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Catalysis Today 65 (2001) 191–194

CATALYSIS TODAY

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Catalytic reforming *n*-octane on Pt–Re/Al_2O_3 catalysts promoted by different additives

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Abstract

The effect of decationized forms of NaY, NaZSM-5 zeolites on the properties of Pt–Re/Al_2O_3 catalyst at *n*-octane reforming has been shown. The promoted additives increase the isomerization activity of catalysts. Activity and selectivity of the modified catalysts depend on both degree of ion exchange and (Si/Al) ratio of zeolites. One hundred percent selectivity of *i*-octane formation is reached at the introduction of promoter additive (element of the V group). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Reforming; Zeolite; Isomerization

1. Introduction

The catalytic reforming allows to increase the yield of fuel with high octane number. At the same time the requirements to the gasoline quality are toughened. It is necessary to create the gasoline with low content of benzene and enriched by *iso*-hydrocarbons. *iso*-Hydrocarbons are ecologically more friendly in comparison with benzene. At present the production of reformulated gasoline with low content of benzene is one of the main problems of petrochemical industry [1–5]. There is a need to develop effective catalysts with high isomerization activity.

At the present time the bifunctional Pt–Re catalysts supported on alumina are mainly used [6,7]. By modification of Pt–Re/Al_2O_3 catalysts by different additives, it is possible to increase their isomerization activity and develop such characteristics as selectivity, thermostability and others [8].

In this report the effect of promoted additives on the properties of Pt–Re/Al_2O_3 catalysts for *n*-octane reforming has been studied.

2. Experimental

The catalysts containing 0.35% Pt, 0.35% Re and 1% Cl were prepared by impregnation of support. The support is a mechanical mixture of γ-Al_2O_3 (S_{BET}: 152.3 m^2/g) and synthetic NaY zeolite with ratio 9:1. The hydrogen forms of zeolite (HY(I), HY(II) and HZSM-5) were used. The main characteristics of H-forms of zeolites are presented in Table 1.

Previously NaY and NaZSM-5 zeolites were exposed to decationization by treatment of NH_4NO_3 solution. Then they were washed by distilled water until reaching of pH 7 and calcined at variable temperature from 573 to 813 K. The degree of decationization was controlled by spectral analysis. If necessary the operation was carried out twice.

The impregnation solution consisting of H_2PtCl_6, $HReO_4$ and HCl was added to support at mixing and

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PII: S0920-5861(00)00584-8

Table 1
The basic characteristics of H-form zeolites

Zeolites	Si/Al	Degree of ion change (%)	S_{BET} (m^2/g)	Relative crystallinity (%)
HY (I)	3.5	60	536.3	94
HY (II)	3.1	90	403.6	89
HZSM-5	34	99	270.2	100

then the mix was exposed at room temperature for 1 h. The examples were formed as extrudates with size 1.5–2 mm. Extrudates were dried on air and calcined at $T = 773$ K for 3 h. Pt–Re–Cl–M/Al_2O_3+HY(II) catalyst was prepared by using of the methodic [9]. Catalysts were studied by X-ray analysis, element analysis, IR-spectroscopy, TPD, BET and electron microscopy. The obtained data are presented in Table 2.

The process was carried out in flow reactor under higher pressure (1.0–2.0 MPa), variation of experiment temperature from 623 to 773 K, feeding flow rate 1.5 h^{-1}, hydrogen flow rate — 1000 ml/h and hydrogen/n-octane = 1.

Before reaction, the catalysts were activated directly in the reactor by air at 773 K (3 h), then by hydrogen at 723 K (2 h).

The reaction products were analyzed on line by gas chromatograph (Chrom-5) equipped with an FID detector at thermoprogrammed heating (3°C/min, column-modified γ-Al_2O_3, Ar).

3. Results and discussion

The results of the study of effect of promoter additives on Pt–Re catalysts are presented in Table 3.

It is shown that isomerization and aromatization activity of Pt–Re/Al_2O_3 catalysts are significantly dependent on decationization degree of NaY-zeolite. It has been shown that the conversion of *n*-octane and product composition at the reforming of *n*-octane over catalyst modified by NaY with 60% decationization degree is dependent on reaction conditions. The increase of experiment temperature from 723 to 773 K at $P = 1.0$ MPa causes the decrease of *n*-octane conversion from 57.8 to 50%. The formation of *i*-octane (21.8 and 16.2%), aromatics (19.3 and 20.1%), *iso*-C_5–C_7 (8.7 and 4.0%) and *n*-C_5–C_7 alkanes (6.6 and 7.4%) has been observed. With increase of pressure from 1.0 to 2.0 MPa the conversion degree decreases from 57.8 to 34.3% at 723 K and from 50.0 to 31.4% at 773 K. The selectivity of *i*-octane varies in the region 27.4–35.0% (Table 3).

The higher decationization degree of zeolite (90%) allows to increase *n*-octane conversion to 76.6% at optimal conditions (723 K, $P = 1.0$ MPa). This catalyst is characterized by high selectivity in isomerization process. At these conditions the selectivity on *i*-octane formation is 44.0%. Probably, the concentration of the acid centers responsible for the isomerization process is higher at 90% decationization degree in comparison with 60%. In result the equilibrium shifts

Table 2
The data obtained by electron microscopy and BET

Catalysts	S_{BET} (m^2/g)	TEM
Pt–Re–Cl/Al_2O_3 + HY(I)	133.0	Both on Al_2O_3 and zeolite: fine-dispersed particles (1.5–2.0 nm) and massive particles (10.0 nm)
Pt–Re–Cl/Al_2O_3 + HY(II)	147.7	Both on Al_2O_3 and zeolite: fine-dispersed particles (2.0–2.5 nm) and massive particles (4.0–5.0 nm) (basically on zeolite surface)
Pt–Re–Cl/Al_2O_3 + HZSM-5	155.3	Both on Al_2O_3 and zeolite: fine-dispersed particles (1.5–2.0 nm) and massive ones (3.0–5.0 nm) are uniformly distributed
Pt–Re–M–Cl/Al_2O_3 + HY(II)	232.2	Both on Al_2O_3 and zeolite: fine-dispersed particles (1.5–2.0 nm) and massive particles (4.0 nm) (basically on zeolite surface)

Table 3
Reforming of *n*-octane on modified Pt–Re–Cl/Al_2O_3 catalysts

Catalyst	*T* (K)	*P* (MPa)	Conversion (%)	Composition of catalysate (%)					Selectivity of *iso*-octane formation
				i-C_8	Benzene	Arenes	Σ*iso*-C_5–C_7	Σ*n*-C_5–C_7	
Pt–Re–Cl/Al_2O_3 + HY(I)	723	1.0	57.8	21.8	1.4	19.3	8.7	6.6	37.8
	773	1.0	50.0	16.2	2.3	20.1	4.0	7.4	32.4
	723	2.0	34.3	12.0	1.5	15.2	2.4	3.2	35.0
	773	2.0	31.4	8.6	2.0	16.5	1.4	2.9	27.4
Pt–Re–Cl/Al_2O_3 + HY(II)	723	1.0	76.6	33.8	0.9	22.8	8.9	10.2	44.0
	773	1.0	60.4	16.2	1.5	26.9	7.0	9.0	26.8
	723	2.0	71.0	31.2	0.01	11.5	12.5	15.8	43.9
	773	2.0	46.0	9.2	1.8	24.4	2.7	7.9	20.0
Pt–Re–Cl/Al_2O_3 + HZSM-5	623	1.0	85.6	14.0	2.8	20.5	21.4	22.0	16.4
	673	1.0	76.6	22.5	0.05	31.7	4.8	8.0	29.4
	723	1.0	72.3	18.5	–	29.3	3.5	11.4	25.6
	773	1.0	69.8	31.7	–	21.0	0.05	13.0	45.4
	623	2.0	91.0	19.0	–	11.4	31.7	28.4	20.9
	673	2.0	81.4	29.0	0.05	26.3	7.5	8.0	35.6
	723	2.0	77.0	21.0	–	26.5	2.0	7.5	27.3
	773	2.0	80.6	45.0	0.05	17.8	0.5	15.0	55.8
Pt–Re–M–Cl/Al_2O_3 + HY(II)	623	1.0	62.0	62.0	0.01	0.01	–	–	100
	673	1.0	55.3	40.0	1.3	12.7	0.01	1.3	72.3
	723	1.0	67.0	27.5	0.8	21.7	8.2	8.8	41.0
	773	1.0	45.0	13.0	0.01	31.8	0.2	0.01	28.8
	623	2.0	62.7	45.0	0.7	0.7	8.5	7.8	71.7
	673	2.0	72.7	64.0	0.01	7.6	0.1	1.0	88.0
	723	2.0	60.0	27.0	0.01	10.5	12.7	9.8	45.0
	773	2.0	73.8	22.4	1.0	39.4	6.5	4.5	30.4
Pt–Re/Al_2O_3	723	2.0	57.3	9.7	5.5	24.1	6.1	11.9	16.9
	773	2.0	70.5	4.0	7.8	41.3	7.0	10.4	5.6

to the isomerization reaction. At the same time the effect of hydrogenation–dehydrogenation function of catalyst was observed at an increase of the process temperature. With temperature increase from 723 to 773 K at $P = 1.0$–2.0 MPa, selectivity on *i*-octane decreases twice and it equals 20.0–26.8%. The content of aromatics increases from 24.4 to 26.9%. The decationization degree influences the catalyst cracking activity. The increase of decationization degree of NaY from 60 to 90% implies the increase of *iso*- and *n*-C_5–C_7 alkanes yield. This process is more active at $T = 723$ K and $P = 2.0$ MPa. The yields of *iso*- and *n*-C_5–C_7 alkanes are 12.5 and 15.8%, respectively.

For comparison the modified Pt–Re/Al_2O_3 catalyst was studied (Table 3). Basically the dehydrocyclization and hydrocracking reactions are presented on this catalyst. The selectivity of *i*-C_8 is significantly lower than on promoted HY catalysts.

The introduction of HZSM-5 zeolites with high change degree (99.0%) and (Si/Al) ratio = 34 into catalyst composition increases the catalyst activity (Table 3). The high *n*-octane conversion is observed at more mild process conditions. The *n*-octane conversion is 85.6 and 91.0% at $P = 1.0$ and 2.0 MPa, respectively ($T = 623$ K). The *iso*-octane yield is 14.0–19.0%. At these conditions significant amount of products of hydrocracking, isomerization and hydrocyclization are formed. Significant formation of C_{9+}-hydrocarbons was observed. Hydrocracking activity sharply grows at low temperature ($T = 623$ K). The maximum yield of *iso*- and *n*-C_5–C_7 are 31.7 and 28.4% ($P = 2.0$ MPa).

The temperature increase from 623 to 773 K implies the conversion decrease from 85.6 to 69.8% at $P = 1.0$ MPa and from 91.0 to 80.6% at $P = 2.0$ MPa. At these conditions the *iso*-octane yield increases to 31.7 and 45.0%, respectively, and the yield of *iso*-C_5–C_7-hydrocarbons decreases from 21.4 to 0.05% and from 31.7 to 0.5%, respectively. The yield of aromatics is 21.0% at $P = 1.0$ MPa and 17.8% at $P = 2.0$ MPa ($T = 773$ K). Also the yield of *n*-C_5–C_7 alkanes decreases. The speciality of this catalyst is the absence of benzene in reaction products. Mainly *p*- and *o*-xylene are formed.

As a promoter for Pt–Re–Cl/Al_2O_3 also the additive of V group element (M) was used. The introduction of this promoter significantly increases the isomerization activity of catalyst (Table 3). Selectivity of *iso*-octane formation reaches 100% at conversion = 62.0%, $T = 623$ K and $P = 1.0$ MPa. With temperature increase (673–773 K) activity and selectivity significantly decrease. At these conditions the yield of aromatics increases from 14.0 to 31.8%.

At pressure increase up to 2.0 MPa the optimal process temperature shifts to high values. Maximum conversion of *n*-octane is 72.7% accompanied by *iso*-octane yield = 64.0% is observed at $T = 673$ K. *Iso*-C_5–C_7 (0.1%) are formed too. The isomerization activity decreases and yield of aromatic hydrocarbons increases (basically *o*- and *p*-xylene) at $T > 673$ K.

It is possible that the high isomerization activity depends on an increase of the concentration of the acid centers and dispersion of metals at modification of catalyst by additive (M). By TEM it has been shown that Pt–Re–M–Cl/Al_2O_3 + HY(II) catalyst is a complex of structures with particle size of 1.5–2.0 and 4.0 nm (Table 2). The particles are uniformly distributed on the surfaces of both Al_2O_3 and zeolite. The particles with size of 4.0 nm are basically distributed on the zeolite surface. The increase of S_{BET} of the modified catalyst was caused by the increase of dispersion of active phase.

4. Conclusions

The obtained data indicate that modification of Pt–Re/γ-Al_2O_3 catalyst by decationized NaY and NaZSM-5 zeolites significantly increases its isomerization activity. It is caused because of high acidity of zeolites, their optimal sizes and pore structures that are favorable to the greater rapprochement of molecules and reaction beginning.

The conversion of *n*-octane increases in the order of: HY(I) < HY(II) < HZSM-5. Consequently the value of ion change degree and (Si/Al) ratio of zeolites affect the properties of catalyst for reforming. HZSM-5 zeolite in comparison with the HY one has higher activity in the hydrocracking reaction at low process temperature and isomerization activity at high temperature.

The multicomponent modification of Pt–Re/Al_2O_3 catalyst allows the increase of its isomerization activity in *n*-octane reforming at mild conditions. Maximum selectivity of *iso*-octane formation is 100% at conversion 62.0%.

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