K-promoted Ni–Mo phyllosilicate catalysts for the synthesis of higher alcohols from syngas

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Abstract: A type of K-promoted Ni–Mo phyllosilicate catalyst (K-(NiMo)Si-PS) has been synthesized for CO hydrogenation to higher alcohols. The optimized K-(NiMo)Si-PS catalyst affords a C_{2+}-OH selectivity up to 64.2%, while the counterpart with the same composition by a deposition precipitation method (K-(NiMo)Si-DP) shows almost inactive under the reaction condition of 3.0 MPa and 513 K. The structure of the catalysts has been characterized by XRD, TEM and H_2-TPR. The results reveal that the K-(NiMo)Si-PS catalyst possesses strong metal–support interactions and well metal dispersion, which are responsible for its superior catalytic performance for the synthesis of higher alcohols from syngas.

Keywords: Phyllosilicate, Ni–Mo-K, Higher alcohols.

1. Introduction

The higher alcohols (C_{2+}–OH) have attracted considerable attention from both academic and industrial interests due to their potential application as fuels, as an octane booster, or as valuable chemical intermediates.[1] Various catalysts have been developed to synthesize higher alcohols from syngas, including modified methanol catalysts, modified Fischer-Tropsch catalysts, Mo-based catalysts and supported noble metal catalysts. On the other hands, phyllosilicates have several unique features, such as high surface area, well metal dispersion and strong metal–support interactions, thereby exhibiting excellent performance for heterogeneous catalysis.[2] Herein, we report that K-(NiMo)Si-PS catalyst can display improved activity and selectivity for higher alcohols from syngas.

2. Experimental

The K-(NiMo)Si-PS and K-(NiMo)Si-DP catalysts were prepared by ammonia evaporation method and deposition precipitation method successively. Performance for synthesis of higher alcohols from syngas was evaluated in a fixed-bed reactor-GC combined system. The catalysts were characterized by means of TEM/SEM/EDS, XRD, H_2-TPR, XPS and so on.

3. Results and discussion

It was experimentally shown that incorporation an appropriate amount of K into the (NiMo)Si-PS pristine could apparently enhance the formation of alcohols (ROH) and suppress the selectivity to hydrocarbons (HCs) simultaneously. When the K/Ni molar ratio increased from 0.1:1 to 0.6:1, the CO conversion decreased rapidly from 22.5% to 2.3%. In order to obtain high *S*(ROH) and *S*(C_{2+}–OH) and low *S*(HCs), the K/Ni molar ratio = 0.5 was optimized as the best. The optimal $K_{0.5}$-(NiMo)Si-PS catalyst could dramatically improve the reactivity to alcohols compared to the $K_{0.5}$-(NiMo)Si-DP catalyst. It can be seen from Table 1 that the selectivity to C_{2+}–OH over $K_{0.5}$-(NiMo)Si-PS reached 64.2%, while no activity was obtained over the compared $K_{0.5}$-(NiMo)Si-DP catalyst under the identical reaction conditions of 3.0 MPa and 240 °C. When the reaction temperature was raised to 300 °C, however, the $K_{0.5}$-(NiMo)Si-DP could present the *S*(ROH) and *S*(C_{2+}–OH) values similar to $K_{0.5}$-(NiMo)Si-PS at 240 °C. The results clearly indicate that the $K_{0.5}$-(NiMo)Si-PS has superior catalytic performance over the $K_{0.5}$-(NiMo)Si-PS counterpart.

Table 1 Catalytic reactivity of K_k-(NiMo)Si-PS and $K_{0.5}$-(NiMo)Si-DP for synthesis of higher alcohols from syngas

Catalyst	S_{BET} / m^2 g^{-1}	Temp. / °C	CO conv. / %	Selec. / %			Alcohol distribution / %	
				HCs	ROH	CO_2	MeOH	C_{2+}–OH
K_0-(NiMo)Si-PS	226.0	240	55.7	75.4	3.6	21	73.3	26.7
$K_{0.1}$-(NiMo)Si-PS	198.3	240	22.5	39.9	26.1	34	58.6	41.4
$K_{0.5}$-(NiMo)Si-PS	83.1	240	7.0	27.4	38.4	34.2	35.8	64.2
$K_{0.6}$-(NiMo)Si-PS	68.4	240	2.3	41.0	38.8	20.2	44.0	56.0
$K_{0.5}$-(NiMo)Si-DP	24.2	240	–	–	–	–	–	–
		300	8.3	27.4	37.9	34.7	33.6	66.4

Reaction conditions: 3.0 MPa, $V(H_2)/V(CO)/V(N_2)$ = 45/45/10, GHSV =3000 mL h^{-1} g^{-1}.

TEM image of $K_{0.5}$-(NiMo)Si-PS (Figure 1A) depicts a perfect fibrous-like structure with homogeneously distribution. The BET surface area (S_{BET}) of $K_{0.5}$-(NiMo)Si-PS arrived 83.1 m^2 g^{-1}, which was 3.4 times that (24.2 m^2 g^{-1}) of the $K_{0.5}$-(NiMo)Si-DP. XRD pattern (Figure 1B) discovered that Ni and Mo species existed in the form of phyllosilicate, which was in accordance with the TEM results. Moreover, the diffraction line ascribed to MoO_3 over the $K_{0.5}$-(NiMo)Si-PS catalyst was of slightly broadness compared to $K_{0.5}$-(NiMo)Si-DP, implying the average particle size might be more or less smaller. From the H_2-TPR spectra (Figure 1C), the main reduction peak of $K_{0.5}$-(NiMo)Si-DP appeared at 500 °C, whereas that of $K_{0.5}$-(NiMo)Si-PS shifted to about 650 °C. The results indicate there exists a stronger metal–support interactions in K-(NiMo)Si-PS, which may benefit the dispersion of Ni–Mo species.

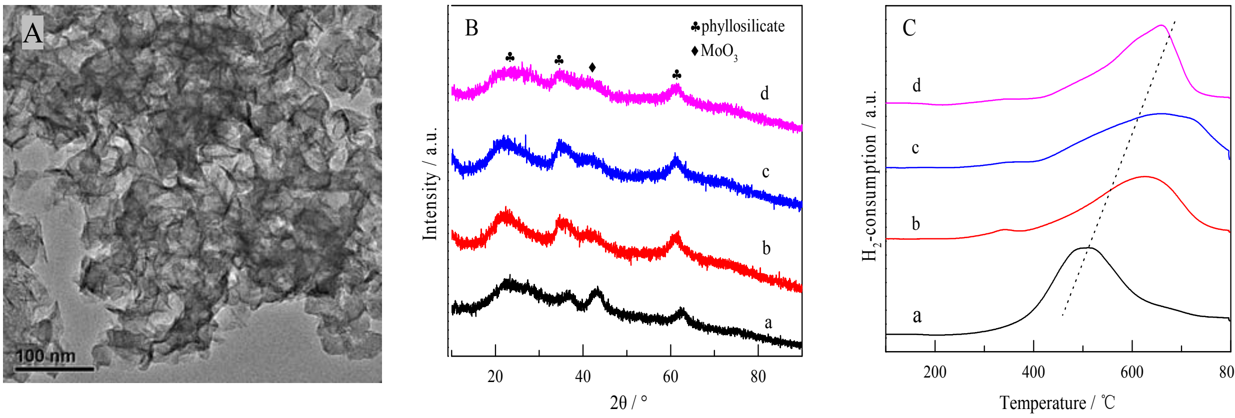

Figure 1. (A) TEM image of $K_{0.5}$-(NiMo)Si-PS , (B) XRD patterns and (C) H_2-TPR profiles of (a) $K_{0.5}$-(NiMo)Si-DP, (b) (NiMo)Si-PS, (c) $K_{0.1}$-(NiMo)Si-PS, and (d) $K_{0.5}$-(NiMo)Si-PS.

4. Conclusions

In summary, the results indicate that the K-promoted Ni–Mo phyllosilicate catalyst K-(NiMo)Si-PS display the enhanced catalytic performance for the synthesis of higher alcohols from syngas. The selectivity toward methanol is decreased markedly but the formation of C_{2+}–OH alcohols is increased considerably. The positive effects in K-(NiMo)Si-PS can be concluded to the increased dispersion of Ni–Mo species and the intensification of metal–support interactions, which is conductive to the formation of higher alcohols.

References

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