

Hydropurification and Hydroisomerisation of Butyl-Mercaptan-Alkane Mixes and Diesel Oil Fractions on Alumo-Iron-Molybdenum Catalysts

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Abstract

Modified alumina-iron-molybdenum (AIM) catalysts have been studied in hydropurification and hydroisomerization both of butylmercaptan-alkane mixture and diesel oil fractions. It has been shown that the modification of alumina-iron-molybdenum catalysts by zeolites and other additives leads to a significant enhancement of their hydrodesulfurization and hydroisomerization activity.

Introduction

Presently the extraction and processing of sulphur and mercaptan containing oils become more extensive. Hydrogen sulfide and light mercaptans are the volatile and high toxic impurities with very strong unpleasant odour [1]. The catalytic hydropurification is used for the extraction of sulphur from oil fractions [1-4]. The process efficiency depends on the catalyst properties and technological parameters.

The catalytic systems based on nickel and cobalt are widely studied in hydropurification of oil fractions. The iron-containing catalysts are not enough studied in this reaction.

In the present study the properties of modified iron-molybdenum catalysts in the conversions of n-alkanes and organic sulphur compounds have been examined.

Experimental

Catalysts were prepared by impregnation of Al_2O_3 support with aqueous solution of ammonium paramolybdate, iron nitrate and by an introduction of zeolites and other additives. The wet samples of catalysts were formed, dried at 150°C and calcined at 500°C for 5 hours.

The activity of AIM catalysts was studied in the hydropurification and hydroisomerization reactions of a model mixture consisting of butyl-mercaptan-alkane and diesel oil fractions. The processes were carried

out in a laboratory fixed-bed flow reactor at various temperatures from 320 to 400°C and space velocity (S.V.) from 1.5 to 3.0 h⁻¹. The pressure was 3.5 MPa. The butyl-mercaptan content in model feeds and in diesel oil fractions are 0.4 and 0.2 wt. %, respectively. The total sulphur content is determined by pyrolytic method of sample burn [5].

The reaction products were analyzed at Chrom-4 gas chromatograph equipped with modified Al_2O_3 column and flame ionization detector. Argon was used as a carrier-gas. The samples were analysed by use of temperature-programmed regime in interval of 40 - 280°C with a heating rate of $3^\circ\text{C}/\text{min}$.

Results and discussion

The results of hydrodesulfurization of butyl-mercaptan-alkane (C_6 , C_{14} , C_{16}) mixture over modified AIM catalysts are presented in Table 1. It is shown that the hydrodesulfurization degree of butylmercaptan-alkane mixture depends on chain length of n-alkanes. The hydrodesulfurization degrees of butyl-mercaptan-hexadecane and butyl-mercaptan-tetradecane at optimal conditions (400°C , 3.5 MPa) are 90.8 and 92.8% on Kt-12 catalyst, respectively, and 88.4 and 91.7% on Kt-13 catalyst, respectively.

At these conditions the conversion of butyl-mercaptan-hexane mixture on Kt-12 catalyst leads to complete removal of sulphur. The hydrodesulfurization degree reaches 100% at 380°C . The activity of Kt-13 catalyst is slightly lower (Table 1). Over Kt-12 and Kt-13 catalysts the hydro-

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desulfurization degree of butylmercaptan-alkane (C_{14} , C_{16}) mixture is increased with increasing of process temperature from 320 to 400°C by 5.2-10.8%. The most hydrodesulfurization degree is observed at 400°C. The further increasing of process temperature does not change significantly the hydrodesulfurization degree. In this case the amount of light hydrocarbons is increased due to the hydrocracking process (Tables 2, 3).

It was shown that the processes of hydro-

isomerization and hydrocracking of n-alkanes carried out in parallel at hydrodesulfurization over Kt-12 catalyst. The maximum n-tetradecane conversion is 91.1% at 350°C (Table 2). The further increase of temperature causes the increase of the catalyst cracking activity. The formation of n- C_1 - C_4 -alkanes is increased from 10.3 to 36.6% with growth of temperature from 350 to 450°C ($P = 3.5$ MPa). Also n- C_5 - C_{13} -alkanes and iso-alkanes are observed among the reaction products. The maximum yield of isoalkanes is 61.9%

Table 1

Hydrodesulfurization of butylmercaptan-(C_6, C_{14}, C_{16}) alkane mixture on modified AIM catalysts ($P_{H_2} = 3.5$ MPa, S.V.=1.5 h⁻¹)

Catalysts	Temperature, (°C)	Hydrodesulfurization degree (%)		
		hexane	tetradecane	hexadecane
Kt-12	320	99.9	87.1	85.6
	350	99.9	90.7	88.1
	380	100.0	91.5	89.5
	400	100.0	92.8	90.8
Kt-13	320	88.0	81.0	77.6
	350	90.4	83.4	81.1
	380	96.1	87.2	85.9
	400	100.0	91.7	88.4

Table 2

The effect of temperature on n-tetradecane conversion over AIM catalysts ($P_{H_2} = 3.5$ MPa, S.V. = 1.5h⁻¹)

Catalysts	Temperature (°C)	Conversion (%)	Composition of catalysate (%)				Selectivity of iso-alkane
			i-alkane	C_1 - C_4	C_5 - C_{13}	unreacted C_{14}	
Kt-12	320	89.0	61.9	10.3	16.8	11.0	69.6
	350	91.1	59.2	11.4	20.5	8.9	65.0
	400	78.7	38.3	26.3	14.1	21.3	48.7
	450	86.5	37.9	36.6	12.0	13.5	43.8
Kt-13	320	44.2	40.7	Traces	3.5	55.8	92.1
	350	54.0	46.6	Traces	7.4	46.0	86.3
	400	50.2	39.0	Traces	12.8	49.8	77.7
	450	57.1	42.5	Traces	14.6	42.9	77.4

Table 3

The effect of temperature on n-hexadecane conversion over AIM catalysts ($P_{H_2} = 3.5$ MPa, S.V. = 1.5h⁻¹)

Catalysts	Temperature (°C)	Conversion (%)	Composition of catalysate (%)				Selectivity of isoalkane
			i-alkane	C_1 - C_4	C_5 - C_{15}	Unreacted C_{16}	
Kt-12	320	63.6	21.1	12.2	30.3	36.4	33.2
	350	46.4	17.1	23.4	5.9	53.6	36.9
	400	69.4	42.7	14.1	12.6	30.6	61.5
	450	79.7	44.1	16.5	19.1	20.3	55.3
Kt-13	320	51.3	34.2	Trace	17.1	48.7	66.7
	350	60.4	29.7	Trace	30.7	39.6	49.2
	400	63.9	28.4	Trace	35.5	36.1	44.4
	450	71.6	33.7	Trace	37.9	28.4	47.1

($T_{\text{exp}} = 320^{\circ}\text{C}$). In more severe conditions (400°C) are optimal for sulphur removal the yield of iso-alkanes decreases to 38.3%. Activity of Kt-13 catalyst in the conversion of n-tetradecane is lower than Kt-12 catalyst one (Table 2). It is shown that hydrocracking direction on the Kt-13 catalyst is presented slower. The reaction products are n- and iso- $\text{C}_5\text{-C}_{13}$ -alkanes and traces of $\text{C}_1\text{-C}_4$ -light hydrocarbons. The maximum n-tetradecane conversion is reached 57.1% at $T_{\text{exp}} = 450^{\circ}\text{C}$. The yield of iso-alkanes is 42.5% at these conditions. The selectivity of iso-alkane formation over Kt-12 and Kt-13 catalysts at optimum reaches 69.6 and 92.1% respectively at $T_{\text{exp}} = 320^{\circ}\text{C}$.

Over Kt-12 catalysts the maximum hexadecane conversion is 79.7% at 450°C (Table 3). In these conditions the yields of iso-alkanes, n- $\text{C}_1\text{-C}_4$ -alkanes and n- $\text{C}_5\text{-C}_{13}$ -alkanes are 44.1, 16.5 and 19.1% respectively. The activity of Kt-13 catalyst is significantly less in compare with Kt-12 catalyst one (Table 2, 3). The maximum hexadecane conversion is 71.6% at 450°C and maximum yield of iso-alkanes (34.2%) is observed at 320°C . Trace amount of n- $\text{C}_1\text{-C}_4$ -alkanes are formed in all temperature range. The cracking properties of catalysts increase with temperature increase. The maximal selectivity on isomer

formation in tetra-decane conversion is observed on the Kt-13 catalyst and is equal 92.1% at 320°C . In the hexadecane conversion the maximum selectivity on isomers is 66.7%.

The analysis of results obtained shows that the Kt-12 and Kt-13 catalysts in the catalytic conversion of butylmercaptan-alkane mix have the polyfunctional properties and simultaneously carried out three processes: hydrodesulfurization of oil fraction from organo-sulphur compounds, hydroisomerization and cracking of alkanes.

The properties of the synthesised polyfunctional catalysts were studied in hydrodesulfurization of a real diesel oil fraction. It has been shown that these catalysts are able to carry out simultaneously the three reaction: hydrodesulfurization, hydrocracking and hydroisomerization. It leads to significant increase of the quality of diesel fuel.

Over unmodified Fe-Mo/ Al_2O_3 (AIM) catalysts the hydrodesulfurization degree is not more than 59.2% (Table 4). Over modified Kt-12 and Kt-13 catalysts the hydrodesulfurization degrees of diesel oil fractions are 81.2 and 92.5%, respectively.

Unmodified AIM catalyst has not the hydroisomerization activity. Freezing point of the fuel after reaction is decreased slightly by $0.5\text{-}0.7^{\circ}\text{C}$ (Table 4).

Table 4

The effect of temperature on hydrodesulfurization of diesel oil fraction ($T_{\text{congelation}} = -12^{\circ}\text{C}$) on AIM-catalysts ($P_{\text{H}_2} = 3.5\text{MPa}$, $S.V. = 1.5\text{h}^{-1}$)

Catalysts	Fe-Mo/ Al_2O_3		Kt-12		Kt-13	
	Hydrodesulfurization degree (%)	Point of congelation ($^{\circ}\text{C}$)	Hydrodesulfurization degree (%)	Point of congelation ($^{\circ}\text{C}$)	Hydrodesulfurization degree (%)	Point of congelation ($^{\circ}\text{C}$)
320	45.4	-12.1	85.9	-23.1	75.2	-21.7
350	52.3	-12.3	91.1	-26.0	76.1	-23.4
380	57.3	-12.5	91.9	-28.5	77.7	-25.3
400	59.2	-12.7	92.5	-29.1	81.2	-26.2

Over modified catalysts the freezing point of fuel after the processes of hydrodesulfurization and hydroisomerization is decreased by $14.2\text{-}17.1^{\circ}\text{C}$ due isomerization of n-alkanes to iso-alkanes. It allows to produce the winter kinds of diesel fuel.

Thus, the developed modified AIM catalysts have polyfunctional properties. These catalysts carried out the reaction of hydrodesulfurization, hydrocracking and hydroisomerization of hydrocarbons. Kt-12 catalyst shows the most catalytic activity.

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