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Review

Advances in bifunctional catalysis for higher alcohol synthesis from syngas

XIAO Kang ^{a,b}, BAO Zhenghong ^a, QI Xingzhen ^a, WANG Xinxing ^a, ZHONG Liangshu ^{a,*},
FANG Kegong ^c, LIN Minggui ^c, SUN Yuhan ^{a,c,#}

^a Low-Carbon Conversion Center, Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai 201203, China

^b University of the Chinese Academy of Sciences, Beijing 100049, China

^c State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, Shanxi, China

ARTICLE INFO

Article history:

Received 30 September 2012

Accepted 7 November 2012

Published 20 January 2013

Keywords:

Higher alcohol

CO hydrogenation

Syngas

Bifunctional catalysis

Dual site

ABSTRACT

Bifunctional catalysis on dual sites plays an important role in higher alcohol synthesis from syngas. It makes use of two types of active sites of which one type dissociates CO and forms surface alkyl species and the other type catalyzes non-dissociative CO adsorption for CO insertion and alcohol formation. To improve catalytic activity for higher alcohol synthesis, it is necessary to design dual sites on the atomic scale to give them high stability. The recent advances in higher alcohol synthesis using bifunctional catalysts are reviewed. The design of the dual sites, the structure of the dual sites on several typical catalyst systems, and the structural evolution of the dual sites during reaction are discussed using our latest research results.

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1. Introduction

Oil is a non-renewable energy source that will eventually be depleted. Due to the oil crisis of the 1970s, extensive research on alternative energies was carried out around the world. One important research area is the conversion of synthesis gas (syngas) [1]. Syngas, a mixture of carbon monoxide and hydrogen, with some carbon dioxide in some cases, can be obtained from various carbon-containing sources such as coal, natural gas, biomass and even organic waste. Many products including methanol, ultra-clean gasoline and diesel, high quality waxes, alcohols, olefins and other chemicals can be obtained from the catalytic conversions of syngas (Scheme 1). One important syngas conversion route is higher alcohol synthesis (HAS).

Higher alcohols, which commonly refer to alcohols higher than methanol, can be used as fuels, fuel additives for octane enhancement, and value added chemicals in fine chemical synthesis [2–4]. Four classes of catalysts have been reported for HAS, which are modified methanol catalysts, modified Fischer-Tropsch (FT) catalysts, molybdenum based catalysts, and rhodium based catalysts. The modified methanol catalysts include the high pressure (HP) and low pressure (LP) types, which were developed by Snam in Italy and Lurgi in Germany. Methanol and *iso*-butanol are the main alcohols produced by modified methanol catalysts [5]. Modified FT catalysts, mainly Cu-Co-based catalysts, were developed by Institut Français du Pétrole (IFP). C₁–C₆ linear primary alcohols are the main products from modified FT catalysts, and the products obey the

* Corresponding author. E-mail: zhongls@sari.ac.cn

Corresponding author. Tel.: +86-21-20325009; Fax: +86-21-20325039; E-mail: sunyh@sari.ac.cn

This work is supported by the National Basic Research Program of China (973 Program, 2011CBA00501), Shanghai Municipal Science and Technology Commission, China (11DZ1200300) and the Foundation of State Key Laboratory of Coal Conversion (11-12-610).

DOI: 10.1016/S1872-2067(11)60496-8

Scheme 1. Syngas generation pathways and conversion routes.

Anderson-Schulz-Flory (ASF) distribution [2]. Molybdenum-based catalysts include molybdenum oxide-, molybdenum sulfide-, and molybdenum carbide-based catalysts. Dow Chemical Company first developed alkali/alkaline metal-doped molybdenum sulfide catalysts for HAS. As with modified FT catalysts, C₁–C₅ straight chain primary alcohols are the main products of molybdenum based catalysts [6]. Rhodium-based catalysts are representative of noble metal-based catalysts, and mainly produce ethanol and other C₂–oxygenates [7]. Although many catalysts have been developed, the selectivity to alcohols, and in particularly higher alcohols, is not high enough and catalyst stability remains poor. Thus developing novel catalysts for HAS with high selectivity and stability is necessary.

There have been many reviews on catalyst preparation, reaction mechanism and kinetics of HAS [8–11]. In this review, the design concept of a dual site (the active site for higher alcohol formation), the structures of the dual site on several typical catalyst systems and the structural evolution of the dual site during reaction are discussed using our latest research results.

2. Summary of recent progress in HAS

Much work has been done on HAS by many groups from around the world to improve the performance of the catalysts and to elucidate the underlying mechanism. Spivey and coworkers in Louisiana State University have carried out significant work on HAS. Recently they used the wet chemical method to prepare a series of Cu-Co alloy nanoparticles and Co@Cu core-shell nanoparticles as model catalysts for HAS [12], and found that the alloy nanoparticles showed higher alcohol selectivity than the core-shell nanoparticles. Unsupported nanoparticles as model catalysts have the benefit of avoiding support effects and are better for the elucidation of the intrinsic function of the metals and the structure of the dual sites. In addition, Spivey and coworkers also used in situ IR to investigate the adsorption states (linear, bridged) and the adsorption sites (metallic Co, oxidized Co) of CO on the surface of Cu-Co and Co, and their relationships with catalytic performance. Goodwin and coworkers in Clemson University investigated component interaction in and the reaction mechanism of a Cu-Co/ZnO catalyst by the multiple product steady state iso-

topic transient kinetic analysis (SSIKA) method [16,17]. The authors proposed that ZnO increased the dispersion of Co, and that Cu did not change the intrinsic activity of Co but Cu on the surface of Co blocked the FT active sites of Co, which improved the selectivity to higher alcohols of the Cu-Co/ZnO catalyst. They also said that a combination of Cu, Co and ZnO gave a high selectivity to oxygenates. Davis and coworkers in University of Virginia worked on rhodium-based and molybdenum carbide-based catalysts [18–21], and Smith and coworkers in University of British Columbia, Canada focused on molybdenum phosphide (MoP)-based catalysts [22–24]. In China, there are also many research groups who have studied HAS in recent years. Zhang and coworkers in Xiamen University developed catalysts using multi-walled carbon nanotubes (MWCNTs). These were transition metal (Co, Ni) doped MWCNT supported catalysts. They found that the MWCNTs significantly improved alcohol selectivity. Both MWCNT supported modified FT catalysts [25,26] and molybdenum based catalysts [27–31] showed higher alcohol selectivity and yield than those without MWCNTs. They found that the MWCNTs did not change markedly the apparent activation energy of the reaction. The promotion effect mainly resulted from an increased concentration of surface species active for HAS and increased hydrogen adsorption by the activation by a chemical state change caused by MWCNT [32]. A work by Bao and coworkers in Dalian Institute of Chemical Physics, CAS that used carbon nanotubes (CNTs) to promote the catalysts is worth noting. They placed Rh inside the CNT and found it to have much higher ethanol selectivity than Rh outside the CNT, and they explained it by the confinement effect [33]. The confinement effect was due to the different electronic states inside and outside of the CNT, which was shown by their theoretical calculation that the inside wall of the CNT is electron deficient while the outside wall is electron rich [34]. Instead of using promoters (e.g. MWCNTs) to improve the performance of the catalyst, Chu and coworkers in Sichuan University focused on novel preparation methods. By using a plasma-assisted method, they synthesized a series of Cu-Fe and Cu-Co-based catalysts for HAS, and showed that the catalysts prepared by the plasma-assisted method gave higher activity and selectivity than those prepared by conventional methods [35–38]. The authors said that the increased activity and selectivity were due to increased specific surface area and disper-

sion and decreased crystal size, that is, the enhanced properties were due to more surface active sites being produced by the plasma-assisted preparation method. In higher alcohol synthesis, the direct synthesis of C_{6+} high molecular alcohols from syngas has also attracted much attention. Recently, Ding's group in Dalian Institute of Chemical Physics, CAS reported an active carbon supported cobalt-based catalyst for the direct synthesis of C_1 – C_{18} linear primary alcohols from syngas under mild conditions [39–41]. Cobalt carbide was believed to be the active species. High molecular mass alcohols ($C_{6+}OH$) can be used for value added fine chemicals, and also find application in fine chemical industries, such as in pharmaceuticals, cosmetics, surfactants, and detergents. The direct synthesis of $C_{6+}OH$ from syngas has both academic and industrial values. However, the separation and purification of the products is a practical problem. In addition to the above research groups, there are also many other groups in China working on HAS, for instance, Mao's group in Shanghai Institute of Technology [42–44], Wang's group in Guangzhou Institute of Energy Conversion, CAS [45, 46], and He's group in Tsinghua University [47]. Our group has worked on HAS for many years and have carried out systematic research on modified FT catalysts and molybdenum-based catalysts (including molybdenum sulfide- and carbide-based catalysts). The results from our group will be discussed in detail in this review.

3. The design of the dual site

HAS is a very complicated catalytic reaction process that involves many reactions occurring in parallel and in sequence. Some reactions are listed below:

Reactions (2) and (3) are typical FT reactions while reaction (4) is the typical methanol synthesis reaction. HAS shares some common surface reactions with FTS and methanol synthesis. However, HAS, FTS, and methanol synthesis also differ in many features. FTS can be considered as a surface polymerization process involving the insertion of methylene into surface alkyl groups in the chain propagation step. The surface alkyls have the termination steps of dehydrogenation to form alkenes or hydrogenation to form alkanes [48,49], as depicted in Scheme 2. There are still debates on the mechanism of methanol synthesis from syngas. It is commonly accepted that CO_2 is the

Scheme 2. Depiction of carbon chain growth and termination in FTS.

Scheme 3. Surface reaction pathway of methanol synthesis.

'real' reactant. CO is first converted into CO_2 by the water gas shift (WGS) reaction, then CO_2 is hydrogenated to form methanol by first forming surface formate and then a methoxy species, as depicted in Scheme 3 [50]. FTS involves chain propagation which needs $C-O$ bond breaking, but it does not involve oxygenation in which an undissociated $C-O$ bond introduces oxygen into the carbon chain. Methanol synthesis needs oxygenation but does not need chain propagation. HAS needs both chain propagation and oxygenation. Chain propagation and oxygenation occur on different sites, so HAS needs a dual site (Scheme 4) on which bifunctional catalysis occurs. On the dual site, one type of active site catalyzes chain propagation and the other type catalyzes oxygenation. The synergism of these two sites leads to the formation of higher alcohols.

Because HAS needs a dual site, increasing the surface concentration of the dual site obviously benefits higher alcohol formation, and any structural change that decreases the concentration of the dual site will lead to decreased higher alcohol selectivity. In addition, it is necessary to keep a balance between these two types of active sites. When one active site outperforms the other, the performance of the catalyst will be reduced. The design concept of HAS catalysts should thus be the construction of the dual site at the atomic scale to maximize the synergism between propagation and oxygenation sites.

4. Structures of the dual sites in some typical catalysts

Although all HAS catalysts need the dual site for higher alcohol formation, the structures of the dual site differ for different types of catalysts. The specific structures of the dual site in some typical catalyst systems are discussed in detail below.

4.1. Modified FT catalysts

Due to the high selectivity to total alcohol and higher alcohols ($C_{2+}OH$), modified FT catalysts, mainly Cu-Co-based catalysts developed by IFP, have attracted much attention. Compared with Cu-Co-based catalysts, Cu-Fe-based catalysts show

Scheme 4. Schematic depiction of the dual site in HAS. M1: chain growth center; M2: oxygenation center. Synergism between M1 and M2 leads to the formation of higher alcohols. Left part depicts the hydrogenation of dissociatively adsorbed CO to form CH_2 .

Scheme 5. CO insertion mechanism on modified FT catalysts [2].

higher activity and C_2+ OH selectivity. In addition, Cu-Fe-based catalysts also exhibit higher WGS activity, which makes them suitable for hydrogen-lean and CO_2 -containing syngas derived from coal or biomass. Research on Cu-Fe-based catalysts have increased in recent years [36,51–57]. A series of CuFeMnZr catalysts developed by our group showed > 50% total alcohol selectivity and > 50% C_2+ OH selectivity. In a 3000 h stability test, no significant decrease in activity or selectivity was observed [3]. In addition, our CuFeMnZr catalysts were successfully scaled-up and have passed the single tube reactor test.

The CO insertion mechanism for higher alcohol formation proposed by Xu et al. [2] is widely accepted for modified FT catalysts (Scheme 5). In the CO insertion mechanism, HAS is treated as a combination of FTS and methanol synthesis, or as a process between FTS and methanol synthesis. The chain initiation (k_a , k_1) and chain propagation (k_p) proceed similarly to the FT reaction to form surface alkyl species ($C_nH_x^*$), and the termination reaction of the alkyl species determines the products formed. Termination by CO insertion (k_{co}) gives alcohols through surface acyl species ($C_nH_zCO^*$) followed by hydrogenation (k_H'), while termination by dehydrogenation or hydrogenation (k_H) gives olefins and paraffins, respectively. It is obvious that alcohol formation competes with hydrocarbon formation. The CO insertion mechanism elucidates why the modi-

fied FT catalysts mainly produced linear primary alcohols and the alcohols obey the ASF distribution with a similar chain growth factor as for hydrocarbons.

The CO insertion mechanism provides the detailed reaction routes of the surface species. However, the detailed structure of the dual site on modified FT catalysts is not clear. Xu et al proposed that the Cu-M (M = Fe, Co, etc.) center is the dual site for higher alcohol formation [2], and this is accepted by many researchers [3,58]. On the Cu-M dual site, CO is dissociated on the FT element (Fe, Co, etc.) and hydrogenated to form methylene species, which initiates chain growth to form surface alkyl species, while CO molecularly adsorbs on Cu and inserts into the alkyl-metal bond to oxygenate the carbon chain. As depicted in Scheme 6, either molecularly adsorbed CO on Cu migrates to the surface of the FT element followed by CO insertion into the C–M bond, or surface alkyl group on the FT element migrates to the Cu site followed by CO insertion to give surface acyl formation. Hydrogenation of the acyl groups gives alcohols. Both routes need the synergism between the Cu and FT elements. The loss of this synergism would decrease alcohol selectivity.

As depicted in Scheme 6, the formation of higher alcohols requires the surface species on one site to migrate to the other site without any side reactions (e.g., hydrogenation and desorption). In order to increase alcohol selectivity, the Cu and FT elements should be in intimate contact with each other on the atomic distance to reduce side reactions. Obviously, a separation of the Cu and FT elements would destroy the synergism of the Cu-M dual site and lead to lower alcohol selectivity. This aspect was studied in detail in our lab [59]. A series of CuFe bimetallic nanoparticles were synthesized as model catalysts for HAS, and the performance of the CuFe catalysts was compared with those of monometallic Fe and Cu nanoparticles and a physical mixture (PM) of monometallic Cu and Fe nanoparticles. Typical results are listed in Table 1. Cu nanoparticles showed no activity under the reaction condition. All CuFe bimetallic nanoparticles gave higher selectivities to total alcohols than Fe and PM. The results indicated that the synergism between Cu and Fe benefited alcohol formation and the synergism only exist on CuFe bimetallic nanoparticles. The Cu-Fe dual site needs the two components to contact each other on an atomic distance. When Cu and Fe were separated from each other as in the case of PM, the surface species on one type of site cannot migrate to the other, and thus alcohol formation was hindered.

On Cu-Co-based catalysts, Blanchard et al. [60] and Baker et al. [61] have proposed another type of dual site, namely, the

Scheme 6. Schematic of alcohol formation on Cu-M dual sites.

Table 1

Catalytic results of Cu-Fe bimetallic nanoparticles and monometallic Fe nanoparticles and PM.

Catalyst	CO conversion (%)	Selectivity (%)		
		ROH	HCS	CO ₂
10Cu1Fe	25.2	23.4	68.1	8.5
3Cu1Fe	20.8	26.2	71.1	2.7
1Cu3Fe	26.5	22.6	68.5	8.9
1Cu10Fe	21.3	18.5	78.9	2.6
Fe	19.6	14.1	75.8	10.1
PM	19.4	13.5	75.9	10.6

Reaction conditions: $T = 220\text{ }^\circ\text{C}$, $p = 6\text{ MPa}$, $GHSV = 6000\text{ h}^{-1}$, $H_2/CO = 2$.

Scheme 7. Depiction of the $\text{Co}^0\text{-Co}^{\delta+}$ dual site.

metallic-oxide Co pair ($\text{Co}^0\text{-Co}^{\delta+}$ pair). On the $\text{Co}^0\text{-Co}^{\delta+}$ dual site, metallic Co^0 is the active site for CO dissociation and chain propagation while $\text{Co}^{\delta+}$ is the active site for CO associative adsorption and CO insertion, as depicted in Scheme 7. The surface reactions on the $\text{Co}^0\text{-Co}^{\delta+}$ dual site are similar to those on the Cu-M dual site. Recently, Spivey et al. [13] investigated CO adsorption on Cu/SiO₂, Co/SiO₂ and Cu-Co/SiO₂ by IR and showed that their results supported the proposal of Blanchard and Baker. The $\text{Co}^0\text{-Co}^{\delta+}$ dual site can explain why Co-based catalysts (without Cu) can produce higher alcohols under certain conditions [62]. It was found that a high dispersion of Co favors higher alcohol formation [60,63]. As the Co-support interaction hinders the reduction of $\text{Co}^{\delta+}$, a high dispersion of Co with a strong metal-support interaction would increase the concentration of $\text{Co}^{\delta+}$ and thus the concentration of the $\text{Co}^0\text{-Co}^{\delta+}$ pair for alcohol formation. The observation that a high dispersion of Co benefited higher alcohol formation indirectly supported the $\text{Co}^0\text{-Co}^{\delta+}$ dual site. It is worth noting that Chaumette et al. [64] found that under careful pretreatment and certain reaction conditions, the Co species in CoZnAl catalysts were mainly $\text{Co}^{\delta+}$ states, and CoZnAl showed a similar performance to CuZnAl with very high methanol selectivity.

4.2. Molybdenum carbide-based catalysts

Levy et al. first reported in 1973 that Group VIB metal carbides have unique physical and chemical properties that are similar to those of the Pt Group noble metals. Since then, metal carbides as a new catalytic material have attracted much attention [65]. Molybdenum carbide (Mo_2C) has long been recognized as a quasi-platinum catalyst with unique properties. In addition, Mo_2C also has the advantage of being inexpensive, sulfur tolerant, and carbon deposition resistant. When used for CO catalytic conversion, Mo_2C catalysts showed good hydrogenation ability with the formation of light hydrocarbons, where methane is the main product. Much work has been done to improve the activity and selectivity of molybdenum-based catalysts. Our group has carried out much research on alkali and Group VIII transition metal-doped Mo_2C catalysts to increase the selectivity to alcohols, esp. to $\text{C}_2\text{-OH}$ alcohols [66–72].

Scheme 8. Mechanism of higher alcohol formation on Mo_2C -based catalysts.

The dual site on Mo_2C based catalysts is suggested to involve two types of molybdenum species [3], namely, the low valence molybdenum (Mo-I , $\text{Mo}^{(0-2)+}$) and the high valence molybdenum (Mo-II , $\text{Mo}^{(4-5)+}$) species, as depicted in Scheme 8. The Mo-I species is the site for CO dissociation, hydrogenation and chain propagation to form surface alkyl species, while the Mo-II species is the site for molecularly adsorbed CO insertion and alcohol formation. A higher concentration of the Mo-II species would increase total alcohol selectivity. However, the corresponding decrease of the Mo-I species would decrease chain growth ability and lead to a lower selectivity to higher alcohols. Thus, it is necessary to balance the two species to get a high selectivity to both total alcohol and $\text{C}_2\text{-OH}$. To improve the alcohol selectivity, additives are commonly used in Mo_2C catalysts. Besides the intrinsic catalytic activity of some additives (e.g., the CO hydrogenation ability of FT elements), all additives affect the selectivity through changing the relative concentrations of the different molybdenum species either directly or indirectly. We have prepared a series of potassium and iron dual-doped $\beta\text{-Mo}_2\text{C}$ catalysts ($\text{K/Fe}/\beta\text{-Mo}_2\text{C}$) by the sol-gel method for HAS. XPS analysis indicated that there are more high valence molybdenum species on the surface when more K was added (Table 2). The change in the surface concentration of the Mo-II species affected the total alcohol and higher alcohol ($\text{C}_2\text{-OH}$) selectivity. As shown in Table 2, the total alcohol selectivity increased with increasing Mo-II concentration, while higher alcohol selectivity (indicated as $\text{C}_2\text{-OH}/\text{MeOH}$) reached a maximum. Low valence molybdenum carbide species have high hydrogenation activity, so methane was the main product with a low concentration of the Mo-II species. With increasing concentration of the Mo-II species, the site for CO insertion and alcohol formation increases leading to improved alcohol selectivity. Meanwhile, a high concentration of the Mo-II species decreases the hydrogenation ability of the catalyst and thus increases the chain growth ability, leading to increased higher alcohol selectivity. However, when the performance of the Mo-II species exceeds the Mo-I species, the chain growth ability becomes low, so the higher alcohol selectivity is decreased. On the other hand, when too much K is added, most of the molybdenum sites stay in the inactive Mo^{6+} state, depressing the performance of the catalyst. Similar results were also observed by other researchers with K-doped Mo_2C catalysts [68,73]. Similar

Table 2

Influence of K amount on surface molybdenum oxidation state and alcohol selectivity of $\text{K/Fe}/\text{Mo}_2\text{C}$ catalyst.

$\text{K}_x\text{Fe}_{0.17}\text{MoC}$	Molar content of $\text{Mo}^{\delta+}$ species (%)				Alcohol selectivity (wt%)	$\text{C}_2\text{-OH}/\text{MeOH}$
	Mo^{2+}	Mo^{4+}	Mo^{5+}	Mo^{6+}		
$x = 0$	12.42	10.99	31.44	45.15	6.11	1.03
$x = 0.1$	5.56	4.38	62.12	27.94	15.66	2.61
$x = 0.2$	2.16	1.35	64.71	31.78	20.99	6.69
$x = 0.5$	—	—	67.54	32.46	39.78	3.01
$x = 0.8$	—	—	60.23	39.77	28.40	1.20
$x = 1.0$	—	—	44.42	55.58	24.84	0.93

Reaction condition: $T = 340\text{ }^\circ\text{C}$, $p = 7.0\text{ MPa}$, GHSV = 4000 h^{-1} , $\text{H}_2/\text{CO} = 2$. XPS was recorded ex situ, so the high valent Mo species might be overestimated due to passivation and aerobic oxidation. However, the regularity of the results was reliable.

to the additives, the support also affects the selectivity through changing the concentration of the molybdenum species. For instance, MWCNT can increase the alcohol selectivity of Mo-based catalysts. Zhang and co-workers found that MWCNTs did not affect the apparent activation energy of the reaction, but changed the chemical state of molybdenum and increased the concentration of the high valence molybdenum species (Mo^{4+} , Mo^{5+}). The authors attributed improved alcohol selectivity to the increased concentration of high valence molybdenum species [27–29,31].

4.3. Molybdenum sulfide-based catalysts

Molybdenum sulfide-based catalysts are good hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) catalysts, and are widely used in the oil industry. After Dow Chemicals and Union Carbide patented alkaline-doped molybdenum sulfide (ADM) catalysts for HAS via CO hydrogenation in the 1970s, many works have been devoted to this type of catalysts by C₁ chemists because of their excellent sulfur tolerance [74–78]. The sulfur tolerance of ADM catalysts avoids the costly process of deep desulfurization of the feed gas. ADM catalysts with high WGS activity are also suitable for hydrogen-deficient syngas. Meanwhile, a high WGS activity consumes much water and thus lowers the water concentration in the final product, which would decrease the cost of product purification. These advantages of ADM catalysts make them suitable for sulfur-containing, hydrogen-lean syngas derived from coal. Our group has performed systematic studies on ADM based catalysts [79–83]. The alkali- and transition metal-doped molybdenum catalysts (M-K/MoS_x, M = Fe, Co, Ni) developed by our group showed total alcohol yield and higher alcohol (C₂+OH) yield as much as 0.40 and 0.16 g/(ml_{cat}·h), respectively. After 2000 h on-stream time under the conditions of 340 °C, 9.5 MPa, H₂/CO = 1.0, and 8500 h⁻¹, no decrease in catalytic activity or selectivity was observed.

ADM-based catalysts give mainly C₁–C₅ linear primary alcohols, and the alcohols obey the ASF distribution, indicating the sequential addition of the monomers. However, chain propagation on ADM catalysts proceeds via CO insertion rather than methylene insertion. The higher alcohol formation mechanism is depicted in Scheme 9. Generally, at least two forms of transition metal promoters exist simultaneously in ADM-based catalysts, namely, the transition metal sulfide (MS_x, M = Fe, Co, Ni) and the Mo containing mixed sulfide (M-KMoS_x). The MS_x phase is active for the dissociation of CO and H₂ for the chain initiation, while M-KMoS_x is the site for CO insertion, chain

Scheme 9. Mechanism of higher alcohol formation and reaction network on M-KMoS_x type catalysts.

Fig. 1. Influence of Co/Mo atomic ratio on the catalytic performance of K-Co-MoS₂ catalyst. (Data from [84]).

propagation and alcohol formation. The MS_x-MKMoS_x pair forms the dual site on ADM-based catalysts. The synergism of the two sites increases alcohol selectivity, and also increases chain growth ability. Furthermore, activated H* species on MS_x that spillover onto M-KMoS_x can increase the activity of the catalysts.

The formation of the M-KMoS_x alcohol formation site on the addition of promoter M increases the alcohol selectivity of ADM-based catalysts. In addition, because of the CO insertion and chain growth activities of M-KMoS_x, the selectivity to higher alcohols also increases on the addition of M. However, excess M would lead to too many MS_x sites on the surface, and the selectivity to hydrocarbons would increase due to the hydrogenation activity of MS_x sites, leading to decreased alcohol selectivity. So promoter M has an optimal amount. These results have long been recognized. For example, Li et al. [84] have seen this phenomenon on the Co-K-MoS₂ catalyst, which is presented in Fig. 1. With increasing Co/Mo atomic ratio, CO conversion increased first and then reached a plateau, and the total alcohol selectivity went through a maximum while the higher alcohol selectivity (indicated as C₂+OH/MeOH) increased steadily. For both high total alcohol selectivity and higher alcohol selectivity, Co has an optimal amount. In Li's study, this optimal amount was 0.5 for the Co/Mo ratio.

Similar results were also found with Ni-KMoS₂ catalyst [79]. La is commonly used to increase the dispersion of active metals. It can suppress the formation of MS_x and promote the formation of M-KMoS_x [85], thus La can increase the active site for alcohol formation and chain propagation, leading to improved total alcohol selectivity and higher alcohol selectivity at the same time. According to this idea, La was added as the promoter to the Ni-KMoS₂ (Ni-ADM) catalyst for HAS. The results were compared with those on the catalyst without La promotion. XRD characterization indicated that there were less NiS_x and more K-Mo-S phases in La-Ni-ADM compared with Ni-ADM (Fig. 2). The catalytic performances showed that both total alcohol and higher alcohol selectivity were increased by the addition of La (Table 3). This work showed that other than adjusting the ratio of the active metals, the addition of promoters is also a way to balance the two active sites to improve the

Fig. 2. XRD patterns of La-Ni-KMoS₂ and related catalysts (Data from [86]). (1) ADM; (2) La-Ni-ADM; (3) Ni-ADM.

performance of the catalyst.

5. Structural evolution of the dual site during reaction

A catalyst for an industrial application should be stable enough during the reaction. However, all catalysts deactivate with time on stream. Many factors account for the deactivation of the catalysts, such as poisoning, carbon deposition, sintering, leaching, phase change and phase separation. The deactivation of HAS catalysts lead to decreased activity and/or alcohol selectivity, esp. C₂+OH selectivity. As the catalytic properties are determined by the structure of the catalyst, there must be some structural change in the catalyst during the deactivation.

In order to investigate the structural evolution of Cu-Fe based HAS catalysts, we synthesized structurally 'simple' CuFe bimetallic nanoparticles as model catalysts and studied the deactivation process [59]. During 288 h time on stream, CO conversion decreased at the early stage and changed little from then on, while the selectivity to alcohols decreased monotonically (Fig. 3). Scanning transmission electron microscopy mapping mode energy dispersive X-ray spectroscopy (Mapping-EDS) characterization showed that the Cu and Fe components were homogeneously dispersed on the catalyst in the fresh and reduced samples, but the Cu and Fe components were significantly separated on the used sample (Fig. 4). It was believed that the phase separation of the Cu and Fe components caused the deactivation of the catalyst. In the early stage of the reaction, the Cu and Fe components were homogeneously dispersed and contact each other on the nanometer scale, leading to good synergism between Cu and Fe and high total alcohol selectivity. During the reaction, the Cu and Fe compo-

Fig. 3. CO conversion and alcohol selectivity changes with time on stream over a Cu-Fe catalyst.

Fig. 4. STEM images of fresh (a), reduced (b) and spent (c) Cu-Fe catalyst. (a1)–(c1) are the corresponding Mapping EDS images. Red for Fe distribution, and green for Cu. The area located in dashed white line square was the scanning area.

nents get separated gradually. As the Cu-Fe dual site gets destroyed, the synergism is weakened and there is decreased total alcohol selectivity with time on stream. Our results indicated that it is necessary to increase the concentration of the dual site and stabilize the dual site during the reaction to maintain high alcohol selectivity. The key to stabilizing the dual site is the prevention of the phase separation of the Cu and Fe components under reaction conditions.

6. Conclusions

A consensus has been reached on the bifunctional catalysis in HAS, but research on the actual structure of the dual site is still lacking due to the complexity of the HAS catalyst system itself and the scarcity of surface characterization methods, esp.

Table 3

Catalytic performance of La-Ni-KMoS₂ and related catalysts.

Catalyst	CO conversion (%)	STY (g/(ml·h))	Selectivity ^a (%)		Alcohol distribution (%)				
			ROH	HCs	C ₁	C ₂	C ₃	C ₄	C ₅₊ ^b
KMoS ₂	22.49	0.12	51.27	48.73	45.07	30.78	15.64	8.14	0.37
Ni-KMoS ₂	39.65	0.14	46.43	53.57	13.10	32.52	31.42	21.29	1.67
La-Ni-KMoS ₂	33.52	0.17	66.05	33.95	11.42	28.03	34.39	23.98	2.17

Reaction condition: $T = 320\text{ }^{\circ}\text{C}$, $p = 8.0\text{ MPa}$, GHSV = 2500 h^{-1} , $\text{H}_2/\text{CO} = 1.0$.

^a CO₂-free. ^b Include C₅+OH, aldehydes, esters and ethers.

those that can be used under the high temperature-high pressure reaction conditions. To avoiding the support effect, unsupported nanoparticles that are simpler are excellent model catalysts for structural studies of the dual site. However, whether the dual site structure in the model catalysts is the same as that in the real catalysts needs confirmation. In situ characterization and characterization and evaluation combined methods are needed to study the catalyst structure under working conditions. Unfortunately, in situ characterization methods esp. for high pressure and high temperature conditions are still very few. The development of more advanced characterization methods is of great importance for studying the active centers of the HAS catalysts. However, more important is the design of more elegant experiments to study the structure of the catalysts, esp. of the catalyst surface under reaction conditions using existing characterization methods.

In addition to the investigation of the structure of the dual site, developing methods to construct and stabilize the dual site is also very important in HAS studies. More efforts are needed to develop controlled preparation methods to obtain dual sites with a specific structure. It is also necessary to investigate the effect of each step in the preparation process on the catalytic performance. In addition, stabilizing the dual site during the reaction process is the key to improving catalyst stability. Therefore it is necessary to elucidate the structure evolution of the dual site during reaction and the underlying mechanism.

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Graphical Abstract

Chin. J. Catal., 2013, 34: 116–129 doi: 10.1016/S1872-2067(11)60496-8

Advances in bifunctional catalysis for higher alcohol synthesis from syngas

XIAO Kang, BAO Zhenghong, QI Xingzhen, WANG Xinxing, ZHONG Liangshu*, FANG Kegong, LIN Minggui, SUN Yuhuan*
 Shanghai Advanced Research Institute, Chinese Academy of Sciences; University of the Chinese Academy of Sciences;
 Institute of Coal Chemistry, Chinese Academy of Sciences

Higher alcohol synthesis is a bifunctional catalytic process occurring on a dual site. There is a need to design the dual site on the atomic scale to give high stability in order to improve catalytic performance.

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合成气制混合醇双功能催化研究进展

肖 康^{a,b}, 鲍正洪^a, 齐行振^a, 王新星^a, 钟良枢^{a,*}, 房克功^c, 林明桂^c, 孙予罕^{a,c,#}

^a中国科学院上海高等研究院低碳能源转化技术与工程中心, 上海201210

^b中国科学院大学, 北京100049

^c中国科学院山西煤炭化学研究所煤转化国家重点实验室, 山西太原030001

摘要: 混合醇合成要求催化剂具备至少两类活性中心, 一类用于解离吸附CO以生成烷基链, 另一类用于非解离吸附CO以使烷基链含氧化生成醇。两类中心通过协同作用共同构成混合醇合成所需的双活性中心。简要综述了近年来合成气制混合醇过程中涉及的双功能催化研究进展, 并以几类典型的催化剂体系为例, 从双活性中心的构筑、典型的双活性中心结构、反应过程中双活性中心结构的演变等方面进行了阐述。混合醇催化剂的研发应从纳米尺度上对催化剂进行设计, 使催化剂表面具有足够多的双活性

中心,并设法稳定催化剂的双活性中心结构.

关键词: 混合醇; 一氧化碳加氢; 合成气; 双功能催化; 双活性中心

收稿日期: 2012-09-30. 接受日期: 2012-11-07. 出版日期: 2013-01-20.

*通讯联系人. 电子信箱: zhongls@sari.ac.cn

#通讯联系人. 电话: (021)20325009; 传真: (021)20325039; 电子信箱: sunyh@sari.ac.cn

基金来源: 国家重点基础研究发展计划(973计划, 2011CBA00501); 上海市科委(11DZ1200300); 煤转化国家重点实验室(11-12-610).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).

1. 前言

由于石油资源的有限性以及20世纪70年代爆发的石油危机,世界各大国均广泛投入了石油替代的研究,其中一个热点便是合成气转化^[1]. 合成气是 H_2 和CO的混合物,有时也含有少量的 CO_2 ,可以从煤、天然气、页岩气、生物质甚至有机垃圾等含碳物质制取,来源广;并且合成气经催化转化可得到种类丰富的产品,如甲醇、汽油、柴油、优质蜡、醇、烯及其它化学品(见图式1),因此合成气转化受到工业界和学术界的重视. 在合成气转化的诸多过程中,从合成气直接制备混合醇(higher alcohol synthesis, HAS)一直备受关注. 混合醇既可替代汽油或作为提高汽油辛烷值的添加剂,又可制备高附加值的精细化学品^[2-4]. 目前已报道的用于混合醇合成的催化剂总体上可归为改性甲醇催化剂、改性费托(FT)催化剂、钼基催化剂和贵金属催化剂四大类. 改性甲醇合成催化剂包括高压和低压两类,分别由意大利Snam公司和德国Lugi公司开发,用来主要合成甲醇和异丁醇^[5]. 改性FT催化剂最早由法国石油研究所(IFP)提出,主要针对Cu-Co系催化剂,合成产物主要为 $C_1\sim C_6$ 直链伯醇,且符合Anderson-Schulz-Flory (ASF)分布^[2]. 钼基催化剂包括氧化钼、硫化钼和碳化钼基几类,最早由美国Dow公司提出,针对碱/碱金属改性的硫化钼基催化剂,主要合成产物为 $C_1\sim C_5$ 直链正构醇^[6]. 贵金属催化剂以铑催化剂为代表,主要合成产物为乙醇等 C_2 -含氧化合物^[7]. 但是,以上催化剂均存在总醇选择性不够高、高碳醇选择性低及稳定性差等问题. 如何进一步发展新催化剂,使其具有更高的总醇选择性,尤其高级醇选择性和稳定性是混合醇合成的研究重点.

有关混合醇合成的综述很多^[8-11]. 这些综述从不同角度总结了混合醇合成领域中涉及催化剂制备、催化机理、反应动力学等方面的研究进展. 本文着重在本课题组的研究工作基础上,探讨双功能催化在混合醇合成中的体现. 在简单介绍国内外研究概况后,将以几个典型的催化剂体系为例,讨论混合醇合成中双活性中心的构

筑、典型的双活性中心结构、反应过程中双活中心结构的演变等方面的最新研究进展.

2. 国内外研究概况

近年来国内外学者在混合醇合成方面做了大量研究,在提高催化剂性能和机理研究方面的工作多有报道. 国外研究团队如美国路易斯安那州立大学Spivey小组在混合醇合成方面做了较多研究,近年该小组制备了Cu-Co合金纳米颗粒及Co@Cu核壳结构纳米颗粒作为模型催化剂用于混合醇的合成^[12]. 研究表明,Cu-Co合金纳米颗粒比Co@Cu核壳结构纳米颗粒具有更高的醇选择性. 采用非负载型纳米颗粒作为模型催化剂的好处在于可以避免载体的影响,有利于研究活性中心结构及活性组分间的相互作用. 同时,该小组还借助原位红外(in situ IR)研究了CO在Cu-Co或Co表面的吸附状态(桥式吸附、线型吸附)和吸附位点(还原态Co、氧化态Co)与催化性能之间的关系^[13-15]. 而美国克莱蒙森大学的Goodwin小组则采用稳态同位素瞬变动力学分析(SSIKA)研究了Cu-Co/ZnO催化剂各组分间的相互作用以及反应机理^[16,17]. 他们认为,Cu覆盖Co表面,选择性抑制烃的生成,而醇的生成不受影响是Cu-Co/ZnO具有较高醇选择性的原因. 但同时他们也提出,只有Cu, Co和ZnO三种组分共存时方具有较好的催化性能. 此外,美国弗吉尼亚大学Davis小组在铑基催化剂和碳化钼基催化剂方面做了相关研究^[18-21];加拿大英属哥伦比亚大学的Smith小组近些年则对MoP基催化剂做了相关工作^[22-24]. 国内也一直在开展合成气制混合醇的相关研究,并取得了较好的研究成果. 厦门大学张鸿斌小组研究发现,多壁碳纳米管和过渡金属(Co, Ni)改性的碳纳米管能显著提高醇的选择性. 碳纳米管负载的改性FT型催化剂^[25,26]和钼基催化剂^[27-31]均表现出比非碳管负载的催化剂优异的性能. 研究者认为,碳管的加入并不改变反应的表现活化能,即反应路径不发生改变,但碳管与活性组分相互作用改变了活性金属的化学状态,使得有利于醇生成的活性中心或活性位点增加,同时氢的

活化能力增加, 导致催化剂上醇选择性显著提高^[32]. 对于碳纳米管负载催化剂的研究中值得一提的是, 大连化学物理研究所包信和小组将铑负载在碳管内部, 由于碳管的限域效应, 负载在碳管内部的铑催化剂上乙醇选择性明显高于负载在碳管外部的^[33]. 这种限域效应可能很大程度上源于碳管内外壁电子状态的不同, 计算表明碳管内部处于缺电子状态^[34]. 四川大学储伟小组从制备方法上着手, 发现等离子辅助制备的催化剂具有比常规方法制备催化剂更高的活性和醇选择性^[35–38]. 他们认为, 等离子辅助提高活性和选择性的原因在于催化剂的比表面积增加, 活性组分的晶粒减小、分散性提高, 即表面活性中心数量增加. 大连化学物理研究所丁云杰小组在混合醇合成研究中发现, 活性碳负载的钴催化剂能用于从合成气直接制备C₁~C₁₈直链伯醇, 高碳醇(C₆以上醇)选择性很高^[39–41]. 他们认为, 碳化钴是高碳醇合成的活性物种. 由于高碳醇可用于制备多种高附加值的精细化学品, 在医药、化妆品和洗涤剂等领域有广泛应用, 所以由合成气直接制备高碳醇具有较大应用价值, 但需要解决产物提纯的实际问题. 除上述研究团队外, 上海应用技术学院毛东森小组^[42–44]、广州能源研究所王铁军小组^[45,46]、清华大学贺德华小组^[47]等在混合醇合成方面均有所研究. 本课题组对改性FT催化剂和钼基催化剂(包括硫化钼基和碳化钼基)均有系统持续的研究, 部分成果将在本文中详细讨论.

3. 双活性中心的结构构筑

混合醇合成过程复杂, 多类反应同时参与, 一些典型的反应如下.

其中(2)和(3)是典型的FT反应, 而(4)是典型的甲醇合成反应. 可见混合醇合成与FT合成及甲醇合成类似, 具有某些相同的表面反应. 但三者的反应过程或催化本质有所不同. FT合成可认为是一个表面聚合过程, 表面烷基链通过不断插入亚甲基物种而增长, 最终脱附生成烯或加氢生成烷, 如图式2所示^[48,49]. 甲醇合成中, 一般认为CO先经水煤气转变(WGS)得到CO₂, CO₂是被直接加氢的反应物, 经过表面甲酸盐物种和甲氧基物种最终

生成甲醇, 如图式3所示^[50]. 费托合成涉及链增长(C–O键断裂), 但无需涉及含氧化过程(CO插入, C–O键保持, 在碳链中引入氧原子的过程); 甲醇合成无需链增长, 反应过程中C–O键保持. 而混合醇合成则同时需要链增长和含氧化过程, 由于二者在不同中心上进行, 故混合醇合成势必需要双活性中心(见图式4), 分别用于碳链增长和含氧化, 二者协同作用生成混合醇.

可见, 要提高醇选择性, 就需要增加混合醇合成催化剂上双活性中心的含量, 任何使得双活性中心解离的变化都将导致醇选择性下降. 另外, 还要求用于链增长和含氧化的两类活性中心到达一定的平衡, 任何一类中心含量过高或过低都将造成催化剂性能下降. 混合醇催化剂设计的理念应是在纳米尺度甚至原子尺度构筑双活性位点, 通过协同作用促进碳链增长及含氧化之间的双功能催化.

4. 典型的双活性中心结构

双活性中心普遍存在于混合醇合成催化剂中, 但对于不同催化剂, 双活性中心具体的结构有所不同. 下面就几类典型的混合醇催化剂体系讨论双活性中心结构.

4.1. 改性FT催化剂

法国石油研究所研发的改性FT催化剂主要针对Cu–Co系列, 由于其较高的总醇选择性和高碳醇选择性而广受关注. 比较而言, Cu–Fe基催化剂具有高活性、高C₂₊OH选择性的特点, 且对WGS催化活性高, 对原料气中CO₂和H₂/CO比的变化不敏感, 很适合以煤或生物质为原料的合成气, 故近年来Cu–Fe基改性FT催化剂的研究也逐渐增加^[36,51–57]. 本课题组开发的CuFeMnZr系列催化剂具有高于50%的总醇选择性和高于50%的C₂₊OH选择性, 稳定性评价已超过3000 h^[3], 并成功完成了单管运行.

对于改性费托催化剂, Xu等^[2]提出的CO插入机理是广为认可的醇生成机理, 如图式5所示. 该机理可以认为是FT反应和甲醇合成的叠加, 或认为是间于FT合成和甲醇合成的反应. 按照该机理, 链引发(*k_d*, *k₁*)和链增长(*k_p*)按照FT反应路径进行, 生成表面烷基物种(C_{*n*}H_{*z*}*), 该物种经不同的链终止步骤得到不同类型的产物. 若链终止经过CO插入(*k_{CO}*)生成表面酰基物种(C_{*n*}H_{*z*}CO*), 然后部分加氢(*k_H*)则生成醇类产物; 若链终止为直接脱附或加氢脱附(*k_H*)则生成烃类产物. 显然, 生成醇和生成烃为竞争反应. CO插入机理很好解释了改性FT催化剂主要生成直链醇且其分布基本符合ASF分布的现象, 同

时也能解释Cu-Co催化剂上醇链增长因子与烃的相同。

CO插入机理给出了表面物种的反应历程,但未给出活性中心结构的信息。目前对于活性中心的结构还不很明确,虽然提出过一些观点,但尚存争议。Xu等^[2]认为,Cu-M(M=Fe, Co等)是混合醇生成的活性中心(双活性中心)。其中,FT组元(Fe, Co等)具有CO解离吸附及链增长的功能,吸附于其上的CO解离加氢形成亚甲基(CH₂)等表面物种,亚甲基聚合形成表面金属烷基物种;而Cu是甲醇合成的活性组分,具有非解离吸附CO及CO插入的功能(见图式6)。该观点得到不少学者的认同^[3,58]。在Cu-M双活性中心上,Cu表面分子态吸附的CO迁移至FT组元表面,插入金属烷基(M-C)键,形成表面酰基物种,后者部分加氢脱附生成醇。或者如Xu等认为,FT组元上的烷基物种迁移至Cu表面,然后CO插入形成酰基物种,最后加氢成醇。无论哪种过程,醇生成都需要Cu与FT组元的协同作用,而这种协同作用的破坏将造成醇选择性下降。

为提高醇的选择性,需要一种中心上的表面物种能迁移至另一种中心上,并尽量避免在迁移过程中发生其它副反应(如加氢)或脱附,这就要求Cu与FT组元的原子尺度接近,且尽可能均匀分布增加界面数量。Cu与FT组元的分离将破坏双活性中心,导致醇选择性下降。以上理论为本课题组研究结果所证实^[59]。为证明混合醇合成中的协同作用,我们合成了一系列Cu-Fe双金属纳米颗粒催化剂用于HAS研究,并与单金属Fe纳米颗粒和单金属Cu和Fe纳米颗粒物理混合物(PM)做了对比,结果列于表1。由于Cu纳米颗粒在反应条件下没有活性,故未列入。由表1可见,所有双金属纳米颗粒上醇选择性均高于单金属Fe和PM。该结果表明,Cu与Fe组分的协同作用有利于醇的生成,而协同作用在CuFe双金属纳米颗粒中方存在,即双活性中心需要Cu及Fe组分在原子尺度接近。当Cu与Fe组分并未原子尺度接近(如物理混合物)时,一种中心上的表面物种不能迁移至另一种中心上,故醇选择性很低。

除Cu-M活性中心外,Blanchard等^[60]和Baker等^[61]还提出,在Cu-Co催化剂上还原态的Co物种和氧化态的Co物种构成双活性中心(Co⁰-Co^{δ+})。Co⁰-Co^{δ+}双活性中心上,还原态Co⁰是CO解离吸附和链增长中心,而氧化态Co^{δ+}则是CO非解离吸附和插入中心,如图式7所示。在该双中心上的表面反应过程与Cu-M类似。最近,Spivey小组通过对Cu/SiO₂, Co/SiO₂和Cu-Co/SiO₂红外表征支持这一观点^[13]。Co⁰-Co^{δ+}双活性中心能很好解释单独Co催化

剂在一定条件下也能用于混合醇合成的事实^[62];并且Co的高分散有利于醇的生成^[60,63]。考虑到Co与载体的相互作用导致钴离子难以还原,高分散Co势必使得氧化态Co^{δ+}物种含量增加,这间接支持了Co⁰-Co^{δ+}双活性中心。值得一提的是,法国石油研究所的Chaumette等^[64]发现,CoZnAl催化剂在适当预处理和反应条件下保持Co为部分氧化态时,CoZnAl具有类似CuZnAl甲醇催化剂性能。

4.2. 碳化钼基催化剂

自1973年Levy等报道VIB族金属碳化物具有类贵金属的催化特性以来,金属碳化物作为一类新型催化材料已引起人们的极大关注^[65]。碳化钼(Mo₂C)被誉为“准铂催化剂”,并具有廉价、耐硫及抗积碳等优点。有关碳化钼催化性能的早期研究通常是与贵金属催化反应体系相联系,以寻求一种能替代Pt, Pd等的非贵金属催化剂。Mo₂C催化剂具有较好的CO加氢反应性能,但主要产物为轻质烷烃,尤其是甲烷。近年来,研究者做了大量工作以提高钼基催化剂的活性和选择性。本课题组对Mo₂C的碱金属改性和VIII族过渡金属改性做了详细研究,在提高醇选择性,特别是C₂₊OH选择性方面取得进展^[66–72]。

碳化钼上醇的生成同样在双活性中心上,需要两类不同活性中心的协同作用,如图式8所示^[3]。两类不同的活性中心分别为低价态的碳化钼物种(Mo-I, Mo^{0–2+})和高价态的钼物种(Mo-II, Mo^{(4–5)+})。低价态钼中心上CO解离吸附并加氢形成表面烷基物种,是链增长中心;而高价态钼中心上CO非解离吸附,是成醇活性中心。要得到高的总醇选择性,就需要成醇中心Mo-II物种含量较多;然而成醇中心比例过高时,双活性中心上链增长能力会降低,使得高碳醇含量减少。在兼顾总醇选择性和高碳醇选择性的情况下,就需要两种物种含量达到一定平衡。一般助剂对Mo₂C催化性能的影响,除助剂本身的催化作用外(如FT组元本身的CO加氢活性),都是直接或间接通过改变碳化钼中钼物种的含量来改变产物选择性的。我们通过溶胶-凝胶法制备了一系列K, Fe双改性的β-Mo₂C (K/Fe/β-Mo₂C)催化剂用于混合醇合成。XPS结果表明,添加的K越多,催化剂表面高价态的钼物种含量越高(见表2),从而影响总醇选择性和高碳醇C₂₊OH选择性。如表2所列,随Mo-II物种含量增加总醇选择性增加,而高碳醇(以C₂₊OH/MeOH表示)选择性有一极大值。当高价态钼含量低时,成醇中心少,由于低价态碳化钼很强的加氢活性,主要产物为甲烷,高碳产物很少。随高价态钼含量增加,成醇中心增加,因而醇选择性增加,并且由于加氢能力降低,链增长能力增加,因而高碳醇含

量也随之增加。然而,当Mo-II物种过高时,用于链增长的Mo-I物种太少,使得高碳醇含量降低。当K含量较大,氧化钼难以还原时,钼很多以无活性的Mo⁶⁺物种存在,导致催化剂性能下降。在K改性的Mo₂C催化剂上也同样观察到类似规律^[68,73]。同样,载体也是通过改变钼物种含量影响催化剂性能的。如张鸿斌小组在研究碳管负载的钼基催化剂时认为,碳管的作用是改变钼的化学形态,使得高价态Mo物种(Mo⁴⁺, Mo⁵⁺)含量增加,从而导致醇选择性增加^[27–29,31]。

XPS为离线测试,由于钝化和空气氧化,与反应过程中的催化剂相比,高价态Mo可能被高估,但数据所显示的规律性不变。

4.3. 硫化钼基催化剂

硫化钼基催化剂是良好的加氢脱硫(HDS)、加氢脱氮(HDN)催化剂,用于石油化工的脱硫工艺中。自20世纪80年代Dow公司和Union Carbide公司报道碱改性的硫化钼催化剂(ADM)具有催化CO加氢合成混合醇的功能以来,此类催化剂以其优异的耐硫性而受到C1研究者的关注^[74–78]。ADM基催化剂的耐硫性可避免耗资巨大的原料气深度脱硫,并且高的WGS活性使得其能适应低氢碳比的原料气,同时产物相对“干燥”,利于后续脱水。这些优点使得ADM基催化剂特别适合于含硫、贫氢的煤基合成气转化。本课题组对ADM基催化剂做了系统研究^[79–83],所开发的M-K/MoS (M = Fe, Co, Ni)系列催化剂总醇收率和C₂₊OH收率分别达0.40g/(ml_{cat}·h)和0.16g/(ml_{cat}·h),并且在340 °C, 9.5 MPa, H₂/CO = 1.0, 空速8500 h⁻¹条件下连续运转2000 h以上没有明显活性和选择性降低。

ADM基催化剂所得产物为C₁~C₅直链正构醇,符合ASF分布规律,表明其碳链为逐步增加过程。与碳化钼基催化剂相同,ADM基催化剂上醇的生成在双活性中心上;所不同的是,链增长为CO插入而非CH₂插入。醇的生成机理如图式9所示。催化剂表面至少存在两类活性中心:MS_x (M = Fe, Co, Ni)中心及M-KMoS_x中心。前者具有解离吸附CO和H₂的功能,可引发链增长,提高反应活性;而后者能非解离吸附CO,是CO插入进行链增长和成醇的活性中心。MS_x上吸附活化的H*可溢流至M-KMoS_x中心上,为加氢提供氢源。两种中心的协同作用(双活性中心),不仅能够提高醇的选择性,也能够一定程度上提高链增长能力。

改性助剂M使ADM催化剂上形成M-KMoS_x成醇中心,助剂M的增加能提高醇的选择性;同时,由于

M-KMoS_x中心的CO插入能力也在一定程度上提高了高碳醇选择性。但是,过多的M将在表面形成过多的加氢成烃的MS_x中心,从而导致醇选择性的下降。该规律早为研究者们所发现,如Li等^[84]在K-Co-MoS₂催化剂上发现,随Co/Mo原子比增加,CO转化率先增加而后趋于平缓,总醇选择性先增加后降低,高碳醇选择性则持续增加(见图1)。综合考虑,Co/Mo有一最佳值在0.5附近。

同样,我们在Ni-KMoS₂催化剂上观察到类似的现象^[79]。由于La具有增加金属分散度的作用,在M-KMoS₂基催化剂上,其能抑制MS_x的形成,并促进M-KMoS_x中心的生成^[85]。即能增加成醇和链增长中心的含量,从而提高总醇和高碳醇的选择性。根据该思路,我们将La添加到Ni-KMoS₂催化剂中。XRD显示,La的加入使得催化剂中NiS_x含量明显减少,而K-Mo-S组分相对较多(见图2)。与未添加La的催化剂相比,总醇(ROH)选择性和高碳醇选择性均有所提高(见表3)。结果表明,要到达两种活性中心的平衡,除调节物料配比外,还可通过添加其它助剂的方法实现。这为催化剂的设计和新型催化剂的开发提供了思路。

5. 反应过程中双活性中心结构的演变

理论上催化剂在反应前后不发生改变,但实际应用中催化剂都存在不同程度的失活。一种具有工业应用的催化剂应具备足够高的稳定性。混合醇催化剂失活原因有多种,如中毒、积碳、活性组分团聚长大、活性组分流失、相转变、相分离等。混合醇催化剂失活主要体现为催化活性及醇选择性下降。催化剂的性能与其结构直接相关,混合醇催化剂的失活过程必然伴随着一定程度的结构变化。

为了更好地研究混合醇催化剂的结构演变,我们选取简单的Cu-Fe双金属纳米颗粒作为模型催化剂,对其失活过程做了考察^[59]。在288 h的反应时间内,CO转化率在初始下降后变化不明显,但醇选择性则持续下降(见图3)。对反应前后样品的表征发现,新鲜催化剂和还原后的催化剂中Cu元素与Fe元素分布较为均匀,但反应后催化剂中Cu与Fe发生严重相分离(见图4)。反应初期,Cu, Fe元素分布均匀,两者紧密接触,Cu-Fe双活性中心保持,有较高的醇选择性;但随反应进行,Cu与Fe物种逐渐分离,Cu-Fe双活性中心结构被破坏,协同作用受限,故醇选择性随在线时间的延长而降低。由此可见,要获得高的醇选择性,必须使催化剂中双活性中心所占比例增加;而要提高催化剂的稳定性,则必须防止反应过程

中相分离的发生.

6. 展望

混合醇合成中的双功能催化在业界已基本达成共识, 但对应的双活性中心结构的研究尚不够深入. 这源于混合醇催化体系本身的复杂和目前精密的表面表征手段还很匮乏, 尤其是在高温高压的反应条件下更为困难. 采用非负载纳米颗粒作为模型催化剂能减小体系的复杂性, 很适合研究活性金属在反应中的行为和活性中心结构, 但是模型催化剂和真实催化剂上活性中心的结构是否完全一致还需要进一步验证. 而要了解工作条件下催化剂的结构, 采用原位表征和表征-评价联用手段在所难免. 但目前能用于反应条件下的原位表征手段还十分稀少. 进一步发展更先进的表征手段对了解混合醇合成催化剂活性中心的结构十分重要. 然而, 更为重要

的是在现有表征手段的前提下如何设计更为巧妙的实验方法对反应条件下的催化剂, 尤其是对催化剂表面进行探测.

在研究双活性中心结构的同时, 如何构筑和稳定双活性中心也是混合醇合成研究的一个重点. 了解双活性中心能告诉我们需要构筑什么样的结构, 但并不能告诉我们如何构筑这样的结构. 这就需要在制备方法上进一步研究, 详细考察催化剂在制备过程的各个基元步骤中发生的结构变化以及这些变化对催化性能的影响. 另外, 保持双活性中心在催化反应过程中不发生变化则是提高催化剂稳定性的关键. 这需要弄清双活性中心在反应过程中发生了何种变化以及这些变化的机理. 总之, 混合醇合成催化剂的研发应从纳米尺度上甚至原子尺度上对催化剂进行设计, 使催化剂表面具有足够多的双活性中心, 并设法稳定催化剂的双活性中心结构.