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Natural Clays of the Kazakhstan Deposits for Catalysts of Cracking

N.A. Zakarina*, L.D. Volkova and O.V.Chshukina

D.V. Sokolsky Institute of Organic Catalysis and Electrochemistry
142 Kunaev St., 480100, Almaty, Kazakhstan

Abstract

Presented paper is devoted to the construction of cracking catalysts based on H-form zeolite Y, modifying by heteropolyacids of 12 row decationzed forms of natural clays of Tagan and Narynkol deposits. Conditions of acid activation were compared for Tagan clay. Chemical composition of clays before and after activation was detected by optical emission spectral method; phase composition was detected with X-ray diffraction. It has been shown that activities of composite catalysts are related to the concentration and sequence of HPA adding. From the results the conclusion was drawn that amount of adding HPA influenced the activity and thermal stability of catalysts prepared on the base of Tagan and Narynkol clays deposits. The synthesized catalysts were studied in a laboratory microimpulse catalytic set by the model reaction of isopropylbenzene cracking at temperature 350-500°C. The optimum compositions of zeolite containing contacts served as the base of creation of cracking catalysts for real raw (kerosene-gas-oil fraction) into quartz reactor with a fixed catalyst bed. These prepared catalysts have demonstrated enhanced thermal stability and high activity. Stronger cracking activity of catalysts prepared on the base of Narynkol clay has been shown.

Introduction

The creation of catalytic technologies with usage of natural raw is economically most advantageous way for a resolution of modern problems of a chemical, petrochemical and oil refining industry. Use of natural clays in constructing the catalysts for the cracking of hydrocarbon raw is an actual task.

The introduced report is dedicated design of modifying catalysts for cracking on the basis of the H-form of a zeolite NaY and decationized forms of natural clays of Tagan and Narynkol deposits with addition of heteropolyacids (HPA) of 12 row. It is known, that HPA are close in structure to zeolites [1,2]. They promote a dispersion of metals on the surface [3,4] of the carrier, resulting to the formation of particles of a cluster type and allocation them in pores of a zeolite [4-6], and also to the growth of heat stability of a contacts [2,4].

Experimental

The natural activated clays were applied by us as a matrix and binder for preparing a series of catalysts. Beforehand the clays were grinded to a fraction 0.25 mm and then was treated with 20% H_2SO_4 at 97°C for 6 hours after that it was washed from ions SO_4^{2-} and dried. Besides, the comparative activation for Tagan clay by 30% sulfuric acid was held at room temperature [7] following by washing.

H-form of zeolite Y (SiO_2/Al_2O_3=4.75) was obtained by standard procedure [8] of ammonium ion exchange in 1M NH_4Cl at 80°C during one hour with the next fourfold decantation with following drying at room temperature and thermal activation at 500°C. The exchange degree of Na^+ to H^+ in zeolite NaY with intermediate calcination was 90.1% detected by optical emission spectral analysis (OESA).

The obtained samples of clays after their calcination at 550°C were mixed with a zeolite (15%), then were moulded in pellets by a size of 2-2.5 mm, and were dried at room temperature within 24 hours and calcinated in temperature range 150-550°C. For an estimation of heat stability all catalysts were exposed to heat treatment at 750°C. The concentrations HPA from 0.3 to 3% were investigated. HPA were added as the modifying components into the catalytic system: zeolite - matrix.

HPA were added by two ways. First way (way 1)

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*corresponding authors. E-mail: orgcat@nursat.kz consisted of impregnation of zeolite-containing composition with heteropolyacid with the subsequent moulding, drying at room temperature and step-by-step incineration at 150-550°C. In second way (way 2) HPA was inputted into clay, a mixture was calcinated at 550°C and then mixed with a zeolite. Subsequently, we acted in the first way.

Catalysts activity was investigated in the micro-impulsive reactor in cracking reaction of model hydrocarbon of isopropyl benzene (IPB) and into quartz reactor with a fixed catalyst bed in cracking of real raw of kerosene-gas-oil fraction (KGF), with T_{boil} = 205-350°C of oil. In the first case the former activity was determined by extent of conversion IPB, in the second – by a petrol fraction yield with end of boiling at 205°C.

The preliminary thermal treatment of catalyst (0.2 g) in IPB cracking was carried out in air stream during 2 hours at 550 and 750°C. Then air was changed for argon that was blown during one hour. The rate of Ar flow was 33 cm^3/min. IPB cracking was investigated in the 350-500°C temperature range. The IPB portion was 4 µl. Stability of the catalyst work was determined by conversion level 4-5 IPB portions. The catalyst (20 cm^3) in the reactor with fixed bed for experiment was placed under quartz layer. Catalytic tests were performed at above mentioned conditions in cracking KGF. Experiment was performed during 20 min and then catalyst was regenerated at 600°C. Feeding flow rate of KGF was 1.5 $hour^{-1}$.

X-ray diffraction analysis (XRD) of catalyst samples was carried out by DRON-4×0.7 – machine with Co-anode.

Results and discussion

According to XRD, the main components of Naryncol clay before acid activation are: α-quartz (5.9); calcite (7.5); muscovite (6.8); dolomite (1.7); hydromiceous (1.9); kaolin (0.1). Numbers in brackets belong to the height (cm) of the most peak intensity on the X-ray patterns above called components. After acid activation phase composition has been changed: α-quartz (9.0); hydromicaceous (2.5); anhydrite (3.48). So it was established by X-ray analysis date that Naryncol clay is classified to number micaceous types. It was defined its raised stability to high temperature affecting. We admit that phase muskowit determines the micaceous character of Naryncol clay.

An elemental composition (AESA) of Narynkol clay before acid activation was, wt.%: Na_2O-1.7; K_2O-2.2; Al_2O_3-17.0; CaO-10.0; MgO-4.0; Fe_2O_3-1.0; SiO_2-64.1; after acid activation was: $\Sigma(Na_2O + + K_2O)$-3.0; Al_2O_3-15.0; CaO-0.3; MgO-0.5; Fe_2O_3-0.3; SiO_2-the rest remaining. The relative increase of content Na and K of into the clay after acid treatment is related with the practically full removal of calcium, magnesium, iron oxides.

Tagan bentonitic clay is Na-montmorillonite of the next chemical composition, wt.%: SiO_2-79.0; Al_2O_3-15.0; MgO-1.1; CaO-0.2; Na_2O-0.8; K_2O- 0.5; Fe_2O_3-0.3 and 3.1 (in the total) impurities of titanium, magnese and strontium oxides; after acid activation was: Al_2O_3-15.0; MgO-0.8; CaO-0.1; $Na_2O < 0.01$; $K_2O < 0.5$; Fe_2O_3-0.2; SiO_2- the rest remaining.

Initial Tagan clay (bentonite) according to X-ray analysis before acid activation is consisted of montmorillonite-(6.0), α-quartz-(3.5); after acid activation was: montmorillonite-(4.2); α-quartz-5.8. There is also the amorphous phase. The amorphous phase is due appeared to destruction of crystal latice of montmorillonite. The bentonitic clay provides bonding strength and plasticity to catalysts.

Table 1 illustrates relation between conversion of IPB and heteropolyacid concentration at 450°C for catalysts prepared by first and second ways for pre-processing temperatures 550 and 750°C.

As follows from the data the addition of HPA to Narynkol clay on first way leads to a monotonic decrease of its activity by T_{treat} = 550°C, while for catalysts prepared by second way the decrease of cracking activity is not so significant. The same results were obtained at the temperatures 350, 400 and 500°C. The catalysts prepared by the second way, are characterized by the greater heat stability. If afterwards treatment at 750°C the conversion of IPB on samples prepared in the first way, is decreased in 10-15%, on the second way - on 8.7%, and for model samples with the optimal content HPA is decreased only on 3.0%. Thus, the catalysts on a base of Narynkol clay, prepared by second way, save high activity after hyperthermal treating at 750°C in cracking IPB. The optimal concentration of HPA is 1%.

The influence of sulfuric acid treating on activity and heat stability of contacts in IPB cracking was tested for Tagan bentonite clay. The obtained results are compared in Figs. 1 and 2 for clay samples (Fig. 1) and 15% zeolite catalysts on its base (Fig. 2). The clay was activated by 20% (A-1, A-2, C-1, C-2) and 30% sulfuric acid (B-1, B-2, D-1, D-2) (conditions 1 and 2, accordingly).

Table 1

Relation between the conversion IPB (a) at 450°C and the concentration HPA for catalysts on Narynkol clay

Concentration HPA, wt.%	α, %			
	Way 1		Way 2	
	T_{treat} = 550°C	T_{treat} = 750°C	T_{treat} = 550°C	T_{treat} = 750°C
0.0	80.3	55.4	80.3	55.4
0.3	78.2	63.0	77.6	70.4
0.5	76.6	67.6	80.1	71.4
1.0	75.6	65.6	74.7	71.7
3.0	63.0	50.0	79.2	71.6

As follows from the data of Figs. 1, 2, the clay, activated at the conditions 1, is more active on 15-20%, than after treating at the conditions 2. The elevation of temperature of clay preprocessing from 550 up to 750°C practically does not effect on activity in cracking reaction and witnesses about its heat stability.

The magnitudes of clay specific surfaces, detected by BET are changed to 71.4 m^2/g for nonactivated clay, to 173.2 and 145.2 m^2/g for samples prepared at the conditions 1 at T_{treat} = 550 and 750°C, respectively, and to 106.5 and 101.9 m^2/g for samples, prepared at the conditions 2.

The adding of a zeolite into clays at conditions 1 increases the activity in 1.3-2.0 times. S_{spec} increases up to 199.7 m^2/g. Variations of catalyst activity with increasing of treatment temperature up to 750°C were not observed. The higher growth of catalysts activity from the zeolite adding under the conditions 2 is rather more appreciable, than under the conditions 1, and it results in almost the same activity are equalized. But catalysts prepared by conditions 2 are less resistant to high temperature so at T_{treat} = 750°C the conversion level of IPB decreases on 12% at cracking temperature 450°C and on 28% at 350°C.

On the basis of the obtained results we conclude about the practical significance of the clay activation at the conditions 1.

Table 2 illustrates relations between transformation extent IPB and HPA concentration at 450°C for catalysts on Tagan clay prepared by first and second ways for preprocessing temperatures 550 and 750°C.

Addition of HPA into catalyst on the base of Naryncol clay resulted to monotonous decreasing of its activity in IPB cracking. The reducing of conversion level on Tagan clay in studied concentration interval from HPA (0.1-3.0 wt.%) was not observed. Addi-

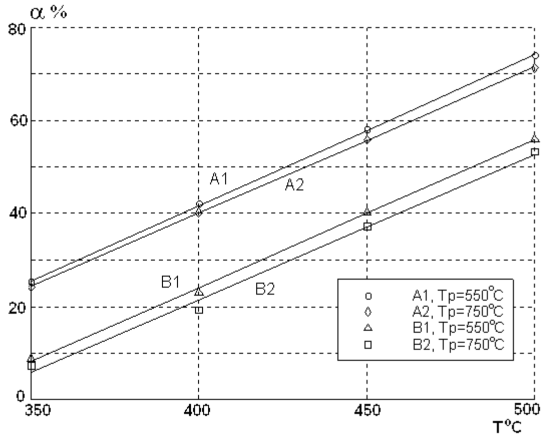

Fig. 1. Relations between conversion level IPB at temperatures of pretreatment 550 and 750°C and cracking temperature 350-500°C for Tagan clay with activation of clay 20% sulfuric acid (A1, A2 – conditions – 1) and 30% sulfuric acid (B1, B2 – conditions – 2).

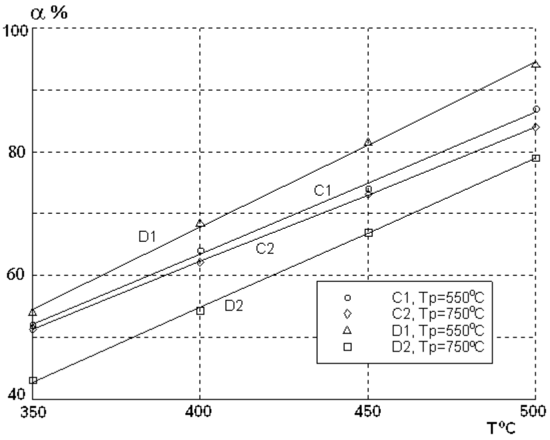

Fig. 2. Relations between conversion level IPB at temperatures of pretreatment 550 and 750°C and cracking temperature 350-500°C for 15% zeolite catalyst on Tagan clay with activation of clay 20% sulfuric acid (C1, C2 – conditions – 1) and 30% sulfuric acid (D1, D2 – conditions – 2).

tion of 1-3 wt.% HPA into catalyst on Tagan clay leads to the increase of activity on 10-14%. Thermal stability of contacts on the base of Tagan clay was higher then on the base of Narynkol clay. Besides catalysts on Tagan and Narynkol clays prepared by second way are more active than by the first way. Rise of temperature preprocessing from 550 to 750°C led to decreasing of IPB conversion level only on 1.7-2.1%. HPA addition according the second way gave better results.

Table 2

Relations between conversion IPB (α) by 450°C treatment and a concentration HPA for catalysts on Tagan clay.

Concentration HPA, wt.%	α, %			
	Way 1		Way 2	
	T_{treat} = 550°C	T_{treat} = 750°C	T_{treat} = 550°C	T_{treat} = 750°C
0	75.0	73.2	75.0	73.2
0.1	78.1	74.5	86.5	84.6
0.3	80.4	76.9	88.2	85.4
0.5	82.5	78.4	88.5	86.5
1.0	84.0	80.2	89.0	87.3
3.0	84.4	79.6	89.3	87.2

The optimum concentration of HPA (1%) was tested for the composite catalysts on the base of Tagan clay at cracking temperature 350-500°C. Table 3 illustrates results of the cracking reaction IPB on two composite catalysts prepared by the first way.

Results of the Table 3 show that the HPA adding leads to a small increase of catalyst activity at all processing temperatures. The superactivity of the catalysts with HPA is conserved after T_{treat}=750°C.

The prepared samples on the base of bentonitic clay, activated by a sulfuric acid at different conditions (1-20% H_2SO_4; 2-30% H_2SO_4), were tested in cracking KGF Kumkol oil. The yields of gasoline were 48.3 and 48.5% for 1 and 2 conditions of activation, respectively. Yields of a fluid phase were 83.0 and 76.4%, gas yields were 14.4 and 20.1%. The increase of concentration of promotive acid from 20 up to 30% probably stimulates formation of strong acid centers that promotes intensification of cracking reaction and leads to lower amount of liquid fraction.

The similar results were obtained when HPA was added to catalysts on the base of Narynkol clay. The increasing of HPA content more then optimum led to the increase of the amount of gaseous cracking products (25.4%).

It is necessary to mentions, that it is possible to obtain the yield of gasoline above 58% at cracking of KGF at optimal HPA concentration on the modified catalyst KL-113 [9] with usage of Narynkol clay.

Conclusion

The main advantages of the clay based catalysts are their high activity and low carbonization. The us-

Table 3

Variation of conversion level of IPB on temperature pretreatment for catalysts on the base of Tagan clay (%) at cracking temperature 350-500°C.

Catalyst on clay	T_{treat} = 550°C				T_{treat} = 750°C			
	350	400	450	500	350	400	450	500
NaHY	52.0	62.1	75.0	84.0	51.3	64.0	73.2	79.0
NaHY+HPA	56.3	70.4	84.0	96.1	55.0	68.3	80.2	87.0

ing of natural clays for synthesis of effective catalysts for cracking reduces the catalyst price. There is a constant source of raw materials for production of such catalysts.

This investigation suggests, that the natural Kazakhstan clays of such deposits as Narynkol and Tagan can be used for constructing of cracking catalysts. The selection of optimal concentrations of the modifying components, the ways of plotting them on matrixes containing activated clays, allows to receive active and thermostable composite catalysts, providing the high yield of gasoline at cracking of real raw.

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