

## Modified Zeolite-containing Pt-Re/Al<sub>2</sub>O<sub>3</sub> catalysts for reforming of C<sub>7</sub>-C<sub>9</sub>-n-paraffins

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### Abstract

The effect of promoter additives to Pt-Re/Al<sub>2</sub>O<sub>3</sub> – zeolite catalysts on their properties at C<sub>7</sub>-C<sub>9</sub> paraffins reforming was investigated. It has been established that a rise of decationization degree of zeolite from 60 to 90% is accompanied by increase of catalyst activity and improvement of quality of final products. On Pt-Re/Al<sub>2</sub>O<sub>3</sub> catalyst modified by 0,6% Re the high conversion of C<sub>7</sub>, C<sub>8</sub>, C<sub>9</sub> – hydrocarbons (74%, 60% and 82% respectively) was observed at P=1.0 MPa, T=623K. The promoter additives allow a rise the selectivity of iso-octane formation to 100% at P=1.0MPa, T=623K. The high stability of catalyst was observed without activation at its test under optimal conditions.

### Introduction

At present, catalytic reforming has an importance for the production of reformulated gasoline [1,2]. It is necessary to use more effective catalysts and the development of new technologies for the improvement of reforming process. Because of the role of processes of both alkylation and isomerization of paraffins, C<sub>4</sub>-C<sub>5</sub> and C<sub>5</sub>-C<sub>9</sub> respectively, is significantly increasing [3,4]. These paraffins are a base of straight run gasoline.

Zeolitic catalysts are more effective ones for these processes [5-7]. Due to certain pore structure they promote more intensive running of the isomerization process than  $\gamma$ -alumina. A new approach to creation of highly effective reforming catalysts is a replacement of part of alumina with synthetic zeolite.

In this report the effect of promoter additives to Pt-Re/Al<sub>2</sub>O<sub>3</sub> –zeolite catalysts on their properties at C<sub>7</sub>-C<sub>9</sub> paraffins reforming was studied.

### Experimental

The catalysts containing 0.35% Pt, 0.35-0.6% Re and 1% Cl were prepared by impregnation method.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $S_{\text{bet}}$  – 152.3 m<sup>2</sup>/g) was modified by synthetic zeolite NaY in hydrogen forms (HY(I), HY(II)). The ratio between Al<sub>2</sub>O<sub>3</sub> and zeolite was 9 : 1.

The impregnation solution consisting of H<sub>2</sub>PtCl<sub>6</sub>, HReO<sub>4</sub> and HCl was added to support at mixing and then kept at room temperature during 1 hour. The examples were formed as extrudates with size 1.5-2 mm. The extrudates were dried on air and calcined at T = 773K during 3 hours.

Previously zeolite was exposed to decationization by treatment of NH<sub>4</sub>NO<sub>3</sub> solution. Then it was washed with distilled water until reaching of pH = 7 and calcined at 813K. The degree of decationization was controlled by spectral analysis.

The process was carried out in a flow reactor under higher pressure (1.0-2.0MPa) with variation of experimental temperature from 623 to 773 K, a feeding flow rate of 1,5 h<sup>-1</sup> and hydrogen flow rate of 1000 ml/h. After two hours of the process and transition to a steady state the periodic sampling for analysis was carried out.

The reaction products were analysed by gas chromatography at thermoprogrammed heating (column – modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>). The catalysts were studied by X-Ray Analysis, BET, electron microscopy, derivatography etc.

### Results and discussion

Selectivity of Pt-Re/Al<sub>2</sub>O<sub>3</sub> –catalysts of reforming combining both isomerization and hydrogenation-dehydrogenation functions depends on the content and

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properties of acid centres. It causes the changes of ratio of products of aromatization and isomerization

of n-alkane on Pt-Re zeolite-containing catalysts with different decationization degree (Table 1).

**Table 1**  
Reforming of N-octane on Pt-Re/Al<sub>2</sub>O<sub>3</sub> + Zeolite catalysts

Catalysts	T, K	P, MPa	Conversion, %	The composition of catalysate, %					Selectivity of i-octane formation
				i-C <sub>8</sub>	Benzene	Arenes	∑ <sub>i</sub> (C <sub>5</sub> -C <sub>7</sub> )	∑ <sub>n</sub> (C <sub>5</sub> -C <sub>7</sub> )	
K <sub>1</sub> Z-1	723	1.0	57.8	21.8	1.4	20.7	8.7	6.5	37.8
	773	1.0	50.0	16.2	2.3	22.4	4.0	7.4	32.4
	723	2.0	34.3	12.0	1.5	16.7	2.4	3.0	35.0
	773	2.0	31.4	8.6	2.0	18.5	1.4	2.9	27.4
K <sub>2</sub> Z-2	723	1.0	76.6	33.8	0.9	23.7	8.9	10.2	44.0
	773	1.0	60.4	16.2	1.5	28.4	6.9	9.0	26.8
	723	2.0	71.0	31.2	traces	11.5	12.5	15.8	43.9
	773	2.0	46.0	9.2	1.8	26.2	2.7	7.9	20.0
K <sub>3</sub> Z-2	723	1.0	63.0	33.8	0.7	17.0	6.4	5.3	54.0
	773	1.0	56.7	18.9	1.3	23.5	6.5	5.9	33.3
	723	2.0	60.5	28.7	traces	10.5	7.8	6.1	47.4
	773	2.0	72.5	19.6	1.4	37.3	8.0	7.6	27.0

The n-octane conversion on catalyst (K<sub>1</sub>Z-1) with comparatively low degree of decationization of NaY-zeolite about 60% is not more than 58%. At this case the selectivity of i-octane is 37.8%. The increase of experiment temperature from 723 to 773K at P=1.0 MPa causes a decrease of i-octane content to 32.4%. With increase of pressure from 1.0 to 2.0 MPa the conversion degree decreases to 34.3 % at 723K and 31.4% at 773K. The selectivity of i-octane varies in region 27.4-35.0%.

The higher decationization degree of zeolite (catalyst - K<sub>2</sub>Z-2) is about 90%, allows to increase n-octane conversion to 77% at optimal conditions (723K, P=1.0 MPa). This catalyst is characterised the high selectivity in isomerization process. In these conditions the selectivity of i-octane formation is 44.0%.

The yield of i-octane depends on reforming process conditions. With temperature increase from 723 to 773K at P=1.0-2.0MPa selectivity of i-octane decrease appreciable and is equal 20.0-26.8%. At the same time the content of aromatics increases by 4.7 and 14.7%, respectively.

On catalyst (K<sub>3</sub>Z-2) with lower content of platinum and higher Re content insignificant decrease of n-octane conversion was observed on comparison with K<sub>2</sub>Z-2. At the same time the selectivity of i-octane formation increases by 3 to 10% at P=1.0-2.0 MPa, T<sub>exp</sub>=723-773K.

Zeolite-containing catalyst K<sub>3</sub>Z-2 has a high activity and selectivity at low experimental temperature in reaction of C<sub>7</sub>-C<sub>9</sub> alkanes (Table 2). The high conversion of C<sub>7</sub>, C<sub>8</sub>, C<sub>9</sub> – hydrocarbons (74%, 60%, 82% respectively) was observed at 623K and 1.0 MPa. Selectivity of isomer formation are 47.0% for i-C<sub>7</sub>, 86.6% for i-C<sub>8</sub> and 54.4% for i-C<sub>9</sub>. The content of aromatics in reaction products is low and varies from 4% to 14%. The increase of both pressure and temperature up to P=2.0 MPa and T=673 K respectively causes the rise of conversion. It occurs due to the increasing of formation of C<sub>5</sub>-C<sub>6</sub> alkanes which are the products of hydrocracking. The total yield ∑(i-C<sub>5</sub>-C<sub>6</sub>) increases by 6.5% at n-octane conversion and by 13.2% at n- nonane conversion.

Additional catalyst modification by acid additive for increase of its isomerization properties results in an increase of the selectivity of i-octane formation up to 100% at P=1.0 MPa, T=623 K (Table 3). The synthesised catalyst (K<sub>4</sub>Z-2) showed a high activity and isomerization capacity at the low temperatures of process (T=623-673 K). The increase of temperature from 623 to 773K at P=1.0MPa decreases the i-octane formation from 100 to 28.8%. At the same time the increase of aromatic formation to 31.8% at P=1.0 MPa and from 1.4% to 40.4% at P=2.0 MPa occurs.

It needs to note that the content of benzene does not exceed 1.3%. Basically p- and orto- xylene are domi-

nated. Earlier [8] the high aromatic ability of the standard Pt-Re/Al<sub>2</sub>O<sub>3</sub> catalyst was showed. 7.8% of benzene was formed on this catalyst at P=2.0 MPa and T=773 K.

The high stability of catalyst K<sub>4</sub>Z-2 was observed without their activation at test under optimal conditions. Its activity did not change during 40 hours of exploitation.

**Table 2**Reforming of C<sub>7</sub>-C<sub>9</sub> paraffins on K<sub>3</sub>Z—2 catalyst

Feed	Experimental conditions	Conversion, %	The composition of catalysate, %						Selectivity of i-alkanes formation
			i-C <sub>7</sub>	i-C <sub>8</sub>	i-C <sub>9</sub>	∑ i (C <sub>5</sub> -C <sub>6</sub> )	∑ (C <sub>5</sub> -C <sub>9</sub> )	∑ aromatics	
n-Heptane	P=1.0 MPa T=623 K	74.0	35.0	17.9	-	1.3	33.5	12.3	47.0
	P=2.0 MPa T=673 K	77.2	41.2	3.8	-	3.5	27.2	14.3	53.4
n-Octane	P=1.0 MPa T=623 K	59.6	0.8	51.6	-	1.5	42.3	3.8	86.6
	P=2.0 MPa T=673 K	74.0	1.2	53.0	-	8.0	30.8	6.9	67.0
n-Nonane	P=1.0 MPa T=623 K	82.2	0.5	0.75	44.7	4.3	44.6	5.2	54.4
	P=2.0 MPa T=673 K	83.0	traces	traces	35.0	17.5	38.8	8.7	42.0

**Table 3**Reforming of N-octane on K<sub>4</sub>Z-2 catalyst

Experimental conditions	Conversion, %	The composition of catalysate, %								Selectivity of i-octane formation	
		i-C <sub>8</sub>	benzene	Toluene	p-xylenes	o-xylenes	∑ i (C <sub>5</sub> -C <sub>7</sub> )	∑ n (C <sub>5</sub> -C <sub>7</sub> )	∑ aromatics		
P=1.0 MPa	T=623 K	62.0	62.0	traces	-	-	-	-	-	traces	100
	T=673 K	55.3	40.0	1.3	2.0	8.4	2.4	traces	1.3	14.0	72.3
	T=723 K	67.0	27.5	0.8	3.5	13.4	4.8	8.2	8.8	22.5	41.0
	T=773 K	45.0	13.0	traces	4.2	18.6	9.0	traces	traces	31.8	28.8
P=2.0 MPa	T=623 K	62.7	45.0	0.7	-	0.7	traces	8.5	7.8	1.4	71.7
	T=673 K	72.7	64.0	traces	1.4	4.8	1.6	traces	1.0	7.8	88.0
	T=723 K	60.0	27.0	traces	1.8	6.5	2.2	12.7	9.8	10.5	45.0
	T=773 K	73.8	22.4	1.0	4.6	24.0	10.7	6.5	4.5	40.4	30.4

The changes may be explained with increase of concentration of supported acid centres as well as dispersion of metals (Table 4).

BET analysis of these catalysts showed an increase of surface area from 133.0 to 232.2 m<sup>2</sup>/g at introduction of promoter additives. By electron

microscopy the fine-dispersed structures with size of 1.5-2.5 nm uniformly distributed on support surface were observed. Also, the massive structures with size of not more 4.0 nm partly were formed. It is possible, the promoter of acid nature increases the specific area of catalyst as well as the dispersion of metals.

**Table 4**  
The data obtained by electron microscopy and BET

Catalysts	S <sub>BET</sub> , m <sup>2</sup> /g	TEM
K <sub>1</sub> Z-1	133.0	Irregular distribution: fine-dispersed particles - 1.5-2.0 nm and massive particles - 10.0 nm
K <sub>2</sub> Z-2	147.7	Irregular distribution: fine-dispersed particles - 2.0- 2.5 nm and massive particles - 4.0-5.0 nm
K <sub>3</sub> Z-2	160.6	Basically: massive particles - 4.0-5.0 nm + fine-dispersed - 2.5 nm
K <sub>4</sub> Z-2	232.2	Regular distribution: fine-dispersed particles - 1.5-2.0 nm and massive particles ~ 4.0 nm

### Conclusions

The modification of Pt-Re/Al<sub>2</sub>O<sub>3</sub> by the decationization of NaY zeolites significantly increases its isomerization activity in the reforming of C<sub>7</sub>-C<sub>9</sub> hydrocarbons. With increase of ion exchange degree of zeolite in catalyst composition the conversion and selectivity are increased. Multicomponental modification of Pt-Re/Al<sub>2</sub>O<sub>3</sub> catalyst allows to increase its isomerization activity in n-octane – reforming at the mild conditions.

### References

1. A.F. Akhmetov, N.R. Saifullin, and K.G. Abdulminev, *Neftehimiya i neftepererabotka*, Vol. 7, p. 42-47 (1998).
2. V.E. Pierce, B.B. Bansal, *Chemical Engineering Progress*, Vol. 82, No. 3, p 27-33 (1986).
3. C.L. Gray, In *National Conf. Of Octane Quality and Reformulated Gasolines*, p. 73 (1992).
4. A. Djezak, *Neftegazovye tehnologii*, Vol. 1, pp. 55-57 (1995).
5. A.A Kamensky, A.A. Kuzmina, V.A. Tremasov, and S.G. Procopuk, *Tem. Obzor*, p. 18-21 (1993)
6. V.G. Stepanov, G.P. Snytnikova, and K.G. Ione, *Neftehimiya*, Vol. 32, No. 3, pp. 243-249 (1992).
7. Ya.I. Isakov, *Neftehimiya*, Vol. 38, No. 6, p. 404-438 (1998).
8. G.D.Zakumbaeva, N.V.Perkas and T.V.Van, *Neftehimiya*, Vol.39, No.4, p.274-277 (1999).

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