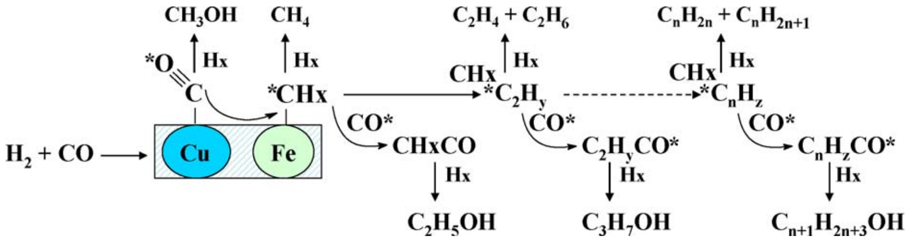


Fig. 1. The stability of the Zn promoted FeCu-based catalyst. Reaction conditions: $T = 260\,^{\circ}C$; $P = 6.0$ MPa; $H_2/CO = 2.0$; $GHSV = 6000\ h^{-1}$.



Scheme 1. Reaction pathway for CO hydrogenation over FeCu-based catalyst.

the degree of homogeneity of the final catalyst, the balance between the chain growth and oxygenate functions, and hence the catalytic performance of mixed alcohols.

2.2. Alkali-doped molybdenum sulfide catalyst

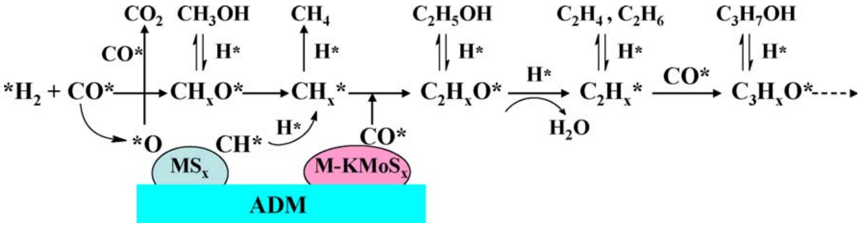
Molybdenum sulfides catalysts possess the excellent sulfur tolerance and high activity for water–gas-shift reaction, being of the promising catalysts for mixed alcohol synthesis. Among them, the alkali-doped molybdenum sulfide catalysts were more attractive for commercial aspects among various MAS catalysts [23–25]. DOW chemical and union carbide firstly developed the ADM catalyst for the production of mixed alcohols [6,26–28]. These catalysts require to be conducted at relatively high reaction temperatures (270–330 °C) and operation pressure of 10–28 MPa with H_2/CO ratio of 1–2. The product mixture over ADM catalyst comprises 70–80% alcohols and 15–30% hydrocarbons on CO_2-free basis. The total alcohol yield can reach 0.3 g/ml(cat)-h, but more than 50% of methanol in the alcohol products [29]. For Cs-doped MoS_2 catalyst, it has been reported that a balance of basic and hydrogenation functions associated with Cs and MoS_2 is required to produce an optimum yield of C_2–C_4 alcohols and to minimize the hydrocarbon formation [29,30]. Thus, a suitable amount of Cs need to added into MoS_2 catalyst to get the excellent catalytic performance.

The 3d transition metals, in particular F–T elements such as Co and Ni, were found to be effective promoters to enhance the alcohol yield as well as C_2^+OH selectivity of MoS_2 catalysts [25,31–34]. Li et al. [35] observed that the total alcohol yield can increased from 69.1 ml/kg(cat)-h to 198.5 ml/kg(cat)-h when cobalt added into $KMoS_2$/C catalyst at a Co/Mo ratio of 0.5. Iranmahboob et al. [36] claimed a higher ethanol yield of about 130 mg/g(cat)-h over Co-modified $KMoS_2$ supported on clay. Our result showed that the promotion effects of Ni were closely related to the structure and morphology of nickel, and the highly dispersed Ni species would lead to high performance of MAS [37–39]. The 17.8% of CO conversion and 81.72% of alcohol selectivity can be obtained at 320 °C, 9.5 MPa and a space velocity of 6000 h^{-1} with a syngas containing an H_2/CO ratio of 2. Generally, it was considered that at least two forms of transition metal promoters simultaneously existed in MoS_2-based catalysts, namely, separated phases of transition metal sulfides and mixed phases such as the so-called "Co-KMoS" and "Ni-KMoS" [40,41]. Scheme 2 outlines the reaction model for CO hydrogenation over the transitional metal promoted ADM catalyst [42]. CO dissociated readily to form surface CHx^* on separated MS_x (M = Fe, Co or Ni) and the formation of methane took place by direct hydrogenation of surface CHx^* species. The non-dissociative adsorbed CO* on the mixed M-KMoS phase then inserts into a metal–methyl carbon bond to produce alcohol precursor, which further hydrogenated or dehydrated to form alcohols and hydrocarbons. This route comprises the chain growth via hydrogenation intermediates and chain growth via oxygenated intermediates [42,43]. Indeed, the concentration of the surface bound C_1 intermediates exerted a far more important influence on the formation of methanol and branched alcohols. The linear chain growth via C_1 intermediate insertion at the end of chain resulted in linear primary alcohols, while the addition via C_1 intermediate resulted in branched alcohols [44–46].

For MoS_2-based MAS catalysts, it has been recognized that the close interaction between Mo and promoter atoms exerted great influence on promotion effects and much efforts including unique preparation methods, modifications by promoters and supporters were attempted to obtain highly dispersed catalysts [47–49]. Moreover, the structural effects of active additives played an important role for CO hydrogenation, namely, small crystallites had advantages to produce alcohols while larger crystallites to hydrocarbons [50,51]. As a potential element, enhancement effects of La modification on MoS_2-based catalysts were expected to improve both dispersion of the active metals and sulfidation of active components by minimizing the Mo–O–La interactions of active species and suppressing the agglomeration of the MoS_2 layers [52]. In our research, the concept of catalyst design included (i) introducing F–T elements to enhance the activity and C_{2+}OH selectivity and (ii) enhancing the interaction between F–T elements and MoS_2 to prolong the life of catalysts. The typical performance of our catalyst was given in Table 1 and Fig. 2. It was found that innovated Ni promoted MoS_2-based catalyst showed extremely higher yield of total alcohols and C_2^+ alcohols which kept above 0.40 g/ml(cat)-h and 0.16 g/ml(cat)-h, respectively. Moreover, the catalyst showed a high stability after running 2000 h.

2.3. Metal carbides catalysts

Transitional metal carbides are a type of metal-derived compounds with the incorporation of carbon in the metal lattice. They have the physico-chemical properties of high melting point and hardness, high thermal and mechanical stability as well as



Scheme 2. Reaction pathway for CO hydrogenation over transitional metal-modified ADM catalyst (M denotes as Fe, Co or Ni).

Table 1
Performance of Ni/MoS_2-based catalyst for mixed alcohol synthesis.

Temp. (°C)	X_{CO}[a] (%)	Selectivity (C-mol%)			STY of Alc[d]. (g/ml(cat)-h)	Liquid product distribution (wt%)			
		HC[b]	CO_2	Alc[c]		C_1OH	C_2OH	C_3OH	C_4OH
300	19.2	24.7	20.1	55.2	0.34	65.6	25.1	7.1	2.2
340	26.5	34.8	22.3	42.9	0.47	56.4	30.0	10.5	3.1

[a] CO conversion.
[b] Total hydrocarbons.
[c] Total alcohols.
[d] Space time yield of alcohols; reaction conditions: $P = 9.5$ MPa, $H_2/CO = 1.0$, GHSV = 8500 h^{-1}.

excellent catalytic performance for hydrogenation, which are similar to those of Pt, Rh and other noble metals [53,54]. Thus, the metal carbides can be used as potential substitutes for noble metal catalysts. Compared with metal sulfides, metal carbides possess superior hydrogen adsorption, activation and transfer capabilities, and then they have potential application in CO hydrogenation reactions.

From a practical view, a highly active, selective and poisoning-resistant catalyst for higher alcohol synthesis is desirable. Transition metal carbides (or nitrides) have attracted much attention for F–T synthesis due to the distinctive properties like noble metals. It has been reported that both molybdenum and tungsten carbides or nitrides were shown to be promising catalysts for CO hydrogenation. Bell and co-workers [55] investigated CO hydrogenation over the HCP and FCC phases of Mo_2C and the FCC phase of Mo_2N. The results showed that the catalytic activity and selectivity of the FCC phases of Mo_2C and Mo_2N were identical. The activity of the HCP phase of Mo_2C was half of the other two catalysts but the olefin selectivity was higher. They attributed the different catalytic performances to the differences in the structure of the principal planes exposed by each phase of the carbide. Lee et al. [56] examined the effect of potassium promotion on F–T synthesis over molybdenum carbide catalysts. They found that the unsupported molybdenum carbide catalyst produced mostly C_1–C_5 paraffins in the hydrogenation of CO at atmospheric pressure. Promotion of the catalyst with K_2CO_3 yielded C_2–C_5 hydrocarbons consisting of 80–100% olefins and reduced the methane selectivity. The selectivity of C_2–C_5 olefins among all hydrocarbon products was 50–70 wt% at CO conversions up to 70%. Leclercq et al. [57] and Woo et al. [58] have elsewhere clearly shown that tungsten and molybdenum carbides produced mainly light alkenes, whereas the formation of alcohols is related to the surface stoichiometry and to the extent of carburization. Mo_2C catalyst promoted by K_2CO_3 has been found to greatly enhance the selectivity to alcohols composed of linear C_1–C_7.

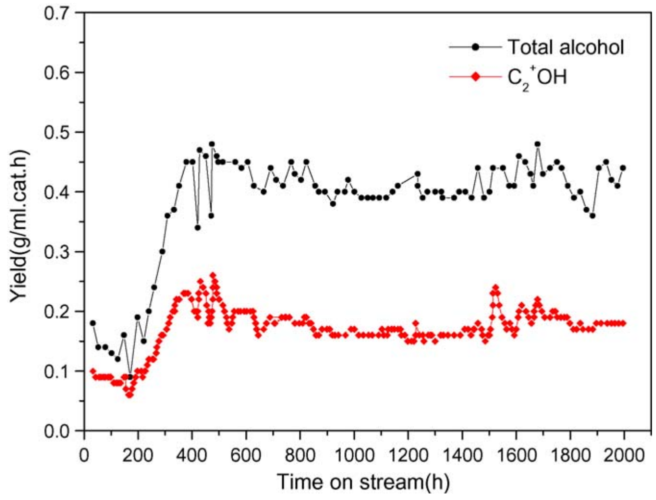


Fig. 2. The performance of MoS_2-based catalyst for 2000 h. Reaction conditions: $T = 340$ °C; $P = 9.5$ MPa; $H_2/CO = 1.0$; GHSV = 8500 h^{-1}.

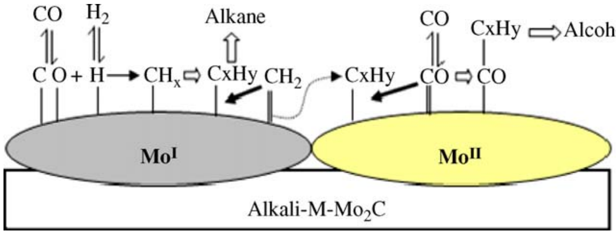
The tentatively proposed reaction pathway for CO hydrogenation over Mo_2C catalyst follows a dual-site mechanism (shown in Scheme 3), similarly to that reported by Muramatsu et al. [59]. There are mainly two kinds of Mo carbide species located on the surface of the catalysts, namely the low valent molybdenum (Mo^I, I = 0–2) carbides and the high valent molybdenum (Mo^{II}, II = 4) carbides [60]. The dissociatively adsorbed CO and H_2 on Mo^I carbide sites form CH_X species and then chain growth of the generated alkyl group is realized via CH_2 insertion. Then the alky group migrates to the Mo^{II} carbide sites, which is inserted by the non-dissociatively adsorbed CO to form acyl species. Finally, the hydrogenation of alkyl group and acyl species over different Mo carbide sites leads to hydrocarbons and mixed alcohols.

Recently, ICC-CAS also made great attempts to develop Fe, Co and Ni promoted metal carbides catalysts for paraffins, olefins and alcohols via CO hydrogenation [61–63]. The initial results showed that Fe, Co and Ni promoters exerted a strong promotion for carbon-chain growth, especially for the stage of C_1OH–C_2OH. We also found that the catalytic activity and selectivity over K/Co/β-Mo_2C catalysts were significantly influenced by the Co/Mo molar ratio, which showed the maximum activity at about 1/8–1/6. The "Co_3Mo_3C" new phase might be responsible for the high activity of higher alcohol synthesis and the "Co_2C" new phase might favor the synthesis of hydrocarbons over Co promoted K/β-Mo_2C catalysts.

The exploitation of our carbide catalysts directed at the high activity and high C–O chain propagation capability for C_2^+OH synthesis through the optimization of carbonization methods and modification by F–T components. Using carbide catalysts, syngas was converted into a range of alcohol components and other co-products such as liquefied petroleum gas (LPG). The typical performances of the modified β-Mo_2C catalysts are given in Table 2. The catalysts showed much higher C_2^+OH selectivity along with sulfur tolerance, expecting to be a new generation catalyst for mixed alcohol synthesis.

3. Reactor and process technology for mixed alcohol synthesis

Besides the exploration of the catalyst with excellent performance, the innovation of reactor and process technology is another



Scheme 3. The tentative reaction pathway for CO hydrogenation over transitional metal-modified Mo_2C-based catalyst (M denotes as Fe, Co or Ni).

Table 2
Performance of modified β-Mo_2C catalyst for higher alcohol synthesis.

Catalysts	X_{CO}[a] (%)	Selectivity (C-mol%)			STY of Alc[d]. (g/ml(cat)-h)	Liquid product distribution (wt%)			
		HC[b]	CO_2	Alc[c].		C_1OH	C_2OH	C_3OH	C_4OH
β-Mo_2C	58.62	46.39	51.81	1.80	0.016	76.85	14.05	6.11	2.99
K/β-Mo_2C	23.43	23.97	49.58	26.45	0.122	45.98	36.15	12.61	5.26
K/Ni/β-Mo_2C	73.05	25.72	50.89	23.39	0.324	34.41	38.44	15.05	12.04
K/Co/β-Mo_2C	40.82	28.32	50.66	21.02	0.156	38.77	38.83	13.72	8.68

[a] CO conversion.
[b] Total hydrocarbons.
[c] Total alcohols.
[d] Space time yield of alcohols; Reaction conditions: $T = 300\ ^\circ C$, $P = 8.0$ MPa, $H_2/CO = 1.0$, GHSV = 2000 h^{-1}.

important aspect for obtaining the higher yield and better selectivity toward higher alcohols with the reducing proportion of by-products in the mixed alcohol synthesis. The higher alcohol yield and selectivity are usually low using the traditional fixed-bed gas phase tubular reactor. Then the double-bed reactor was designed to maximize the formation of methanol from syngas over the first catalyst bed at lower reaction temperature and to promote the C–C bond-forming steps and subsequent formation of higher alcohols. In the isobutanol synthesis, it has been reported that the isobutanol productivity was more than doubled by using the dual-bed $Cs/Cu/ZnO/Cr_2O_3||Cs/ZnO/Cr_2O_3$ catalyst as compared with the single-bed $Cs/Cu/ZnO/Cr_2O_3$ catalyst [1,64]. Now, the double-bed reactors are mainly used for the synthesis of branched alcohols due to their higher stability than that of linear alcohols.

As a kind of hydrogenation reaction, mixed alcohol synthesis process basically converts carbon monoxide to the products consisting mainly of the mixed C_1–C_6 alcohols and more or less paraffin hydrocarbons with variable carbon-chain length. This brings a highly exothermic effect that results in the generation of hotspots, facilitating the carbon deposition and the sintering of catalyst particles. Thus, the rapid removal of the reaction heat is also a major consideration for the design of suitable reactors. The slurry-bed reactor has been introduced into alcohol synthesis due to its better heat transfer, mass transfer and the possibility of online catalyst replacement. To carry out the alcohol synthesis in a slurry-bed reactor can suppress the production of CO_2 and by-product formation. The selectivity of alcohols reached a high level (see Fig. 3) at lower temperatures than 300 °C, but the higher catalyst activity was needed [65]. The supercritical synthesis process appeared to solve most of the problems for both methanol and higher alcohol synthesis. By using a suitable supercritical solvent, the equilibrium for methanol synthesis may shift beyond the thermodynamic limitation, and the selectivity for higher alcohol synthesis is expected to be improved. Furthermore, the heat transfer in both cases was improved also to alleviate the 'hotspot' phenomena. The process has been succeeded for both methanol and ethanol synthesis in our laboratory [66], and progress has been made in higher mixed alcohols synthesis with the main product of isobutanol.

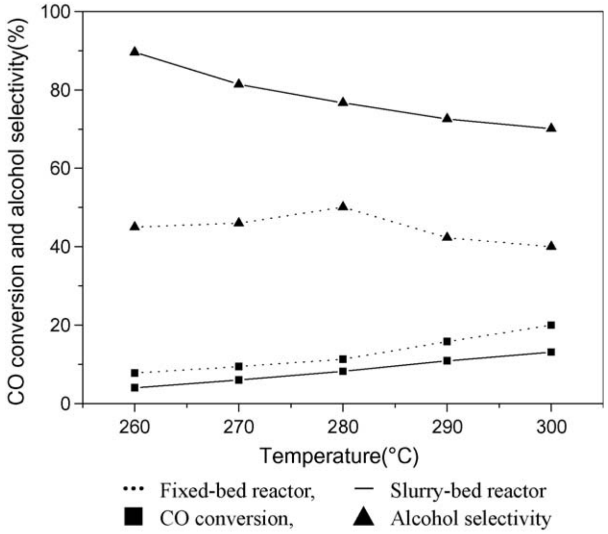


Fig. 3. Catalytic performance for alcohol synthesis in different reactors. Reaction conditions: $P = 10.0$ MPa; $H_2/CO = 2.0$; GHSV = 12,000 h^{-1}.

4. Challenges and perspectives

As one of the alternative routes to the petroleum pathway, the mixed alcohol synthesis bring new life due to the increasing demands for liquid fuels and the fading supply of oil reserves. Although many efforts have been made to facilitate the technology progress of mixed alcohol synthesis, some uncertainties and risks exist in this process. CO hydrogenation to produce mixed alcohols is not only the more complicated reaction process than syngas-to-liquids processes such as F–T synthesis, but also no commercial plants exist solely for the manufacture of mixed alcohols from syngas. The catalyst stability, catalyst sensitivities to impurities, catalyst intensity and reaction performance under scale-up conditions are needed to investigate in detail. There are not sufficient evaluation about the overall process feasibility to produce the desired alcohols and the ability to scale-up the process to a commercial level. Besides, the by-products such as water, hydrocarbons and CO_2 are needed to the comprehensive utilization for obtaining higher benefit at low cost level. Nevertheless, the most crucial is to achieve higher C_2^+ alcohols selectivity with comparable alcohol productivity considering the commercial production of mixed alcohols. Besides the deep understanding of mechanism for mixed alcohol synthesis, the future shall still emphasize the further developing highly efficient catalyst and integrated process technology to meet the economic viability and market demands for oxygenates fuels.

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