Synthesis of Higher Alcohols from Syngas over Fe/K/ β -Mo₂C Catalyst

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Abstract Fe/K/ β -Mo₂C catalysts were prepared by the temperature-programmed-reaction (TPRe) method and tested for higher alcohols synthesis (HAS). The catalysts exhibited high catalytic activity and selectivity to higher alcohols (C₂⁺OH). The effect of Fe/Mo molar ratio on the catalytic performance of HAS was investigated and the best one was at Fe/Mo molar ratio of 1/14. It could be concluded that the Fe promoter exerted strong promotion for carbon chain growth, especially for the stage of C₁OH to C₂OH. The "Fe₃Mo₃C" and "Fe₃C" phases formed over Fe promoted K/ β -Mo₂C catalysts, which might be responsible for the high activity of higher alcohols and hydrocarbons synthesis, respectively.

Keywords Fe/K/ β -Mo₂C catalyst \cdot Higher alcohols synthesis \cdot Syngas

1 Introduction

The higher alcohols synthesis (HAS) via syngas is considered as a potential alternative for clean fuels as well

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as chemicals [1, 2]. However, the application of such an attractive synthesis still suffers from the lack of high performance catalysts. It's the reason that development of catalysts with high efficiency and selectivity for higher alcohols has been one of the key objectives of research.

According to the literature, molybdenum carbide exhibits some properties similar to those of noble metals [3] and the application of molybdenum carbide in the field of catalysis has attracted more and more attention. Molybdenum carbide catalysts have been recognized as being effective for the methanation and/or Fischer-Tropsch synthesis of light hydrocarbons [4, 5]. While Lecercq et al. [6] reported that the formation of alcohols is related to the surface stoichiometry and to the extent of carburization over the molybdenum carbide catalyst. Promotion of molybdenum carbide with K₂CO₃ has been found to greatly enhance the selectivity to alcohols composed of linear C1-C7 [7]. Thus, molybdenum carbide could be a potential catalytic material for alcohol synthesis. Generally, the Fischer-Tropsch elements (Fe, Co and Ni) were used as promoters because of their strong ability to promote carbon chain growth in HAS [8-10].

In our previous work, the K/Fe/ β -Mo₂C catalyst was studied for mixed alcohols synthesis and exhibited potential catalyst for HAS [11]. But the reaction conditions and compositions are not optimized for the catalyst. So the catalyst is expected to perform better under appropriate conditions. Thus, Fe doped K/ β -Mo₂C catalysts with different Fe content were developed for HAS in the present work. They display a better performance for HAS and the characteristics of Fe/K/ β -Mo₂C for higher alcohols synthesis from syngas are also investigated.

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2 Experimental

2.1 Catalyst Preparation

The catalysts prepared through Temperature-Programmed-Reaction (TPRe) method [12]. In detail, the β -Mo₂C was prepared by direct carburization of the MoO₃. The Fe/K/ β -Mo₂C catalyst was prepared as follows: firstly, Fe(NO₃)₃. 9H₂O and (NH₄)₆Mo₇O₂₄·4H₂O aqueous solutions were prepared separately and then mixed with required Fe/Mo molar ratio under constant stirring for 2 h, followed by aging, filtrating, drying, and then calcined at 773 K for 4 h. Following grinding to a fine powder, the oxide precursor was converted to FeMo carbide via TPRe. K₂CO₃ modification was accomplished by physically mixing K₂CO₃ with the final carbide, and then the mixture was calcined at 773 K for 2 h under Ar. In all cases, the K/Mo molar ration was of 0.2 [13].

2.2 Characterization Methods

BET surface areas of catalysts were determined by N₂ adsorption at 77 K using ASAP-2000 Micromeritics instrument. X-ray powder diffraction (XRD) patterns of the samples were obtained on a Rigaku D/Max 2500 powder diffractometer using Cu K α radiation as the X-ray source. Elemental analysis was acquired on Atomscan 16 ICP-AES instrument (TJA, USA). The X-ray photoelectron spectra (XPS) was recorded on a XSAM800 spectrometer (Kratos, UK) using an Al Ka X-Ray source, the base pressure of the chamber was less than 2 × 10⁻⁷ Pa. The binding energy was corrected with the energy of C1s (284.8 eV) for carbon contaminant.

2.3 Catalyst Testing

The catalytic reactions were carried out using a stainless steel fixed-bed reactor with 1.0 mL (40–60 mesh) of catalyst. Both gaseous and liquid products were analyzed offline by gas chromatography. H₂, CO, CH₄ and CO₂ were determined by thermal conductivity detector (TCD) with a TDX-101 column. The water and methanol in liquids were also detected by TCD with a GDX-401 column. The alcohols were analyzed by flame ionization detector (FID) with a Porapack-Q column. The carbon balance and mass balance were 100 \pm 5%.

3 Results and Discussion

3.1 Structural Properties of Fe/K/β-Mo₂C Catalysts

The XRD patterns of samples are shown in Fig. 1. In Fig. 1A, it can be seen that K/β -Mo₂C-based catalysts all



Fig. 1 XRD patterns of K/ β -Mo₂C-based catalysts with different Fe content. (*a*) Fe/Mo = 0 (*b*) Fe/Mo = 1/16 (*c*) Fe/Mo = 1/14 (*d*) Fe/Mo = 1/12 (*e*) Fe/Mo = 1/10

had definitive phase of the molybdenum carbide with hexagonal close packed (HCP) structure [14] (2θ = 34.48°, 38.08°, 39.48°, 52.18°, 61.58°, 69.68°, 74.68° and 75.68° for β -Mo₂C [1 0 0], [0 0 2], [1 0 1], [1 0 2], [1 1 0], [1 0 3], [1 1 2] and [2 0 1], respectively). For K/ β -Mo₂C catalyst, the peaks at 2 θ value of 49.5 and 66.7 might be related to "K–Mo–C" entities [13]. For Fe/K/ β -Mo₂C catalysts, the peak intensity corresponding to the β -Mo₂C decreased with increasing Fe/Mo molar ratio. Further investigation revealed that the weak signals at 42.6° and 46.5° might correspond to Fe₃C [15], and weak signals at 44.5° might correspond to Fe₃Mo₃C [16], which formed during the preparation (Fig. 1B).

The surface compositions of Fe/K/ β -Mo₂C catalysts are listed in Table 1. The Fe/Mo ratio and the K/Mo increased for the Fe/K/ β -Mo₂C catalysts compared with the K/ β -Mo₂C catalyst. The surface Fe content was all higher than its nominal preparation, it could be concluded that there is β -Mo₂C segregation of the Fe/K phases to the surface, and

Table 1 Surface composition of the K/β -Mo₂C-based catalysts (calculated from XPS data)

Catalyst n(Fe)/n(Mo)	Surface composition/mol%					Atom ratio		
	Мо	Fe	K	С	0	Fe/ Mo	K/ Mo	Fe/ Mo ^a
0	11.76	_	6.43	52.78	29.03	_	0.55	_
1/16	9.45	1.29	5.79	51.02	32.42	0.13	0.61	0.058
1/14	8.68	1.93	5.29	52.28	30.77	0.22	0.61	0.067
1/12	7.61	2.52	5.59	54.03	30.41	0.33	0.71	0.077
1/10	7.13	2.85	5.04	53.32	32.67	0.39	0.67	0.095

^a Based on ICP results



Fig. 2 XPS spetra of Mo 3d and Fe 2p with different Fe/Mo molar ration. (a) Fe/Mo = 0 (b) Fe/Mo = 1/16 (c) Fe/Mo = 1/14 (d) Fe/Mo = 1/12 (e) Fe/Mo = 1/10

probably that behaving as a support for the dispersed ironcontaining phases. Namely, the iron promoter is enriched on the surface. Also, the surface K content was all higher than its theory preparation, which suggested that K promoter was enriched on the surface of catalyst.

3.2 XPS Characterization

The Mo 3d and Fe 2p XPS spectra are displayed in Fig. 2. They showed the presence of Mo 3d in different chemical state. The three main peaks with binding energy (B.E.) located at 228.4, 232.5, and 235.5 eV. According to the literature, the peak at 228.4 eV was unambiguously attributed to Mo atoms in the carbide form [17]. The peak at B.E. of 232.5 eV was attributed to Mo⁴⁺ species [16]. The peak at 235.5 eV was assigned to Mo⁶⁺ species, which was characteristic of oxidized phase, resulting from the passivation step [14]. When adding Fe to K/ β -Mo₂C catalyst, the B.E. of Mo 3d shifted to higher B.E. value again with the Fe/Mo molar ratio increased. Simultaneously, the intensity of the peaks became weaker.

The XPS spectra of Fe 2p of Fe/K/ β -Mo₂C sample is also presented in Fig. 2. The XPS spectra of Fe 2p

exhibited two large peaks, at 724.6 and 711.6 eV for the Fe $2p_{1/2}$ and Fe $2p_{3/2}$ signals [18]. Simultaneously, a narrow Fe $2p_{3/2}$ peak appearing at 706.9 eV is characteristic of iron in iron carbides [19]. The iron carbide could increase the selectivity to oxygenates [20]. In addition, the peaks of Fe 2p shifted to lower binding energy as the iron content increased. It also indicated that there was a strong effect between iron and molybdenum. In terms of catalytic performances of CO hydrogenation reaction, Fe promoter, as a electronic promoter, released the electron density and transferred to molybdenum. Thus, the increased proportion of molybdenum in an oxidative environment might be favorable to the alcohols synthesis.

3.3 Effect of the Fe Promoter on the Catalytic Performance

The catalytic performance for HAS in steady state over the K/β -Mo₂C-based catalysts are given in Tables 2 and 3. For K/β -Mo₂C catalyst, the CO conversion was 40.46% and the yield of alcohols achieved 0.10 g/mL h. In alcohols products (see Table 3), the methanol selectivity was high (about 40.40%). For Fe/K// β -Mo₂C catalyst, the optimum of Fe/Mo molar ratio was about 1/14. At the Fe/Mo molar ratio of 1/14, the CO conversion increased to 50.25% and

Table 2 Performance of CO hydrogenation over Fe/K/ β -Mo₂C catalysts

Catalyst <i>n</i> (Fe)/ <i>n</i> (Mo)	CO conv. (%)	Yield (g/(mL	h))	Selectivity (C%)		
		Alcohols	Hydrocarbons	Alcohols	Hydrocarbons	CO ₂
0	40.46	0.10	0.11	15.24	34.34	50.24
1/16	38.93	0.11	0.17	19.20	25.60	55.19
1/14	50.25	0.14	0.22	22.69	27.60	49.70
1/12	46.72	0.12	0.21	18.03	28.15	53.81
1/10	36.91	0.08	0.15	16.37	27.91	55.71

Reaction conditions: T = 593 K, P = 7.0 MPa, GHSV = 4,000 h⁻¹, $n(H_2)/n(CO) = 2.0$

Table 3 Alcohols distribution over Fe/K/ β -Mo₂C catalysts

Catalyst n(Fe)/n(Mo)	Alcohols distribution (wt%)						
	MeOH	EtOH	PrOH	BuOH	C ₅ ⁺ OH		
0	40.40	48.03	9.56	1.90	0.11		
1/16	31.98	49.75	13.46	4.17	0.64		
1/14	28.71	52.72	13.63	4.17	0.62		
1/12	27.94	48.40	15.36	6.73	1.57		
1/10	25.14	46.33	17.63	9.04	1.86		

Reaction conditions: T = 593 K, P = 7.0 MPa, GHSV = 4,000 h⁻¹, $n(H_2)/n(CO) = 2.0$

the selectivity to alcohols also increased. As the Fe content further increased, the selectivity to C_2^+OH , especially the propyl alcohol and butyl alcohol, increased remarkably, but the selectivity to hydrocarbons greatly increased. Thus, it could be concluded that Fe promoter has dual function in CO hydrogenation, one is to favor the higher alcohols, and the other is to promote the hydrocarbons synthesis. Namely, there is a synergistic interaction between the Fe and Mo, and the "Fe₃Mo₃C" new phase might be responsible for the high activity of higher alcohol synthesis. The remarkable effect of Fe promoter might be ascribed to its own intrinsically activity for carbon monoxide hydrogenation especially methanation, and the "Fe₃C" new phase might responsible for the synthesis of hydrocarbons.

The typical change in CO conversion and selectivity of alcohols with time on stream over Fe/K/ β -Mo₂C (Fe/Mo = 1/14) catalyst is shown in Fig. 3. Initially, the catalyst showed high CO conversion and relatively low selectivity to alcohols. Gradually, the CO conversion decreased and alcohol selectivity increased with time on stream. After about 72 h, a pseudo steady state was



Fig. 3 Stability test of Fe/K/ β -Mo₂C catalyst (Fe/Mo = 1/14)

obtained. During the experimental period (192 h), the catalyst showed a constant activity and selectivity. In addition, other catalysts also exhibited similar trends. Generally, molybdenum carbide-based catalyst has an induction period in Fischer–Tropsch reaction [21]. For Fe/ K/β -Mo₂C catalyst, a part of the surface oxygen on the catalyst probably reacted with carbidic carbon and was removed from the uppermost surface layer during this induction period [22]. It was also reported that during the induction, some surface carbon atoms of carbide and some deposited carbon species were eliminated [22].

3.4 Effect of Iron on Chain Propagation

Anderson-Schulz-Flory (A-S-F) distribution of The hydrocarbons and alcohols is given in Fig. 4. Over both K/β -Mo₂C and Fe/K/ β -Mo₂C catalysts, the distribution of hydrocarbons obeyed linear. While alcohols showed a significant deviation of methanol, they did not obey the traditional linear A-S-F distribution. Except for methanol, it was worth noting that the C2-C4 alcohols still followed a liner distribution plot. For Fe/K/ β -Mo₂C catalyst, the chain-growth probability (P in Fig. 4) of alcohols was of 0.19, which was higher than that of K/β -Mo₂C catalyst (0.12). It seemed that iron promoter exerted strong promotion for carbon chain growth, especially for the stage of C_1OH to C_2OH . It was noted that the chain-growth probability of hydrocarbons of Fe/K/ β -Mo₂C catalyst was increased from 0.29 to 0.33. Combined with the XRD results, the chain-growth probability of hydrocarbons might be attributed to the phase Fe₃C. And the high selectivity to alcohols, especially for C_2^+OH was assigned to new phase "Fe₃Mo₃C" in Fe/K/β-Mo₂C catalyst, together with the "K-Mo-C" entities. It could be speculated that the "Fe₃Mo₃C" and "K-Mo-C" species might be the active sites for HAS.

4 Conclusion

A novel Fe/K/ β -Mo₂C catalyst was prepared and tested for HAS. The catalyst revealed high performance for HAS via syngas. The catalytic performance over the catalyst was obviously influenced by the Fe/Mo molar ratio. The optimized Fe/Mo molar ratio was of 1/14 for HAS. Furthermore, the iron promoter exerted strong promotion for C–C growth. The phase, "Fe₃Mo₃C", might be responsible for the high selectivity of C₂⁺OH. And the "Fe₃C" phase favors the hydrocarbons synthesis over the Fe/K/ β -Mo₂C catalyst.

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Fig. 4 A-S–F plots of alcohols and hydrocarbons over the catalysts. **a** K/β -Mo₂C **b** $Fe/K/\beta$ -Mo₂C (Fe/Mo = 1/14)

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