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K/Ni/β-Mo_2C: A highly active and selective catalyst for higher alcohols synthesis from CO hydrogenation[☆]

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Abstract

Nickel and potassium promoted β-Mo_2C catalysts were prepared for CO hydrogenation to higher alcohols synthesis. The results revealed that β-Mo_2C produced mainly hydrocarbons, but the addition of potassium resulted in a remarkable selectivity shift from hydrocarbons to alcohols over β-Mo_2C. Moreover, it was found that potassium enhanced the ability of chain propagation of β-Mo_2C catalyst and led to a higher selectivity to C_2^+OH. The addition of nickel further enhanced higher alcohols synthesis, which showed the optimum at 1/8–1/6 of Ni/Mo molar ratios. The characterization suggested that there might be a synergistic effect of potassium and nickel on β-Mo_2C, which favored the alcohols synthesis. The production of alcohols appeared to be relevant to the presence of Mo^{4+} species, whereas the formation of hydrocarbons was closely associated with Mo^{2+} and/or Mo^0 species on the surface of β-Mo_2C-based catalysts.

Keywords: K/Ni/β-Mo_2C; Higher alcohols synthesis; CO hydrogenation

1. Introduction

The higher alcohols (C_1–C_5 mixed alcohols) synthesis (HAS) from natural gas or coal via syngas is considered as a potential alternative route for clean fuels as well as chemicals [1–2]. The catalytic synthesis of higher alcohols from CO hydrogenation was first reported in 1920s. However, the application of such an attractive synthesis still suffers from the lack of high performance catalysts. Thus, great efforts are still being made to improve both activity and selectivity of catalysts [1].

As a new type of material, carbides of transition metals receive a great attention with molybdenum carbide being the most promising [3,4]. Insertion of carbon atoms into the lattice of molybdenum leads, due to lattice expansion, to the appearance of a narrower metallic type band with a density of states at the Fermi level similar to that of noble metals [4]. Recently, molybdenum carbides reported to be active for synthesis of light hydrocarbons in the liquefied petroleum gas range from carbon monoxide and hydrogen [5,6]. Woo et al. [7] revealed that in the field of CO hydrogenation, molybdenum carbides produce mainly light alkanes, whereas modification with potassium was found to greatly enhance the selectivity to alcohols composed of linear C_1–C_7. Investigations of molybdenum carbides were also carried out in Fischer-Tropsch synthesis. Synthesis of hydrocarbons from CO/H_2 over cobalt or ruthenium promoted molybdenum carbides have been evidenced by Constant et al. [6] and the results indicated that molybdenum carbide gave light hydrocarbons and alcohols, the addition of Ru decreased the alcohol production whereas Co increased the formation of heavy hydrocarbons. Our previous studies also revealed that molybdenum carbides (both β-Mo_2C and α-MoC_{1-X}) mainly produced light hydrocarbons [8]. By adding potassium as a promoter, both β-Mo_2C and α-MoC_{1-X} showed a remarkable selectivity shift from hydrocarbons to alcohols. Moreover, potassium enhanced the ability of chain propagation of β-Mo_2C and α-MoC_{1-X} with higher selectivity to C_2^+OH. And the K/β-Mo_2C catalyst was far more active and selective than K/α-MoC_{1-X} catalyst in terms of catalytic performance of HAS [8].

As reported by others [9–12], the transition metals (such as Co, Ni, Rh, Pd) were found to be able to improve the catalytic

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activity and selectivity of C_2^+ alcohols due to their strong ability of hydrogenation and chain propagation over MoS_2-based catalysts. In our previous studies [13–15], Fe, Co and Ni promoted molybdenum carbides were used for higher alcohols synthesis from syngas, the results revealed that Ni modified K/β-Mo_2C catalyst was shown to be highly active and selective towards the synthesis of mixed alcohols, especially for the C_2^+OH production. Nickel is an excellent methanation component but other catalytic capabilities have been neglected for a long time. Recent researches on Ni-containing catalysts such as Na-NiO-TiO_2, Ni-SiO_2 and Cu-Mn-Ni suggested that nickel had potential to promote mixed alcohols synthesis due to the strong ability of CO insertion [16–18]. As a result, a series of nickel modified β-Mo_2C catalysts in the presence of potassium were prepared and investigated for their performance of mixed alcohols synthesis in the present paper.

2. Experimental

2.1. Catalyst preparation

Molybdenum carbides were prepared through Temperature-Programmed-Reaction (TPRe) method as described elsewhere [8,15,19]. In detail, the β-Mo_2C and Ni/β-Mo_2C with the hexagonal close packed (HCP) structure were prepared by direct carburization of the MoO_3 and NiMo oxide precursors, respectively. The oxide precursor for NiMo bimetallic carbide was prepared using mixtures of an aqueous solution of nickel nitrate ($Ni(NO_3)_2 \cdot 6H_2O$; 99%) and an aqueous solution of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$; 99%). The compounds were dissolved in water at 353 K under stirring, which produced a viscous mixture. The solid products were dried at 353 K overnight, heated above 673 K for 4 h, and then cooled to room temperature. TPRe was carried out under atmospheric pressure in a flow of 20.0 vol% CH_4/H_2 gas mixture and the temperature linearly increased from room temperature (RT) to 973 K. Then the samples were quenched to RT and gradually passivated with 1.0 vol% O_2/N_2 before exposure to air. K_2CO_3 modification (K/Mo = 1/5) was accomplished by physically mixing K_2CO_3 with the final carbide, and then the mixture was calcined at 773 K.

2.2. Characterization methods

X-ray powder diffraction (XRD) patterns of the tested catalysts were obtained on a Rigaku D/Max 2500 powder diffractometer using Cu Kα radiation as the X-ray source. Scanning electron microscopy (SEM) images were carried out using a LEO 438VP SEM (5 KV). The X-ray Photoelectron Spectra (XPS) was recorded on a PHI-5300 spectrometer (Physical Electronics, USA) using an Al Kα X-Ray source, the base pressure of the chamber was less than 2×10^{-8} Pa.

2.3. CO hydrogenation

CO hydrogenation was conducted with a fixed-bed, stainless flow reactor with 2.0 ml of catalysts (pellets, 40–60 mesh). The products were analyzed by 1790-GC, and H_2, CO, CH_4 and CO_2 were analyzed by thermal conductivity detector (TCD) equipped with a TDX-101 column. The water and methanol in liquids were also detected by TCD with a GDX-401 column, but the alcohols and hydrocarbons were analyzed by flame ionization detector (FID) with a Propake-Q column.

3. Results and discussion

3.1. Structural and morphological properties

The XRD patterns of the samples are shown in Fig. 1, it can be seen that β-Mo_2C-based catalysts all had definitive phase of the molybdenum carbide with HCP structure [20] ($2\theta = 34.4°$, 38.0°, 39.4°, 52.1°, 61.5°, 69.6°, 74.6° and 75.6° for β-Mo_2C [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). With the promotion by potassium, the intensity of peaks assigned to β-Mo_2C became slightly weak. Meanwhile, there appeared new diffraction peaks with 2θ values of 49.5° and 66.7°, it could be tentatively assigned to mixed ‘‘K-Mo-C’’ entities, which were analogous to ‘‘K-Mo-S’’ in the K/MoS_2 catalysts. For K/Ni/β-Mo_2C catalyst, the intensity of peaks assigned to β-Mo_2C became weaker and diffraction peaks corresponding to the metallic Ni were detected (2θ values was at 44.5° and 51.3°) [21,22], and the intensity of Ni metal became strong as the Ni content increased.

The SEM micrographs of samples indicated that β-Mo_2C showed regular morphology of hexagonal particles. However, modified by potassium, the surface of β-Mo_2C appeared to be decorated by small clusters, which might be related to K_2CO_3 and/or ‘‘K-Mo-C’’ particles. For K/Ni/β-Mo_2C catalyst, morphological differences among these samples were evident. When nickel content was low, the surface of the β-Mo_2C appeared to be covered with a great deal of small-conglutinated particles and showed an irregular shape. Moreover, a progressive surface decoration was observed as a function of the concentration of promoter nickel in these micrographs (see Fig. 2c). With relatively higher nickel content, larger particles were formed on the surface of β-Mo_2C. Combined with XRD

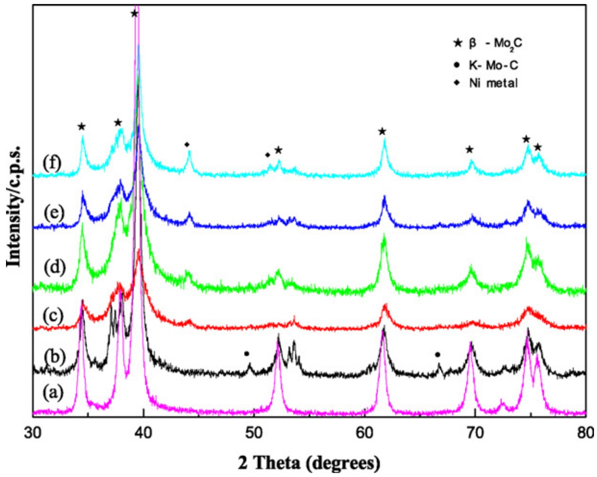

Fig. 1. XRD patterns of the catalysts with different Ni/Mo molar ratios (a) β-Mo_2C, (b) K/β-Mo_2C, (c) 1/10, (d) 1/8, (e) 1/6 and (f) 1/4.

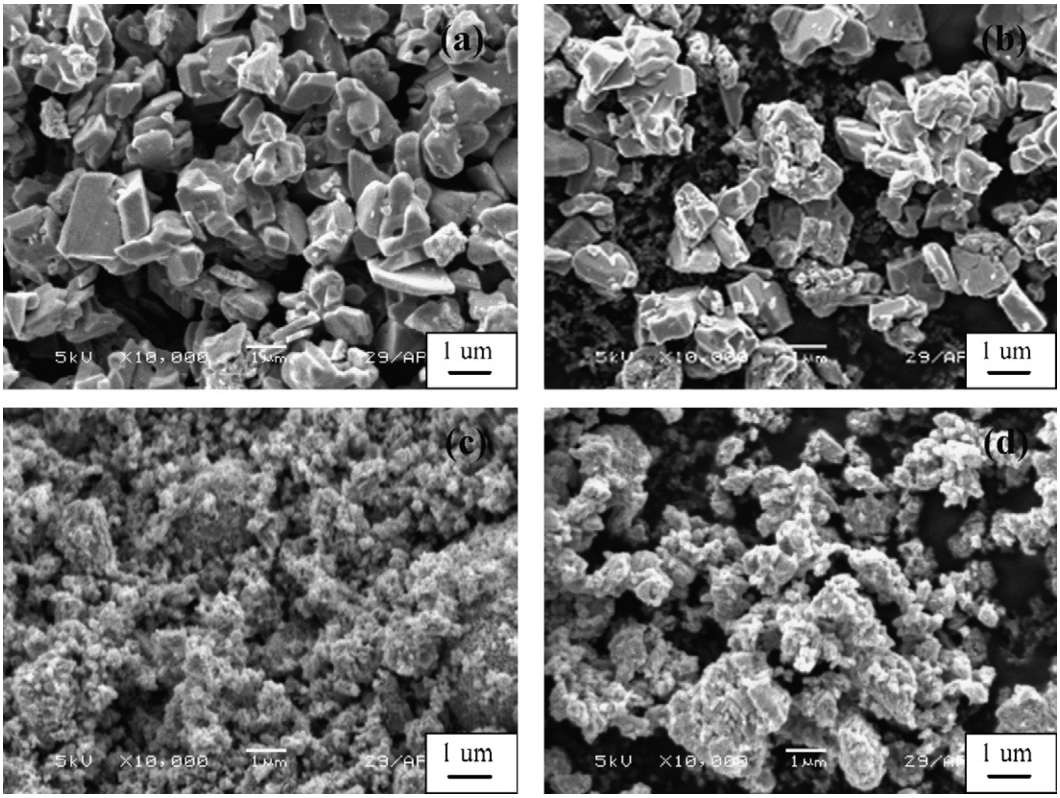

Fig. 2. SEM micrographs of catalysts (a) β-Mo_2C, (b) K/β-Mo_2C, (c) K/Ni/β-Mo_2C (Ni/Mo = 1/8) and (d) K/Ni/β-Mo_2C (Ni/Mo = 1/4).

analysis, the large particles might be related to the assemblies of Ni metal (see Fig. 2d). As the catalysts for mixed alcohols synthesis, the interaction between Mo and promoters and the dispersion of catalysts exerted great influence on the catalytic performance [23,24]. Catalysts with small crystallites had an advantage to produce alcohols while larger crystallites led mainly to methane [9]. In the present case, remarkable changes of morphology and structure caused by Ni promoter indicated that the performances of mixed alcohols synthesis might be related closely to the structural effect of nickel.

The surface compositions of β-Mo_2C-based catalysts are listed in Table 1. It showed that the surface content of K was higher than its stoichiometry, indicating that the K promoter existed in the form of ‘‘K-Mo-C’’ particles on the surface of catalysts, which was consistent with SEM observation. Also, the ratio of surface content of carbon to molybdenum was much higher than its theoretical stoichiometry, namely, 0.5, suggesting that amorphous carbon was deposited on the catalysts and was unavoidable during the preparation procedure. However, it was worth noting that the surface content of Ni was much lower than its stoichiometry. These suggested that there was strong interaction between Ni and β-Mo_2C. Combined with the SEM observation, the remarkable changes of morphology and structure of β-Mo_2C could be attributed to the nickel fully inserted into the bulk of β-Mo_2C.

Table 1
Surface composition of K/Ni/β-Mo_2C catalysts with different Ni loadings[a]

Catalyst, n(Ni)/n(Mo)	X_{Mo}	X_{Ni}	X_K	X_C	X_O
β-Mo_2C	15.53	–	–	56.15	28.32
K/β-Mo_2C	11.49	–	8.65	45.24	34.62
1/10	17.01	1.26	6.60	50.09	25.04
1/8	14.23	1.09	5.89	56.41	22.38
1/6	12.58	0.97	5.44	57.55	23.46
1/4	13.43	1.42	6.87	54.21	24.07

[a] Calculated from XPS data (Mo3d, Ni2p, K2p, C1s and O1s).

3.2. The synergistic effect of potassium and nickel on β-Mo_2C

The Mo3d, Ni2p, K2p and C1s XPS spectra are presented in Fig. 3. It showed the presence of Mo3d in several oxidation states located at 228.4 eV, 232.5 eV, and 235.5 eV. For β-Mo_2C, two species with a $Mo3d_{5/2}$ binding energy (B.E.) around 229 eV were identified, the first one assigned to Mo^{2+}(228.4 eV) and the second to Mo^{4+}(229.4 eV). The $Mo3d_{5/2}$ peak at the lower B.E. (228.4 eV) was consistent with the carbidic phase [25], no metallic molybdenum being detected. Higher B.E. signals were also observed on β-Mo_2C catalyst, at about 231.8 eV and 232.5 eV, assigned to Mo^{5+} and Mo^{6+} of $Mo3d_{5/2}$, respectively [20], and these peaks were characteristic of oxidized phases, resulting from the passivation step. Modified by potassium, the position of $Mo3d_{5/2}$ shifted to lower B.E., the intensity of Mo^{2+} decreased and the ratio of Mo^{2+} to Mo^{4+} remarkably reduced compared with those of on β-Mo_2C. The addition of nickel to K/β-Mo_2C, the XPS spectra changed remarkably. The intensity of signals assigned to Mo^{2+} and Mo^{4+} increased simultaneously and the position shifted to higher B.E. Meanwhile, a new signal

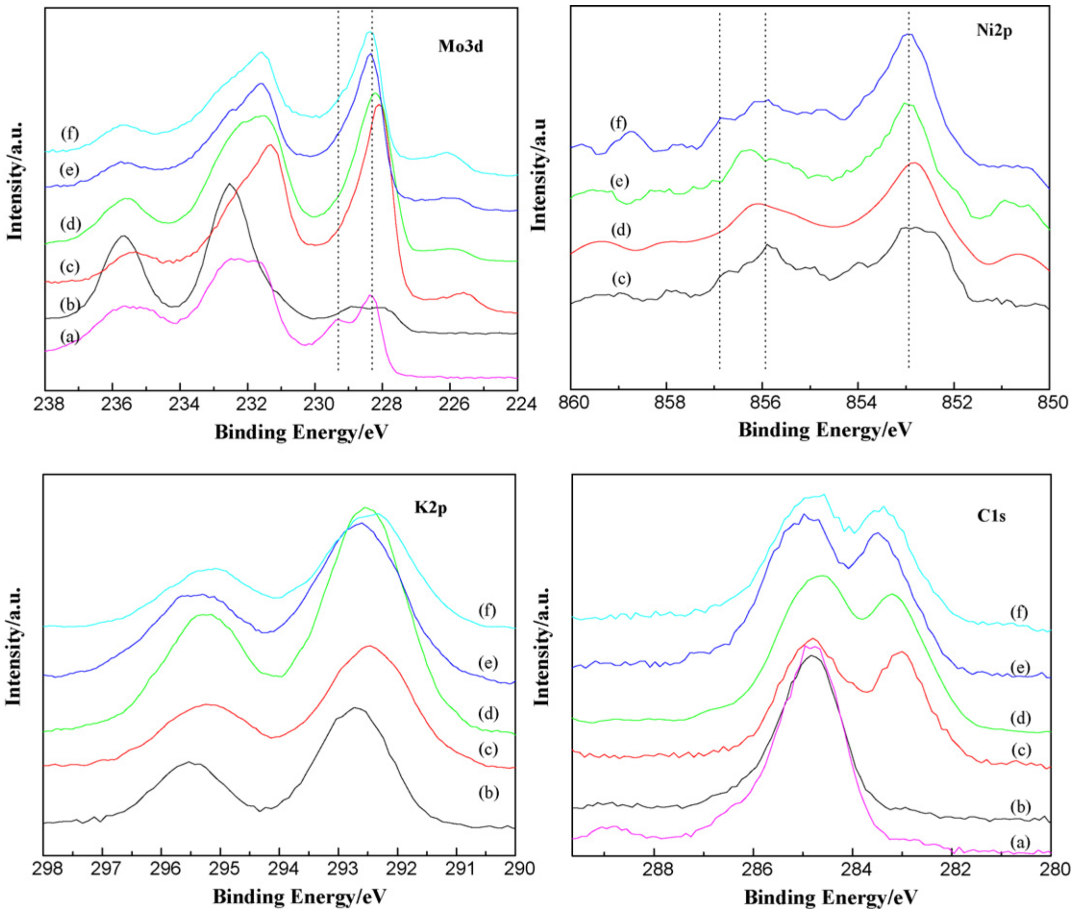

Fig. 3. Mo3d, Ni2p, K2p and C1s XPS spectra of K/Ni/β-Mo_2C catalysts with different Ni/Mo molar ratios (a) β-Mo_2C, (b) K/β-Mo_2C, (c) 1/10, (d) 1/8, (e) 1/6 and (f) 1/4.

appeared at the 225.7 eV, which could be assigned to Mo^0 [20]. However, these signals became weak as the Ni content further increased. From the Ni2p spectra, the signals shifted to higher B.E. as Ni content increased. For $Ni2p_{3/2}$, the signals at the 855.9 eV and 856.8 eV might be assigned to Ni^{2+} [26]. Laniecki et al. reported that the presence of Ni^{2+} enhanced the reducibility of Mo species and was responsible for the improvement of the catalytic performance [27]. The signal at the 852.8 eV might be assigned to Ni^0 and its intensity became strong with increasing the Ni content [26], this generally indicated electron donation to Mo atoms [28]. The electron interaction between nickel and molybdenum resulted in the increased d-orbital occupation in molybdenum atoms, which further increased the intrinsic activity. Nikolova et al. reported that the addition of nickel resulted in the middle value of the Mo^{4+} contribution, as compared to the unsupported Mo sample [29]. In terms of catalytic performances of CO hydrogenation reaction (see below), the increase in the number of Mo^{4+} on the surface of β-Mo_2C might favor the alcohols synthesis, whereas the lower valence of Mo ($Mo^{2+}$and Mo^0) might favor the hydrocarbons synthesis [30,31].

The K2p spectrum primarily showed two strong XPS peaks, in all cases, the intensity of signals almost remained the same. However, addition of Ni to K/β-Mo_2C, the position shifted to lower B.E., however, it shifted to higher B.E. again. As mentioned above, the electron transferred from nickel to molybdenum increased the intrinsic activity and had strong interaction between K and Mo, which made the signals of potassium shift to lower B.E., and this effect became weak as the Ni content increased. The C1s spectra primarily showed three XPS peaks. For β-Mo_2C and K/β-Mo_2C catalysts, the signals almost remained the same. The signal at 284.8 eV was attributed to amorphous carbon as reported by several authors [32–35]. The signal at 288.6 eV was attributed to the carbon atoms involved in carbonate species (C=O), and was due to contamination [34,35]. Further investigation revealed the weak signal at 283.5 eV might correspond to a carbon bonded to a metal in a carbide form [32–35]. Because amorphous carbon formed by the pyrolytic reaction was accumulated on molybdenum carbides, the signals of C1s at 284.8 eV was very strong. Thus, the signal for the carbon atoms in the carbide form was very weak. However, promoted by potassium and nickel, the deposited carbon was greatly suppressed and the signal (283.5 eV) for the carbon atoms in the carbide form became strong.

3.3. Catalytic performances

The results of carbon monoxide hydrogenation over the β-Mo_2C-based catalysts are given in Table 2. For β-Mo_2C

Table 2
Performance of CO hydrogenation over K/Ni/β-Mo_2C catalysts[a]

Catalyst, $n(Ni)/n(Mo)$	CO Conv./C%	STY/g/(L h)		Selectivity/C%[b]		C_2^+OH/C_1OH (C-atom)
		ROH	C_2^+OH	ROH	CH_x	
β-Mo_2C	58.6	15.7	3.5	3.7	96.3	0.42
K/β-Mo_2C	23.4	122.1	65.9	52.6	47.4	1.80
1/10	58.1	174.1	121.8	35.7	64.3	2.27
1/8	73.0	324.2	206.1	47.3	52.7	2.88
1/6	77.7	302.8	216.3	43.7	56.3	3.81
1/4	81.3	291.3	218.5	38.4	61.6	4.99

[a] Reaction condition: $T = 573$ K, $P = 8.0$ MPa, GHSV = 2000 ml/g cat./h, $n(H_2)/n(CO) = 1.0$.

[b] Calculated on a CO_2 free basis.

catalyst, the CO conversion was high and hydrocarbons were the major products, only little alcohol was formed. In alcohol products, methanol was the main one, about 70.0 C% (see Fig. 4). Modified by potassium, the CO conversion over β-Mo_2C catalyst was reduced approximately from 58.6 C% to 23.4 C%, yet the main products shifted from hydrocarbons to alcohols and the STY of alcohol achieved 122.1 g/(L h). In alcohol products, the methanol was depressed and the value of C_2^+OH up to about 64.0 C% (see Fig. 4). Obviously, the addition of Ni to K/β-Mo_2C catalyst led to a sharp increase in both the activity and selectivity to C_2^+OH. Compared with β-Mo_2C and K/β-Mo_2C catalyst, the proportion of methanol was further suppressed and C_2^+OH became the major liquid products. This indicated that nickel had strong ability to promote the carbon chain growth.

For K/Ni/β-Mo_2C catalyst, the optimum of Ni/Mo molar ratio was about 1/8–1/6. At Ni/Mo molar ratio of 1/8, a high CO conversion rate of 73.0 C% was obtained, and the STY of alcohol reached the maximum, 324.2 g/(L h). At the Ni/Mo molar ratio of 1/6, the CO conversion up to 77.7 C% and the selectivity to alcohols was slightly reduced. As the Ni content further increased, the selectivity to C_2^+OH, especially the C_3OH and C_4OH, increased remarkably, but the selectivity to hydrocarbons greatly increased. Thus, it could be concluded that Ni promoter had dual function in CO hydrogenation, one was to favor the higher alcohols synthesis due to its strong ability of CO insertion, and the other was to promote the hydrocarbons synthesis due to its strong ability of CO dissociation [16–18]. Combined with XRD and SEM observation, the aggregated Ni particles might favor the synthesis of hydrocarbons and highly dispersed Ni in the catalysts favored the synthesis of alcohols.

The typical change in CO conversion and selectivity of alcohols with time on stream is shown in Fig. 5. Initially, K/β-Mo_2C catalyst showed high CO conversions and relatively low selectivity to alcohols. The CO conversions decreased and alcohol selectivity increased with time on stream, and a steady state was obtained after 72 h. The catalyst exhibited a constant activity and selectivity up to 144 h without any deactivation. Generally, molybdenum-based catalysts for mixed alcohols synthesis from CO hydrogenation had an induction period [23]. For molybdenum carbide, a part of the surface oxygen on the β-Mo_2C catalyst probably reacted with carbidic carbon and was removed from the uppermost surface layer during this induction period [6]. It was also believed that during the induction, some surface carbon atoms of carbide and some deposited carbon species were eliminated before the catalysts had enough hydrogenation ability [36].

3.4. Effect of potassium and nickel on chain propagation

For β-Mo_2C catalyst, the distribution of hydrocarbons and alcohols had similar linear Anderson-Schultz-Flory (A-S-F) plots (see Fig. 6), the chain-growth probability P were 0.62 and 0.26, respectively [37]. Modified by potassium, the distribution

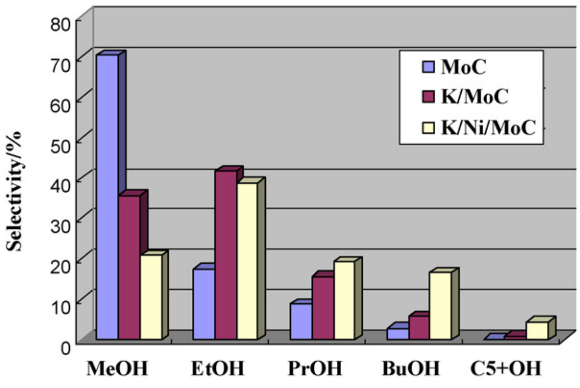

Fig. 4. Distribution of alcohols over β-Mo_2C-based catalysts with K/Mo = 1/5 and Ni/Mo = 1/6.

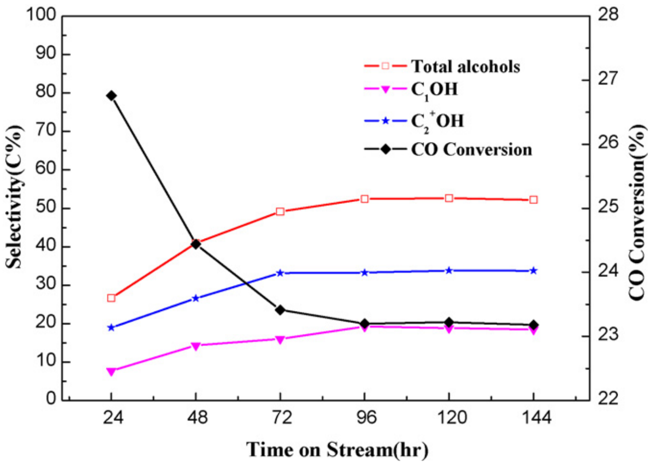

Fig. 5. The change in CO conversion and selectivity of alcohols with time on stream.

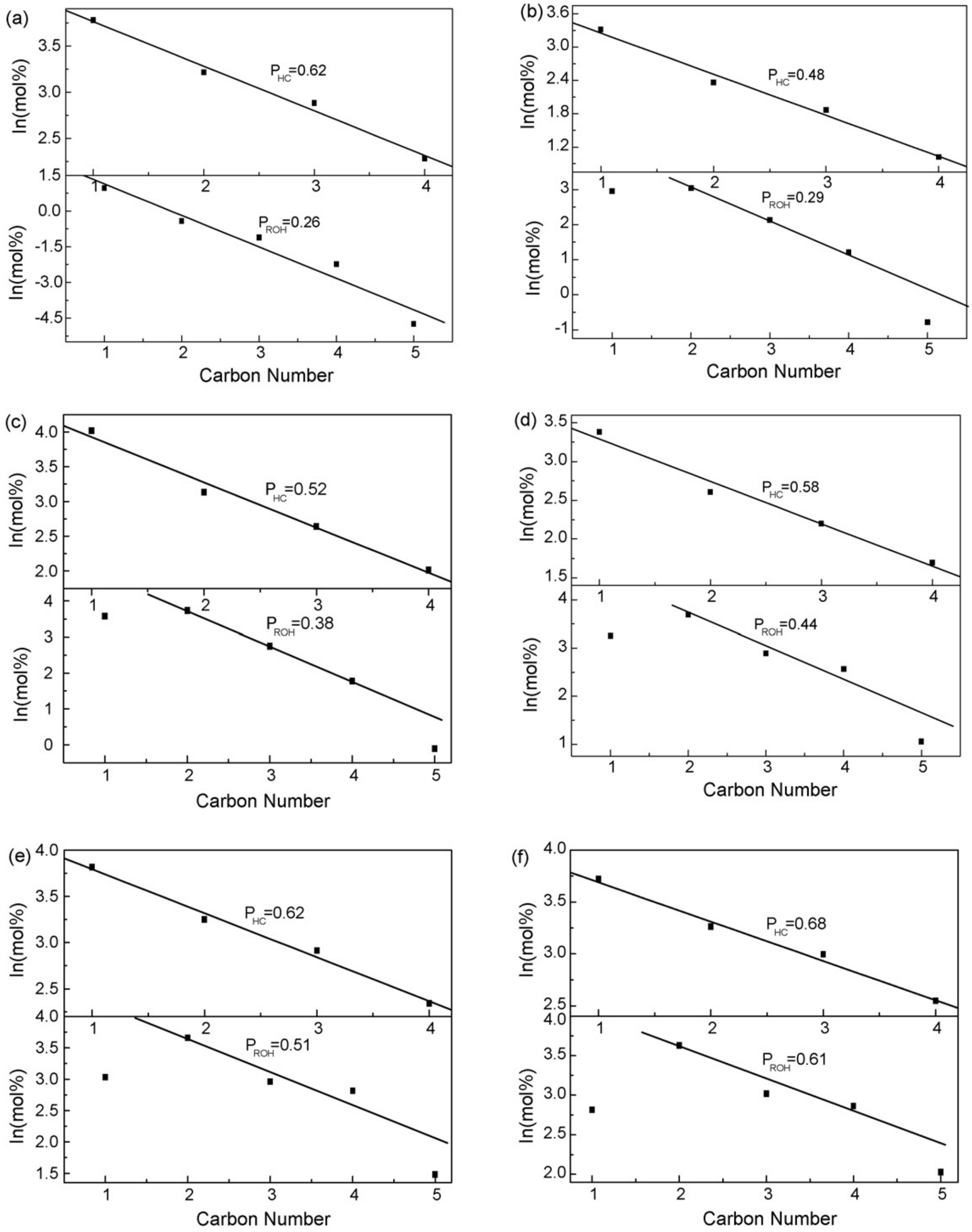

Fig. 6. A-S-F plots of alcohols and hydrocarbons over the catalysts with different Ni/Mo molar ratio (a) β-Mo_2C, (b) K/β-Mo_2C, (c) 1/10, (d) 1/8, (e) 1/6 and (f) 1/4.

of hydrocarbons still obeyed the linear A-S-F plot. However, the alcohols gave a unique deviation in the case of methanol, indicating a different reaction mechanism for alcohols formation over K/β-Mo_2C catalysts. However, it was worth noting that the C_2–C_4 alcohols still followed the linear distribution plot and the chain-growth probability *P* of 0.29 was obtained, which the value for the alcohols production was quite different from that of the production of hydrocarbons. Promoted by both potassium and nickel, β-Mo_2C showed similar types of A-S-F plots of hydrocarbons and alcohols to K/β-Mo_2C catalyst. The chain-growth probability of hydrocarbons and alcohols increased simultaneously as the Ni/Mo molar ratios increased from 0.48 to 0.68 and from 0.29 to 0.61, respectively. It meant that potassium exerted a positive function on the whole chain propagation to produce alcohols and nickel further enhanced the activity and selectivity to C_2^+OH. The main difference of reaction mechanism over K/Ni/β-Mo_2C and β-Mo_2C catalysts lied in chain propagation of C_1OH to C_2OH. For K/Ni/β-Mo_2C catalyst, a surface phase such as the ‘‘K-Mo-C’’ was responsible for the higher value of C_2^+OH with Ni further enhanced the chain propagation to produce alcohols, especially for the C_1 to C_2 conversion.

Due to the bifunctionality of nickel, namely, the formation of corresponding precursor of alcohol (CH*x*) and the strong ability of CO insertion [12], it was likely that over the K/Ni/β-Mo_2C catalyst, the ‘‘K-Mo-C’’ phase was the active site for the alcohols synthesis, and highly dispersed Ni further enhanced the ability of chain growth to produce C_2^+OH, whereas the aggregated Ni particles led to the severe methanation. However, in terms of XPS results and catalytic performance of β-Mo_2C-based catalysts, it could be concluded that the formation of alcohols might be attributable to the presence of Mo^{4+} species, whereas the products of hydrocarbons was closely associated with Mo^{2+} and/or Mo^0 species on the surface of the catalysts as reported by Muramatsu et al. and Zhang et al. [30,31].

4. Conclusions

A series of nickel promoted β-Mo_2C in the presence of potassium were prepared and tested for mixed alcohols synthesis. The main products over β-Mo_2C catalyst were hydrocarbons. The addition of potassium led to a remarkable shift of the products from hydrocarbons to alcohols, however, promoted by both potassium and nickel, β-Mo_2C exhibited highly active and selectivity to C_2^+OH with the maximum at Ni/Mo molar ratio of 1/8–1/6. This was due to the strong promotion for carbon chain growth by nickel, especially for the stage of C_1OH to C_2OH. The formation of alcohols could be attributed to the presence of Mo^{4+} species, whereas the products of hydrocarbons was closely associated with Mo^{2+} and/or Mo^0 species on the surface of the catalysts.

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