K/Ni/β-Mo$_2$C: A highly active and selective catalyst for higher alcohols synthesis from CO hydrogenation[☆]

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Abstract

Nickel and potassium promoted β-Mo$_2$C catalysts were prepared for CO hydrogenation to higher alcohols synthesis. The results revealed that β-Mo$_2$C produced mainly hydrocarbons, but the addition of potassium resulted in a remarkable selectivity shift from hydrocarbons to alcohols over β-Mo$_2$C. Moreover, it was found that potassium enhanced the ability of chain propagation of β-Mo$_2$C 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$_2$C, 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$_2$C-based catalysts.
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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$_2$C and α-MoC$_{1−X}$) mainly produced light hydrocarbons [8]. By adding potassium as a promoter, both β-Mo$_2$C 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$_2$C and α-MoC$_{1−X}$ with higher selectivity to C$_2{}^+$OH. And the K/β-Mo$_2$C 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

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$(NO_3)_2$·$6H_2O$; 99%) and an aqueous solution of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}$·$4H_2O$; 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

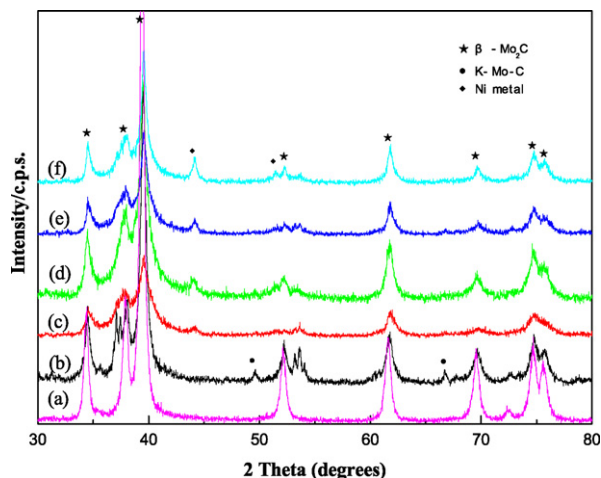Fig. 1. XRD patterns of the catalysts with different Ni/Mo molar ratios (a) β-Mo_2C, (b) K/β-Mo_2C, (c) 1/10, (d) 1/8, (e) 1/6 and (f) 1/4.