Light olefins synthesis from syngas over Sulfide-Zeolite bifunctional catalyst

Haibo Zhou, **Su Liu, Yangdong Wang ***
State Key Laboratory of Green Chemical Engineering and Industrial Catalysis, Shanghai Research Institute of Petrochemical Technology, SINOPEC, Shanghai, 201208, China

Abstract:

Bifunctional catalysts consisting of metal oxide and zeolite have been reported to perform excellent light olefins selectivity from syngas and attract much attention. We demonstrate here that a new sulfide (MoS_2) – zeolite (SAPO-34) bifunctional catalyst which could catalyze the production of light olefins. The side reaction of methanation and hydrogenation of olefins to paraffins are suppressed by the introduction of potassium. Characterization results show that the introduction of potassium could enhance the formation of K–Mo–S structure, at which the alcohol precursor formed. The optimized bifunctional catalyst performs 61.2% C_2-C_4 olefins selectivity, beyond the limitation of Anderson-Shultz-Flory distribution.

Keywords: synthesis gas, light olefins, bifunctional catalyst.

1. Introduction

The development of the global economy leads to a rising demand for light olefins, which are the basic chemical raw materials. Recently, a series of bifunctional catalysts consisting of metal oxide and zeolite have been reported to perform excellent light olefins selectivity from syngas and attract much attention [1, 2]. Many studies have revealed that the challenge of selective conversion of syngas to light olefins lies in the suppression of the methane formation and hydrogenation of olefins [3].

In this article, a new sulfide (MoS_2) – zeolite (SAPO-34) bifunctional catalyst was studied for syngas conversion to light olefins. It was found that, the side reaction of methanation and hydrogenation of olefins to paraffins was suppressed by the introduction of potassium to MoS_2. Characterization results showed that the introduction of potassium could enhance the formation of K–Mo–S structure, at which the alcohol precursor formed. The optimized bifunctional catalyst MoS_2-0.6K+SAPO-34 performed 12.5% CO conversion and 61.2% C_2-C_4 olefins selectivity.

2. Experimental

The unsupported MoS_2-based catalysts were prepared by co-precipitation method [4]. Briefly, aqueous solutions of acetic acid (CH_3COOH) and ammonium tetrathiomolybdate ($(NH_4)_2MoS_4$) were simultaneously added to a container under continuous stirring. Hydrogen ion reacted immediately with the thiomolybdate and a black suspension was formed. The precipitate was aged at 70 ℃ for 2 h, and then filtered. The filtered cake (precipitate) was repeatedly rinsed with ethanol. The solid was dried at 100 ℃ for 12 h, followed by mixing with K_2CO_3 to thermal decomposition at 500 ℃ under N_2 for 2 hour to obtain unsupported MoS_2 catalysts. The MoS_2 catalysts promoted by potassium are denoted as MoS_2-xK (x= 0, 0.2, 0.4, 0.6, 0.8, 1.0), where x is the molar ratio of K/Mo.

3. Results and discussion

To expand the application bifunctional catalysts and search appropriate CO activation sites with strong CO conversion capacity and weak hydrogenation ability of olefins, the performance of several representative alcohol synthesis catalysts coupling with SAPO-34 are investigated and compared in Table 1.

LiFeMnRh/SiO_2+SAPO-34 showed high CH_4 selectivity of 74.0%. While, the C_2-C_4 paraffins became the to the mainly products over CuZnAl+SAPO-34 and CoMoS-0.6K/AC+SAPO-34 bifunctional catalysts.

MoS_2-0.6K with weaker hydrogenation ability might prevent the olefin intermediate products from further hydrogenation, so high C_2-C_4 olefins selectivity could be achieved over the Sulfide-Zeolite system.

Table 1. Catalytic test results over $LiFeMnRh/SiO_2$, CoMoS-0.6K, CoMoS-0.6K/AC, CuZnAl with and without SAPO-34 [a]

Catalysts	CO conversion	Organic product selectivity (CO_2 free)					C_2-C_4 olefin/paraffin
		CH_4	C_2-C_4 olefins	C_2-C_4 paraffins	C_{5+} hydrocarbons	Oxygenates	
$LiFeMnRh/SiO_2$ + SAPO-34 [b]	21.7	74.0	1.4	22.7	0.3	1.6	0.06
CoMoS-0.6K/AC + SAPO-34 [b]	3.4	8.6	5.5	75.8	3.6	6.5	0.07
CuZnAl+ SAPO-34 [b]	37.9	3.6	1.6	90.8	4.0	0	0.02
MoS_2-0.6K+SAPO-34 [b]	19.7	14.6	58.9	22.5	3.7	0.3	2.62

[a] Reaction conditions: p = 4.0 MPa, GHSV = 4000 h^{-1}, T = 400 ℃, $n(H_2)/n(CO)$= 1.

[b] Mass ratio of alcohol catalysts:SAPO-34 = 1:1.

Table 2 compared the catalytic performance of the K modified MoS_2+SAPO-34 bifunctional catalysts. MoS_2+SAPO-34 provided 70.4% CH_4 with a high CO conversion, but seldom C_2-C_4 olefin was formed. Modification of the MoS_2 with K_2CO_3 yielded more than 80% C_2-C_4 hydrocarbons and reduced the methane selectivity. It is notable the C_2-C_4 olefin/paraffin ratio increased with the mount of K increased.

Our results suggested that the CO hydrogenation sites significantly affected the product distribution in the subsequent conversion of C_1 intermediate. C_1 intermediate would easily be reduced to CH_4 over MoS_2 [5], which exhibited highest hydrogenation activity, rather than desorbed and migrated to the coupling active sites. K was found to be effective additive to weaken the hydrogenation ability of MoS_2 [5, 6]. With the introduction of K, CO conversion and CH_4 selectivity decreased, while more C_1 intermediate was able to migrate to the coupling active sites, resulting the increase of the C_{2+} product selectivity. The hydrogenation of olefins to paraffins could lead to the consumption of olefins. By weakening the hydrogenation ability, the introduction of K could suppress the side reaction, and enhance the C_2-C_4 olefin/paraffin ratio. So, a balance of hydrogenation and coupling functions associated with K and MoS_2 was required to produce an optimum yield of C_2-C_4 olefins and to minimize the paraffins formation. And, 60% K introduction could significantly enhance the production of light olefins from syngas.

Table 2. Catalytic test results over MoS_2-xK+SAPO-34 bifunctional catalysts with different K loadings [a]

Catalysts	CO conversion	Organic product selectivity (CO_2 free)					C_2-C_4 olefin/paraffin
		CH_4	C_2-C_4 olefins	C_2-C_4 paraffins	C_{5+} hydrocarbons	Oxygenates	
MoS_2 + SAPO-34	75.4	70.4	-	29.5	0.1	0	0
MoS_2-0.2K+SAPO-34	39.0	18.9	35.2	40.2	4.9	0.8	0.88
MoS_2-0.4K+SAPO-34	25.9	13.7	48.3	33.3	4.3	0.4	1.45
MoS_2-0.6K+SAPO-34	19.7	14.6	58.9	22.5	3.7	0.3	2.62
MoS_2-0.8K+SAPO-34	16.9	16.1	56.8	22.5	4.0	0.6	2.52
MoS_2-1.0K+SAPO-34	15.9	12.3	51.2	30.9	5.4	0.2	1.66

[a] Reaction conditions: $m(MoS_2\text{-}xK):m(SAPO\text{-}34)$= 1:1, p = 4.0 MPa, GHSV = 4000 h^{-1}, T = 400 ℃ , $n(H_2)/n(CO)$= 1.

4. Conclusions

Light olefins synthesis from syngas over the Sulfide-Zeolite bifunctional catalyst has been investigated in this work. By the introduction of potassium, the hydrogenation ability of MoS_2 catalyst was weakened, the side reaction of methanation and hydrogenation of olefins to paraffins was suppressed. The optimized bifunctional catalyst MoS_2-0.6K+SAPO-34, which performed 19.7% CO conversion and 58.9% C_2-C_4 olefins selectivity, could significantly enhance the production of light olefins from syngas. Due to the resistance to sulfur poisoning and high olefin/paraffin ratio, the Sulfide-Zeolite bifunctional catalyst showed potential application prospect in the light olefins synthesis.

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