



Hydropurification of Catalytically Cracked Gasoline

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Abstract

New polyfunctional catalysts for hydrodesulphurization, hydroisomerization and hydrogenation of catalytically cracked gasoline have been developed. The activity of synthesized catalysts was studied for the above processes in flow conditions on a fixed bed at various temperatures and space velocities of the feed. Activity of studied catalysts depends on the nature of modified additives. Catalyst KT-17 modified by the zeolites HZSM-5, HY and other additives have high hydro-desulfurisation, hydroisomerization and hydrogenation activities compared to catalyst KT-18. The residual sulphur content is less than 0.01% in processed gasoline which corresponds to European standards. Decreasing of concentration of olefin with high octane numbers has small influence on octane number of catalytically cracked gasoline hydro-treated on KT catalysts. It is related with high degree of isomerisation of n-alkanes to isoalkanes. Temperature interval of 320-380°C is found to be suitable for high hydro-desulfurisation activity with simultaneous decrease of olefin content and increasing isoalkanes concentration. Increasing of space velocity of raw material feed from 2.0 to 6.0 hour⁻¹ results in decreasing of desulfurisation degree from 97.3 to 91.1% and output of isoalkanes from 43.1 to 37.0%, increasing of olefins content in the reaction products from 11.9 to 33.0%. Catalysts KT-17 and KT-18 have poly-functional properties; reactions of hydro-desulfurisation, hydro-isomerisation and hydrogenation take place simultaneously and allow producing low sulfur, high octane and stable gasoline.

Introduction

Secondary refining processes including cracking and coking is becoming more relevant due to the necessity of residual oil processes. The gasoline of secondary processes contains high amount of sulphur, nitrogen and unsaturated hydrocarbons in comparison with distilled gasoline. The usage of motor fuels that contain sulphur and nitrogen compounds leads to environment pollution. At present Ecological and economic requirements on quality and cost of the motor fuels is increasing, that require stringent of purification process to be used with due consideration to the attendant pollution [1-4].

During hydro purification of secondary processed gasoline hydrogenation of olefins takes place simultaneously with the reaction of hydro desulfurisation that considerably decreases the octane number of hydro-processed material. For the processes of hydro-purification alumino-nickel-molybdenum and alumino-cobalt-molybdenum catalysts are used. However

the existing catalysts of hydropurification do not satisfy the increased requirements of gasoline quality. New effective catalysts that can promote deep hydro-purification and lead to high quality of motor fuel, is being searched for. Perspective proposition is the development of effective catalysts that allow carrying out the several catalytic processes of hydrotreatment of gasoline of secondary processes

Experimental

The new polyfunctional catalysts of hydropurification, hydroisomerization and hydrogenation were developed by modification of alumino-nickel-molybdenum catalysts (ANM) by zeolites of different types (HY, HZSM-5, other additives).

The catalysts were prepared by the impregnation of zeolite and aluminum oxide mixture in aqueous solution of ammonium paramolybdate, nickel nitrate. This also included the introduction of modifying additives. The wet samples of the catalysts were formed in granules, dried at 150°C (5 hours) and calcined at

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500°C for 5 hours. Catalysts were activated by sulfuration with free sulphur at 150°C pressure 0.7 MPa during 3 hours then at 200°C pressure 2.5 MPa (3 hours) and at 320°C during 2 hours.

The activity of the synthesized catalysts were studied at the processes of hydropurification, hydroisomerization and hydrogenation of catalytically cracked gasoline under flow conditions in fixed bed mode in the temperature interval of 320-400°C, at a pressure 3.5 MPa, space velocity of raw material feed being varied between 2.0-6.0 hour⁻¹.

The content of sulphur was determined by the pyrolytic method. [5]. the carbon content of the reaction products was analyzed by chromatography "Chrom-4" with column filled with specially processed γ -aluminum oxide by "Supelco" firm.

Results and discussion

The results of initial fractional content analysis and hydropurified catalytically cracked gasoline are shown in Table 1. Fractional content of gasoline after hydrogenation process depends on nature and structure of catalyst. According to the data of Table 1 the temperature of the boiling end of gasoline is slightly increased during hydroprocessing of catalytically cracked gasoline at the catalyst KT-18.

The fractional composition of the catalytically cracked gasoline with catalyst KT-17 doesn't change

Table 1

Fractional content of initial and hydro-treated catalytically cracked gasoline T = 380°C, P = 3.5 MPa, V_{vol} = 5.0 hour⁻¹

Catalyst	Fractional content, °C				
	b.b.p	10%	50%	90%	e.b.p.
Primary catalytically cracked gasoline	43	54	94	159	170
KT-18	42	56	104	163	185
KT-17	41	55	97	162	173

b.b.p. – beginning boiling point; e.b.p. – ending boiling point

compared to the raw material. Activity of the catalysts depends on the nature of modified additives (Table 2). Catalyst KT-17 modified by the zeolites HZSM-5, HY and other additives shows high hydro-desulfurisation, hydro-isomerization and hydrogenation activities comparing with catalyst KT-18.

Catalyst KT-18 differs from KT-17 because it does not contain HZSM-5. The degree of hydro-desulfurisation at temperature of 380°C on catalysts KT-17 is 94.8% and on the catalyst KT-18 is 91.1%. The residual sulphur content is less than 0.01% in processed gasoline that corresponds to European standards. The content of iso-alkanes on the catalysts KT-18, KT-17 is increased from 27.3 to 34.3 and 37.3 respectively. Simultaneously concentration of olefins

Table 2

Hydrodesulfurisation, hydroisomerization and hydrogenation of catalytically cracked gasoline on KT-17 and KT-18 catalysts (P = 3.5 MPa)

Catalyst	Temperature, °C	Space velocity, hour ⁻¹	Content of		Degree of hydrodesulfurisation, %	Octane number	
			olefins, %	isoalkanes %		RON	MON
Primary catalytically cracked gasoline			44.3	27.3		89.5	79.0
KT-18	320	5.0	33.2	31.1	83.3	83.7	74.3
	350	5.0	31.1	32.5	87.7	84.8	73.7
	380	5.0	30.7	34.3	91.1	85.7	73.5
	400	5.0	29.4	35.1	92.3	85.3	73.9
KT-17	320	2.0	19.5	33.1	86.8	80.6	75.9
	320	5.0	30.9	34.1	89.6	84.8	77.5
	350	5.0	28.5	36.8	92.0	86.5	78.2
	380	5.0	28.2	37.3	94.8	88.8	78.9
	400	5.0	27.9	38.7	96.7	89.0	79.0

RON - octane number by the research method; MON- octane number by the motor method

in the reaction products is decreased from 44.3% to 30.7 % and 28.2% respectively that led to considerable increase of gasoline stability. It is necessary to note that the decrease of the concentration of olefin with high octane numbers has small influence on octane number of catalytically cracked gasoline which is hydrotreated on KT-17 catalysts. It is associated with high isomerization degree of n-alkanes and olefins to isoalkanes, characterized by high octane numbers as well. Output of gasoline is 97 -98%.

It is shown in Table 2 that increasing of temperature from 320 to 400°C leads to increase of hydrodesulfurisation activity from 9.0 to 9.9%. The considerable increase in the degree of hydrodesulfurisation is observed with increase of temperature in the interval of 320-380°C. It is also observed that considerable decrease of olefins content and increase of concentration of isoalkanes. At temperatures higher than

400°C degree of the hydrodesulfurisation doesn't change practically, light boiled hydrocarbons appear in the reaction products due to hydrocracking process that decreases output of gasoline.

Volume velocity of raw material feed affects the hydrodesulfurisation, hydro-isomerization and hydrogenation activities of the catalyst KT-17. This showed increasing of volume velocity from 2.0 to 6.0 hour⁻¹ causes decreasing of hydro-desulfurisation from 97.3 to 91.1%, decreasing of output of isoalkanes from 43.1 to 37.0% and increasing olefin content in the reaction products from 11.9 to 33.0%. As shown in Table 3, increasing of raw material feed cause increasing of octane numbers of gasoline, because of increasing of olefins and isoalkanes content due to hydroisomerization reaction. Optimum volume velocity of raw material feed is 4-5 hour⁻¹ to produce high quality gasoline.

Table 3

Effect of volume velocity of the feed on catalyst KT-17 activity in reactions of hydrodesulfurisation, hydroisomerization and hydrogenation of catalytically cracked gasoline. T = 380°C, P = 3.5 MPa.

Space velocity of raw material feed, hour ⁻¹	Degree of hydrodesulfurisation, %	Content of		Octane number	
		isoalkanes, %	olefins, %	RON	MON
2	97.3	43.1	11.9	79.0	75.2
3	96.8	41.9	15.5	82.1	76.0
4	95.6	39.7	20.9	85.3	77.2
5	94.8	37.5	28.2	88.8	79.0
6	91.5	37.0	33.0	89.5	78.9

Study of catalysts surface and porosity by the low temperature adsorption of nitrogen (method BET) showed that specific surface of catalysts KT-18, KT-17 is equal to 280 and 300 m²/g respectively. Pore sizes 30-50 Å dominated in these catalysts. According to electron microscopic studies catalysts are highly dispersed, their sizes are 20-40 Å. Modification of ANM catalyst contributes to formation of high disperse heteronuclear clusters with complex content that are active in the reaction of hydropurification, hydroisomerization and hydrogenation [1,2,6].

Conclusions

New catalyst formulations for hydroprocessing KT-17 and KT-18 were developed and synthesized

by modification of ANM catalyst with zeolites of different types and the other additives. Activity of the catalysts is studied in the processes of hydrodesulfurisation, hydroisomerization and hydrogenation of catalytically cracked gasoline.

It is shown that developed catalysts KT-17 and KT-18 have poly functional properties. During the hydro-processing of catalytically cracked gasoline on these catalysts reactions of hydro-desulfurisation, hydro-isomerisation and hydrogenation take place simultaneously and low sulfur, high octane and stable gasoline is produced.

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