The Iron-containing Catalysts in the Petrochemical Processes

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Abstract

The iron-containing catalysts modified by zeolites, copper, nickel and other additives have been studied in the process of hydrorefining of butylmercaptan (C_4H_9SH) -alkane (C_5H_{12}, C_6H_{14} or $C_{10}H_{22}$) mixture and of the real gasoline and diesel oil fractions. It has been shown that the iron-containing modified catalysts posses the multi-functional properties. The processes of hydrodesulfurisation, hydroisomerization and hydrocracking run in parallel over these catalysts. The catalysts studied show the high hydrodesulfurisation activity. Conversion of butylmercaptan over these catalysts is about 100% at 400°C, P = 3.5 MPa and H_2/feed = 250/1. It has been established, that the conversion of butylmercaptan in model mixes over KTZ-13 is decreased with increase of molecular weight of hydrocarbons in the following order: $C_5H_{12} > C_6H_{14} > C_{10}H_{22}$.

After hydrorefining, hydroisomerization and hydrocracking of the real diesel fraction the temperature of freezing of the final product is decreased by 9.7-17.1°C. Introduction of zeolites (HY, HZSM and clinoptilolite) in composition of the iron-containing catalysts allowed to increase the adsorptive properties of catalysts concerning to hydrogen and oil products. The big pore diameter facilitates the transport of the reactant molecules into pores and of the reaction products from pores.

Introduction

In the world, the production and refining of sour and mercaptan oil and gas condensate is increasing year by year. In Kazakhstan the significant oil supplies are characterized by high content of mercaptan, particularly the *Tengiz*, *Zhanazhol* and *Karachaganak* gas condensates.

The natural gas and gas condensate are widely used as fuel. Oil gases and gas condensate contain mercaptan and other sulfur-containing compounds as impurities. They are highly toxic and affect human health. They corrode the equipments and pipe lines. Sulfur dioxide formed during the burning of sulfur-containing compounds pollutes the atmosphere. Therefore it is necessary to clean gases from sulfur-containing compounds before their use in transport vehicles. Depending on deposits, the content of sulfur in natural gas can vary in a wide range. The laws on environmental protection require the deep cleaning from poisons.

The processes of hydropurification are widely used in the petroleum refining for extraction of sulfur and nitrogen-containing compounds from oil fractions [1-4]. These processes improve the quality and stability of fuel. The corrosion of equipments as well as atmospheric pollution are also decreased.

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Experimental

Catalysts were prepared by impregnation of Al_2O_3+HY, Al_2O_3+HZSM and Al_2O_3 + clinoptilolite mixed supports with aqueous solution of $(NH_4)_6\cdot 4H_2O$, $Fe(NO_3)_3\cdot 9H_2O$, $Cu(NO_3)_2\cdot 2H_2O$ and with the introduction of other additives. The wet samples of catalysts were formed as granules, dried at 100 - 150°C for 5 hours at a heating rate of 20-30°C/hour and calcined at 500°C for 5 hours.

The activity of catalysts synthesised was studied in hydrodesulfurisation of a model mixture consisting of butyl-mercaptan (C_4H_9SH) - alkane (C_5H_{12}, C_6H_{14}, $C_{10}H_{22}$) mix and of the real gasoline and diesel oil fractions.

The process is carried out in a laboratory-built fixed-bed flow reactor at various temperatures from 320 to 400°C and space velocity (V) from 1.5 to 3.0 hr^{-1}. The space velocity of hydrogen-containing gas was 250 m^3/m^3. The pressure was 3.5 MPa. The total sulphur content is determined by pyrolytic method of sample burn [5]. The butyl-mercaptan content in model feeds is 0.4 wt.%. The sulphur content in initial gasoline and diesel oil fractions are 0.1 and 0.22 mass % respectively.

Results and Discussion

The hydrodesulfurisation activity of iron-containing catalysts has been evaluated for butylmercaptan conversion. As seen from the values given in Table 1 the catalysts exhibit high hydrodesulfurisation activity. The highest activity at hydrodesulfurisation of butylmercaptan – alkane mix is observed over KTZ-11 and KTZ-12 catalysts. Practically, mercaptan sulfur is completely removed in the temperature range 320-400°C. The observed conversion degree of mercaptan is 99.8-99.9%.

Over catalysts supported on clinoptilolite (KTZ–13) the conversion degree of mercaptan is slightly less than over catalysts of KTZ–11 and KTZ–12. Increase of hydrocarbon molecular weight (C_5-C_{10}) decreases of hydrodesulfurisation activity over this catalyst.

Table 1

Hydrodesulfurisation of butylmercaptan (C_4H_9SH) - alkane (C_5H_{12}, C_6H_{14}, $C_{10}H_{22}$) mix over multi-component iron-containing catalysts at P_{H_2}=3.5 MPa, V=1.5 hr^{-1}

Catalyst	T_{exp}, °C	The degree of mercaptan conversion, %		
		C_5H_{12}	C_6H_{14}	$C_{10}H_{22}$
5%Fe-10%Mo-4%Cu-2%Ni Al_2O_3-HY (KTZ-11)	320	99.9	99.9	99.8
	350	99.9	100	99.8
	380	100	100	99.9
	400	100	100	99.9
5%Fe-10%Mo-4%Cu-2%Ni Al_2O_3-HZSM (KTZ-12)	320	99.9	99.9	99.8
	350	100	99.9	99.9
	380	100	100	99.9
	400	100	100	99.9
5%Fe-10%Mo-4%Cu-2%Ni Al_2O_3-10% clinopt. (KTZ-13)	320	95.7	88.0	85.8
	350	98.6	90.4	87.6
	380	100	96.1	92.7
	400	100	100	96.4

During hydropurification mercaptan is converted to appropriate hydrocarbon and sulfur (Eq. 1).

$$C_4H_9SH + H_2 \rightarrow C_4H_{10} + H_2S \qquad (1)$$

Hydrogen sulfide (H_2S) formed is recovered by dissolution in cadmium chloride (Eq. 2):

$$H_2S + CdCl_2 \rightarrow 2HCl + CdS \downarrow \text{ (yellow deposition)} \qquad (2)$$

In industry the conversion of hydrogen sulfide into sulphur dioxide and its subsequent catalytic reduction to obtain elemental sulphur is effected though conventional Claus's process [1].

Over these modified iron-containing catalysts hydrodesulfurisation reaction takes place in parallel with the hydroisomerization and hydrocracking reactions. So the formed C_5H_{12}-$C_{10}H_{22}$ alkanes of normal and iso-stucture are the base of straight-run gasoline. In Table 2 the results on hexane conversion over KTZ-12 and KTZ-13 are presented. C_1-C_4 – gases, C_5^+ - normal hydrocarbons and C_4-C_6 – iso-alkanes are observed in reaction products. With increase of temperature from 320 to 450°C the degree of hexane conversion over KTZ-12 increases from 49.3 to 75.7%, at the same time the yield of gaseous reaction products is also increased (Table 2). The maximum selectivity on isomers at the hexane conversion is 46.4% at 350°C. The further increase of temperature to 450°C results in selectivity decrease to 27.3%.

Table 2

The effect of temperature on hexane conversion over KTZ-12 and KTZ-13 at P_{H_2}=3.5MPa, V=1.5 hr^{-1}

Catalyst	T_{exp}, °C	C_6H_{14} conversion, %	The composition of reaction products, %			Non-reacted product	Selectivity on isomers, %
			Iso-alkane	C_1-C_4	C_5	C_6	
KTZ -12	320	49.3	21.2	20.5	7.6	50.7	43.0
	350	60.4	28.0	23.5	8.9	39.6	46.4
	400	73.8	26.9	45.8	1.1	26.2	36.5
	450	75.7	20.7	53.7	1.3	24.3	27.3
KTZ -13	320	3.9	1.2	2.7	traces	96.1	30.8
	350	6.6	2.5	3.7	0.4	93.4	37.9
	400	9.4	3.1	5.8	0.5	90.6	33.0
	450	15.7	1.9	12.0	1.8	84.3	12.1

The data on hexane conversion over KTZ-13 demonstrate that the cracking and isomerization activity is significantly less than for KTZ-12. Thus, the maximal yield of isomers is 37.9% at 350°C.

The hydrodesulfurisation activity has been investigated by use of the real gasoline. It was possible to increase the space velocity of feed from 1.5 to 3 hr^{-1} due to the high activity of KTZ-11, KTZ-12 and KTZ-13 catalysts. The degree of hydrodesulfurisation is 96.5, 97.1 and 89.4% respectively at 400°C, P_{H_2}=3.5 MPa, V=3 hr^{-1} (Table 3). The residual sulfur content in gasoline after reaction in these conditions are 0.0035, 0.0029 and 0.0106 mass %, which meet the environmental requirements.

Table 3

Hydrodesulfurisation of gasoline oil fraction over multifunctional iron-containing catalysts at P_{H_2}=3.5 MPa, V = 3 hr^{-1}

Catalysts	T_{exp}, °C	The residual sulfur content, %	Hydrodesulfurisation degree
KTZ -11	320	0.0087	91.3
	350	0.0068	93.2
	380	0.0042	95.8
	400	0.0035	96.5
KTZ -12	320	0.0095	90.5
	350	0.0069	93.1
	380	0.0033	96.7
	400	0.0029	97.1
KTZ -13	320	0.0169	83.1
	350	0.0145	85.5
	380	0.0124	87.6
	400	0.0106	89.4

For the reason to improve the diesel characteristics the hydrodesulfurisation of the real diesel fraction has been studied over these catalysts. The degrees of hydrodesulfurisation are 91.8, 92.5 and 81.2% respectively at 400°C. The residual sulfur content after the process is no more than 0.05 mass % (Table 4).

Table 4
Hydrodesulfurisation of diesel oil fraction ($T_{freezing}$ = -12°C) over multifunctional iron-containing catalysts at P_{H_2}=3.5 MPa, V=3 hr^{-1}

Catalysts	T_{exp}, °C	Residual sulfur content, mas. %	Hydrodesulfurisation degree, %	Tfreezing of reaction product, °C
KTZ -11	320	0.0301	86.3	-22.0
	350	0.0233	89.4	-24.7
	380	0.0215	90.2	-27.0
	400	0.0180	91.8	-27.8
KTZ -12	320	0.0310	85.9	-23.2
	350	0.0195	91.1	-26.0
	380	0,0178	91.9	-28.5
	400	0.0165	92.5	-29.1
KTZ -13	320	0.0545	75.2	-21.7
	350	0.0525	76.1	-23.4
	380	0.0487	77.1	-25.3
	400	0.0413	81.2	-26.2

At the production of diesel, the part of summer-grade diesel is 89, of winter-grade one is 10 and of arctic one is 1%. At the same time the necessity in winter diesel is satisfied only by 30-40% [7,8]. One of the most effective methods for production of diesel with low temperature of freezing is the process of their hydroisomerization and hydrocracking. The temperature of freezing of diesel after processes of hydro refining, hydroisomerization and cracking over KTZ-11, KTZ-12 and KTZ-13 catalysts is decreased by 9.7-17.1°C. The activity of KTZ-11 and KTZ-12 is significantly higher than that of KTZ-13. It needs to noted that there is a change of diesel color after process. For example, the initial diesel had the dark-yellow color and after catalytic process the diesel with light-yellow color was obtained. It may indicate the improvement of diesel characteristics.

It is known that the efficiency of catalysts is increased with increase of surface available for contact with reagents. The iron-containing catalysts studied have the high developed surface (Table 5). Zeolites (HY, HZSM and clinoptilolite) in the composition of iron-containing catalysts allow to increase the adsorptive properties of catalysts concerning to hydrogen and oil products. The big pore diameter facilitates the transport of the reactant molecules into pores and reaction products from pores. The total pore volume is 0.21 and 0.26 cm^3/g for KTZ-11 and KTZ-12 respectively.

Conclusion

The data reported show, that the multifunctional iron-containing catalysts promote almost complete extraction of the mercaptan sulfur from the model mix of butyl-mercaptan (C_4H_9SH) – alkane (C_5H_{12}, C_6H_{14}, $C_{10}H_{22}$). Over KTZ -13 catalyst the decrease of hydrodesulfurization degree is observed with increase of hydrocarbon molecular weight in the process temperature range 320-380°C in the following order: $C_5H_{12} > C_6H_{14} > C_{10}H_{22}$.

It was shown that over these catalysts parallel with hydrodesulfurisation the processes of hydroisomerization and of hydrocracking occur. Also catalysts

Table 5
The physico-chemical properties of synthesized catalysts

Characteristics	Catalysts		
	KTZ -11	KTZ-12	KTZ -13
Specific surface area, m^2/g	166.7	199.3	158.6
Bulk density, g/cm^3	0.77	0.79	0.75
Total pore volume, cm^3/g	0.21	0.26	-
Specific mechanical strength, kg/cm^2	24.7	30.9	23.8

synthesized show the high hydrodesulfurisation activity at hydro-refining of gasoline and diesel oil fractions. The residual sulfur content in gasoline and diesel fractions is less than 0.01 and 0.05 mass % respectively. It corresponds to the environmental requirements. After hydro-refining, hydro-isomerization and hydro-cracking the temperature of freezing of diesel fraction is decreased by 9.7-17.1°C.

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