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Synthesis of higher alcohols from syngas over Fischer–Tropsch elements modified K/β-Mo_2C catalysts

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Abstract

Fischer–Tropsch elements (Fe, Co and Ni) modified K/β-Mo_2C catalysts were prepared and investigated for their performance in CO hydrogenation. The results revealed that Ni or Co modified K/β-Mo_2C catalysts were shown to be highly active and selective towards the synthesis of mixed alcohols, especially for the C_2^+OH production, but Fe caused a negative effect. Ni or Co led to a decrease in apparent activation energies for C_1–C_4 alcohols, whereas Fe caused a slight increase for methanol and the decrease for C_2–C_4 alcohols. As a result, the promotion effects of Fischer–Tropsch elements were different and followed the sequence: $Ni \gg Co > Fe$ for the activity and $Ni > Co > Fe$ for the C_2^+OH alcohol selectivity.

Keywords: K/β-Mo_2C; Fischer–Tropsch elements; Higher alcohols synthesis

1. Introduction

Since 1973, when Levy and Boudart [1] reported that WC displayed reactivity similar to Pt for hydrogenation reactions, there has been considerable interest in the catalytic properties of metal carbides, particularly of the group VI transition metals. As a new type of catalytic material, molybdenum carbide might be used as a cheaper substitute for catalysts of various reactions [1]. It has been shown to be promising catalysts for CO hydrogenation [2–4], hydrodenitrogenation (HDN) [5], hydrodesulfurization (HDS) [5], hydrocarbon isomerization [6], etc. [7,8].

In the field of syngas chemistry, the studies of molybdenum carbides have attracted more attention. Molybdenum carbides have been reported to be active for synthesis of light hydrocarbons in the liquefied petroleum gas range from carbon monoxide and hydrogen [2,9]. Leclercq et al. [3] and Woo et al. [4] have clearly revealed that molybdenum carbides produced mainly light alkanes, whereas the formation of alcohols is related to the surface stoichiometry and to the extent of carburization [3]. Promotion of molybdenum carbide by potassium has been found to greatly enhance the selectivity to alcohols [4]. Investigations of molybdenum carbides have also been 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. [9] and the results reveal that molybdenum carbide give light hydrocarbons and alcohols, the addition of Ru decrease the alcohol production whereas Co increase formation of heavy hydrocarbons. Our previous studies also reveal that molybdenum carbides (both β-Mo_2C and α-MoC_{1-X}) produce mainly light hydrocarbons, only little alcohols are obtained. For both β-Mo_2C and α-MoC_{1-X}, the additions of potassium as a promoter, result in remarkable selectivity shift from hydrocarbons to alcohols. Moreover, the potassium promoter enhances the ability of chain propagation of β-Mo_2C and α-MoC_{1-X} with higher selectivity to C_2^+OH

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[10]. Our results also reveal that the K/β-Mo_2C catalyst is far more active and selective than *K*/α-MoC_{1-X} catalyst in terms of catalytic performance of HAS, and its optimum of K/Mo molar ratio was about 1/5 [10]. It appears that molybdenum carbides could be potential catalytic materials for CO hydrogenation reactions.

As reported elsewhere [11–14], the addition of 3d transition metals (such as Co, Ni, Rh and Pd) is found to be able to improve the catalytic activity and selectivity of C_2^+ alcohols over MoS_2-based catalysts. In this regard, it can be speculated that the 3d transition metals may also have positive effect on HAS from CO hydrogenation over β-Mo_2C-based catalysts, and much less information is available. According to the literature [2,4,9,10], the promotion effects of Fischer–Tropsch elements over the β-Mo_2C-based catalysts for HAS are not studied systematically at present. In this work, the Fischer–Tropsch elements modified K/β-Mo_2C catalysts were prepared for HAS and the characteristics of β-Mo_2C-based catalysts for mixed alcohols synthesis were also investigated.

2. Experimental

2.1. Sample preparation

The molybdenum carbide prepared through Temperature-Programmed-Reaction (TPRe) method and it could be found elsewhere [10,15,16]. In detail, the β-Mo_2C and *M*/β-Mo_2C (M = Fe, Co, Ni) with the hexagonal close packed (HCP) structure were prepared by direct carburization of the MoO_3 and MMo oxide precursors, respectively. The oxide precursors for bimetallic carbides were prepared by mechanically mixing a stoichiometric amount of the corresponding nitrate, e.g. $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ or $Ni(NO_3)_2 \cdot 6H_2O$ with $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, the mixture was then calcined at 673 K for several hours. 6.0 g of the oxide precursor (particle size 0.7–1.2 mm) was placed in the reactor supported on a quartz wool plug. The quartz tube reactor (i.d. = 0.8 cm and length = 40 cm) was heated with an electric furnace (Lindberg, model 55031), and the reactor temperature was controlled using a programmable temperature controller (Omega, CN-2010). TPRe was carried out under atmospheric pressure in a flow of 20.0 v% CH_4/H_2 gas mixture. The temperature was linearly increased at the rate of 60 K/h from room temperature (RT) to 973 K, where it was maintained for additional hours. Then the samples were quenched to RT and gradually passivated with 1.0 v% O_2/N_2 before exposure to air. K_2CO_3 modification (K/Mo = 1/5) was accomplished by a post-doping procedure after synthesis of the final carbide. The alkalinization was carried out by physically mixing K_2CO_3 with the final carbide, and then the mixture was calcined at 773 K to obtain catalysts. The as-prepared catalysts all had definitive phase of the β-Mo_2C [16] ($2\theta = 34.4°$, 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).

Table 1
Catalytic performance of CO hydrogenation over the samples[a]

Catalyst[b]	CO Conv. (C%)	STY (g/(L · h))		Selectivity (*C*%)[c]	
		ROH	C_2^+OH	Alc.	CHx
K/β-Mo_2C	23.41	122.06	65.93	52.60	47.40
K/Co/β-Mo_2C	40.76	156.43	99.58	42.59	57.41
K/Ni/β-Mo_2C	73.00	324.21	206.13	44.91	55.09
K/Fe/β-Mo_2C	22.01	75.15	42.46	41.95	58.05

[a] Reaction condition: $T = 573$ K, $P = 8.0$ MPa, GHSV = 2000 h^{-1}, $n(H_2)/n(CO) = 1.0$.
[b] M(M = Co, Ni, Fe)/Mo = 1/8, K/Mo = 1/5.
[c] Free of CO_2.

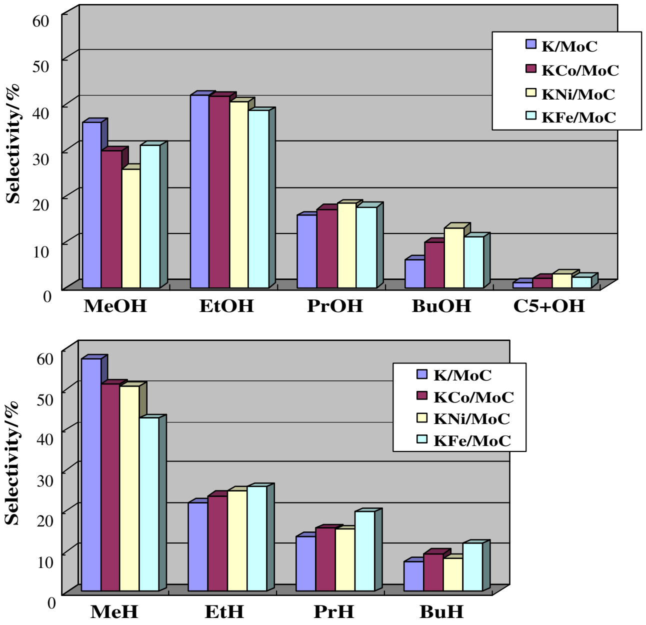

Fig. 1. The product distribution of alcohols and hydrocarbons over the samples.

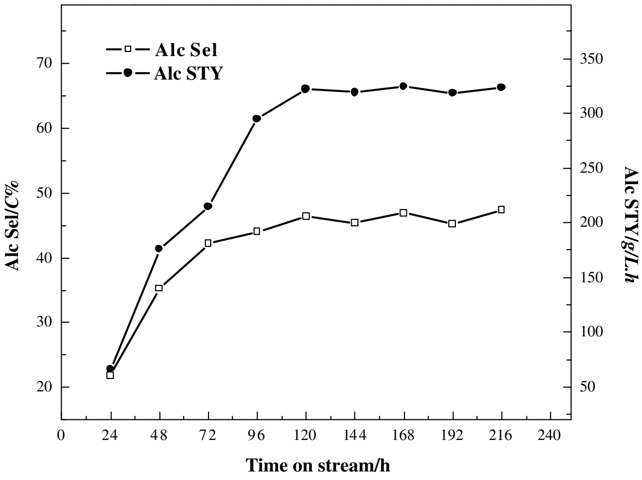

Fig. 2. Stability test of K/Ni/β-Mo_2C catalyst.