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Kazakhstan Natural Clays Based Catalysts for Isomerization of n-Hexane

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Abstract

Isomerization of n-hexane was carried out in the presence of hydrogen over Pt- and Pt-Re- supported on the matrix of complex composition (natural klinoptilolite clay, alumina-silica gel) and alumina. Pt- catalysts on the compost containing clinoptilolite clay, alumina-silica-gel, decationed and exchanged zeolite (HCeY) showed the isomers selectivity at a wide range of temperature interval (350-450 ^oC). It was shown that the high activity and selectivity of studied catalysts correlated with the concentration of strong and medium acid sites on the surface of catalysts.

Introduction

Isomerization of light n-alkanes which leads to branched alkanes is important for the production of a high octane number gasoline with low content of aromatics and lead [1-2]. The reactions of isomerization are limited by balance of isomers transformations, thus the low temperatures promote an increase in the content of high octane isomers. The reactions proceed over a stationary layer of the catalyst at the presence of hydrogen.

Skeleton isomerization of n-alkanes is carried out, as a rule, over bi-functional catalysts with two types of active sites: metallic ones for dehydrogenation (Pt, Pd, Ir) and acidic ones for isomerization (special zeolite materials).

Recently the tendency of design catalyst on the basis of mixed matrixes including both natural and synthetic zeolites and also other components, has been observed. The latter promotes the increase of surface acidity, catalyst life and regular distribution of active sites on the catalysts surface. It is supposed, that developed methods of catalyst preparation will help to produce high effective catalysts for this process.

The aim of the work was to investigate the influence of decationing and modification of zeolite component of Pt and Pt-Re catalysts, supported by semi-synthetic natural klinoptilolite matrix, on distribution and strength of acidic sites of the catalysts and their activity in isomerization of n-hexane.

Experimental

In order to increase mechanical durability of the catalyst grains we used γ-Al_2O_3 or alumina-silica gel (ASG). Matrixes for catalysts were prepared by mixing of components.

Natural clay containing 65% of klinoptilolite zeolite was treated with 0.25% HCl solution in order to remove Ca, Mg, Na, Fe impurities. During the treatment, acidic sites are forming and pores are expanding together with de-cationing. At the same time, crystal structure of alumina-silica frame remains unchanged. We treated zeolite NaY ($SiO_2/Al_2O_3 = 4.6$) with NH_4NO_3 in order to remove Na ions completely from all the cavities. Then we carried out ion exchange with Ce^{3+} to stabilize H-Y form of the zeolite.

Support was impregnated 0.35 mass % of Platinum by solution of H_2PtCl_6; Rhenium (0.35 mass %) by impregnation with ammonium perrhenate.

n-Hexane isomerization was carried out in a laboratory flow reactor at atmospheric pressure under the following conditions: volume of catalyst is 5 ml, H_2/n-hexane ratio - 3.5, flow rate - 0.82 h^{-1}, temperature 250-450 °C. A chromatograph with capillary columns was used for qualitative analysis of products. Fig.1 shows apparatus scheme for isomerization of n-hexane.

Method of ammonia temperature programmed des-

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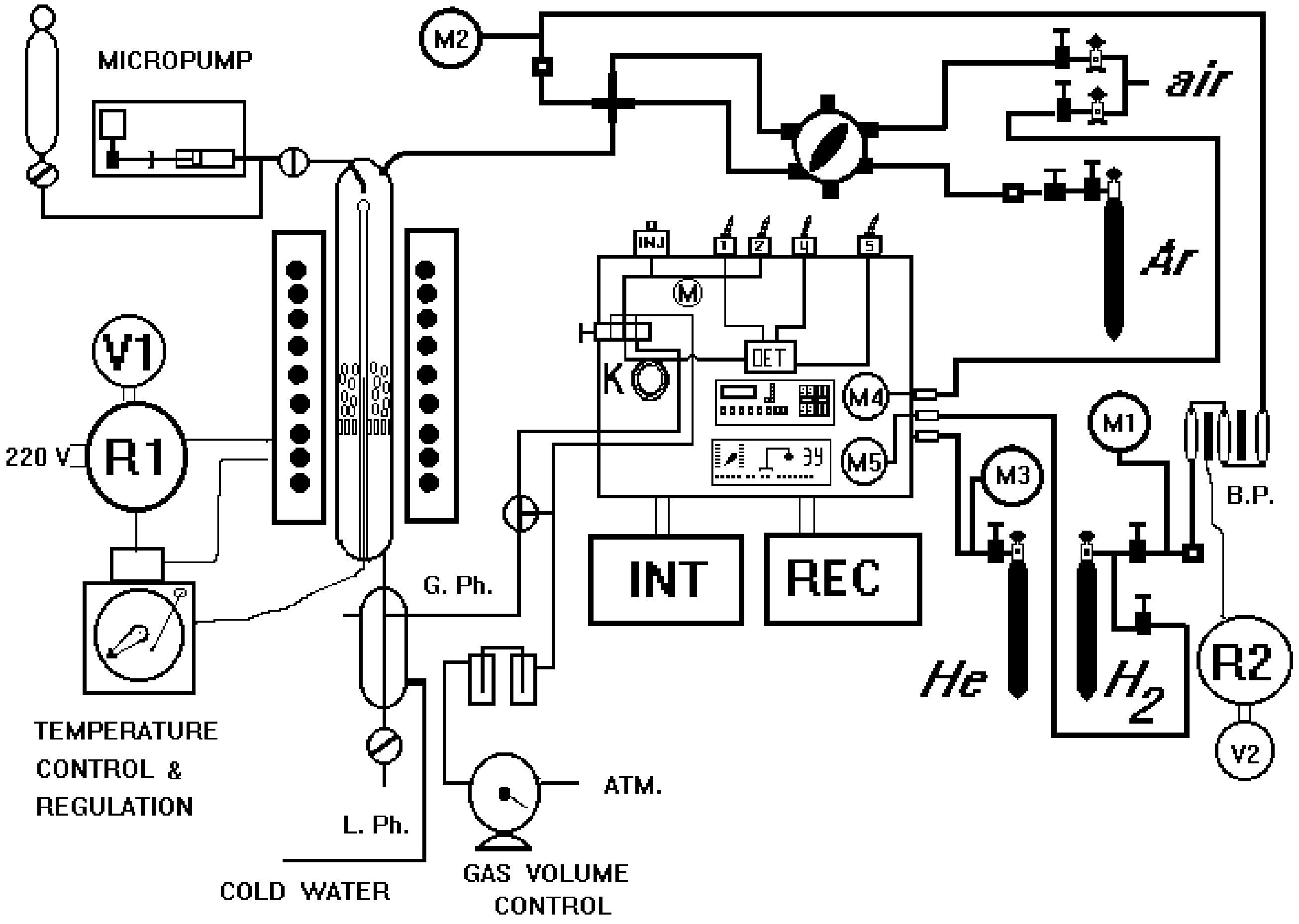

Fig.1.Apparatus for measuring the catalytic activity in reaction of isomerization of n-hexane. (INT - integrator; REC - recorder; H.P. - bloke of hydrogen purification; G.Ph.- gas phase; L.Ph. - liquid phase; K -capillary column; M 1-5 - manometers)

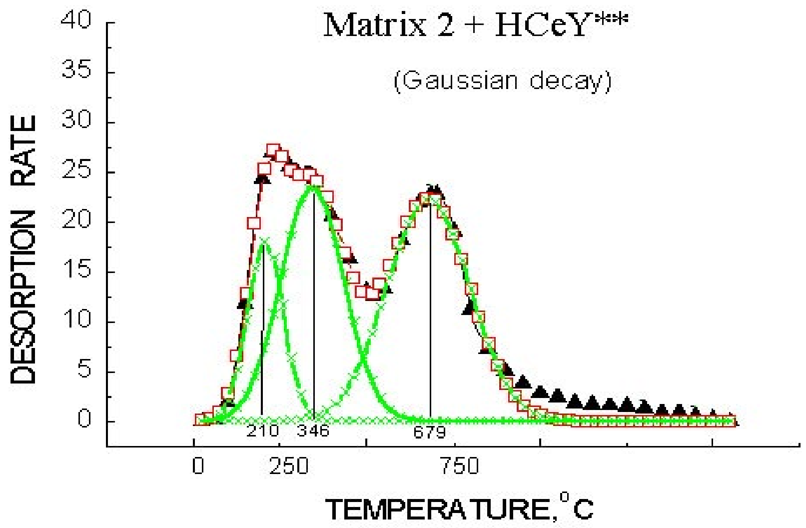

Fig.2. Deconvolution analysis results of the NH_3-TPD spectrum in case of the one sample. Legend: (—▲—) experimental data; (— X —) calculated curves for desorption from three different types of sites; (—□—) theoretical curve of overall desorption.

orption was used for determination of acidic sites concentration.. Measurements, in the range 25 - 750 ^{o}C, were performed in a conventional flow apparatus using a linear quartz reactor, at heating rate of 7.5 K/min and He carrier flow rate 100 is ml/min. The desorption process was monitored by a catarometer connected with reactor on line. Deconvolution analysis results of the ammonia spectra have shown that experimental and theoretical curves are practically identical. It may be observed on the spectrum of one of the samples (Fig. 2).

Results and discussion

The initial clay, as a rule, contains in the structure alkaline and rare metals, which reduce acidity of its surface. Therefore, the clay previously activated in acids at heating. During the process of treatment by acid it occurs, both decationation, formation of acidity centres and expansion pores and channels in structure of clinoptilolite. Thus the crystallite structure of alumina-silica frame is kept [3].

According to element analysis, ion exchange with Ce^{3+} is effective after almost complete removal of Na ions from the zeolite (to less than 0.6 mass %). Ion exchange with cerium helps to remove strongly bonded Na ions from hardly accessible NaY zeolite cavities and to stabilize H-Y form. Fig.3 shows the ammonia-TPD spectra of the initial samples (a) and impregnated samples (b).

It is seen from Fig.3 and Table 1., that two-fold treatment of the zeolite with $Ce(NO_3)_3$ yields three time increase in the concentration of acidic centers as compared to one time treatment, due to an increase in strong acidic centers concentration. Similar situation is observed at Pt/matrix + HCeY catalysts.

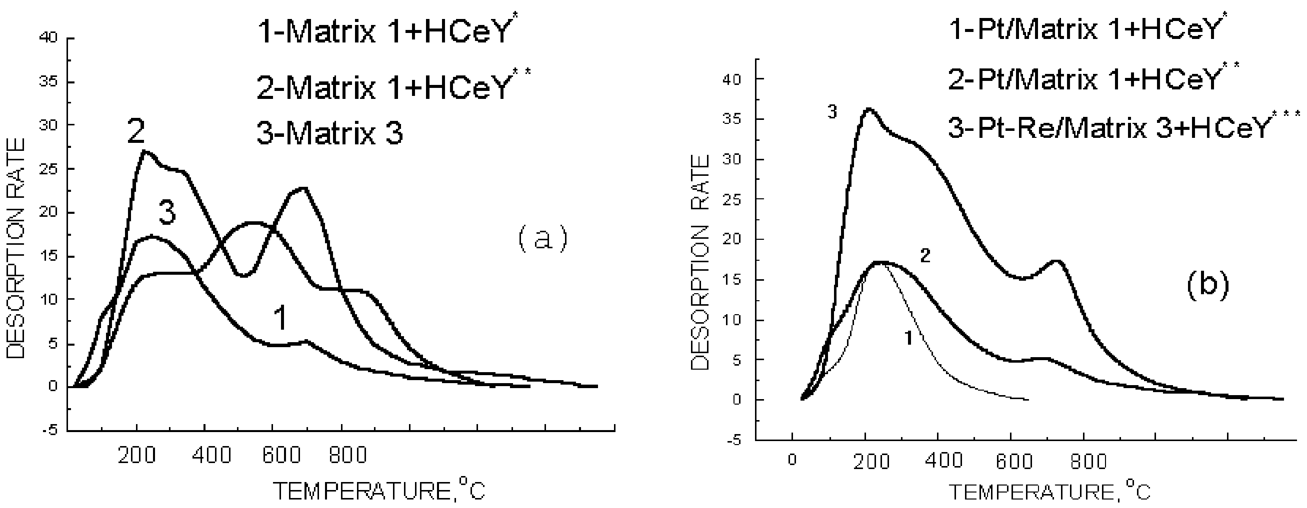

Fig. 3. TPD spectra of NH_3 for the catalysts used in this work. (a) - initial samples: Matrix 1 - Clay + Alumina; Matrix 3 - Alumina (Ketjen)

Table 1.

Concentration and distribution of acidic sites on the initial samples and catalysts.

Catalyst	Center of the peak, ^{o}C (gauss analyze)			Distribution of active sites, mmol NH_3/g (cat)			
	1	2	3	Total amount	1	2	3
Matrix 3	198	407	705	512.8	64.7	282.3	165.8
Matrix 1 +HCeY*	204	261	728	243.5	59.0	143.9	40.6
	210	346	679	762.7	125.4	283.4	353.9
Pt/ Matrix 1+HCeY *	201	249	560	207.6	109.4	89.1	9.1
Pt/ Matrix 1+HCeY **	184	315	612	402.5	92.7	166.2	143.6
Pt-Re/ Matrix 3+ HCeY ***	190	349	692	945.5	156.7	498.6	290.2

*- number of zeolite treatments with $Ce(NO_3)_3$ (markings the same as in the Fig.3)

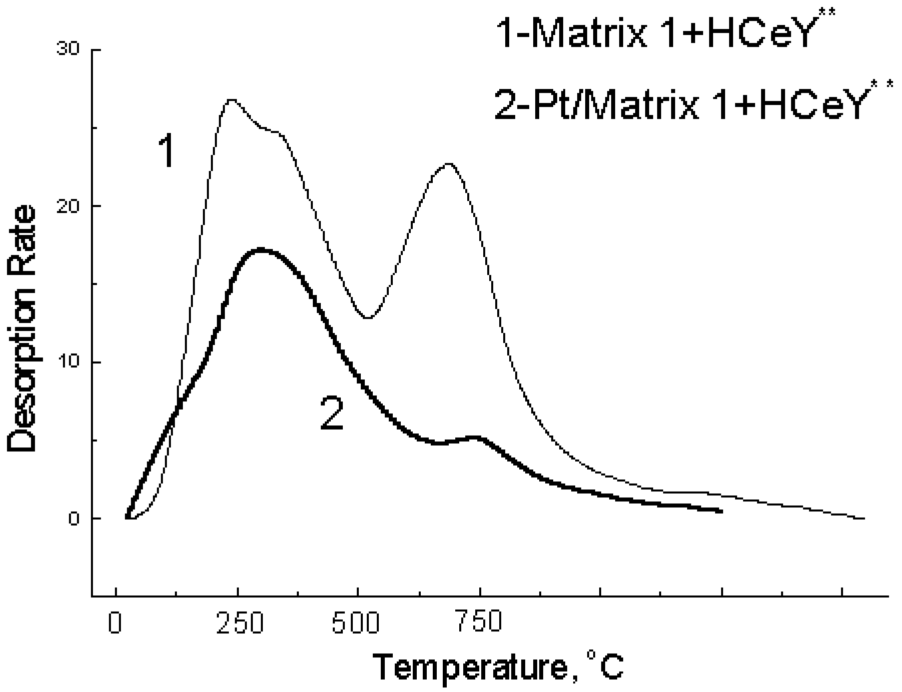

Fig. 4. TPD spectra of ammonia for samples without and with platinum.

However, it is necessary to point out that concentration of acid centres in the presence of active metal, in contrast with initial sample, is decreasing. It may be observed on the Fig.4, where the spectrum of one of the initial samples and the spectrum of this sample, but impregnated with Platinum are shown.

n-Hexane isomerization is more complete over the catalyst which has passed 2-fold treatment with $Ce(NO_3)_3$ solution. Thus, n-hexane conversion at 450°C over catalyst with 2- and 1-fold treatment was 44.7% and 31.6% respectively (Table 2). Compared with 350°C at this temperature cracking of the products is increasing. This reduces the selectivity for isomers up to 88.6% and 83.4% respectively. Using of ASG as a component of the support after 3-fold cerium treatment suppresses the cracking and reduces the activity of the catalysts, but the selectivity is 99.7%.

It is known that Re input lets increase thermal stability of catalysts [4]. We synthesized Pt-Re catalyst with optimum matrix composition. Total concentration of acidic centers on it was 945.5 μmol NH_3/g (cat). Tests of the catalyst showed that in the same tempera-

Table 2

n-Hexane isomerization over Pt- and Pt-Re catalysts

Catalyst	Rate of n-hexane conversion, %			Selectivity according to isomers, %		
	Temperature, ^{O}C			Temperature, ^{O}C		
	250	350	450	250	350	450
Pt/ Matrix 1+HCeY *	1.2	28.2	31.6	99.9	98.4	83.4
Pt/ Matrix 1+HCeY **	1.6	34.3	44.7	99.9	98.6	88.6
Pt/ Matrix 2 + HCeY ***	1.3	26.3	38.7	98.5	99.7	99.7
Pt - Re/ Matrix 3 + HCeY ***	1.1	33.6	53.2	99.1	99.8	97.6

* - number of treatments of the zeolite with $Ce(NO_3)_3$ solution
Matrix 1 – clay + alumina
Matrix 2 - clay + ASG
Matrix 3 – alumina (Ketjen)

ture interval it is more active than the other catalysts, but its selectivity is a bit less than for catalyst supported by natural clay matrix. Besides, the C7-C8 hydrocarbons appear on this catalyst.

Conclusions

Complex matrix from natural clinoptilolite clay and Pt- , Pt-Re- catalysts on these matrixes and alumina have been systematically studied by ammonia TPD method. Developed catalysts containing natural and synthetical zeolites, showed high activity and selectivity in reaction of isomerization of n-hexane at temperature interval (350-450 ^oC) and atmospheric pressure. Conversion of n-hexane over the Pt-Re/matrix 3+HCeY*** reached 53.2 mass.% and selectivity 97.6 % at 450^oC. Pt/matrix 2 + HCeY***- catalyst was showed 38.7 mass.% conversion and selectivity 99.7% at the same temperature. Our results reveal that the application of natural clinoptilolite in complex matrix leads to an increase in isomer selectivity in reaction of n-hexane hydroisomerization. From the TPD experiments, it can be concluded that reactivity in n-hexane isomerization reaction is controlled by both medium and strong acid sites on all the catalysts.

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