

## EFFECT OF THE CONCENTRATION OF ACIDIC CENTERS IN NiNaY ZEOLITE ON TOLUENE CONVERSION

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NiNaY zeolite has been studied in toluene conversion performed at an elevated pressure. The influence of the concentration of the acidic Brønsted sites on the disproportionation and the hydrodealkylation activity of NiNaY samples is discussed.

Превращения толуола при повышенном давлении были исследованы в системе Ni-цеолит У. Обсуждается влияние концентрации кислотных центров Брэнстэда на активность образцов Ni-цеолита У в реакции диспропорционирования и гидродеалкилирования толуола.

The reduction of NiNaY zeolite by  $H_2$  leads to the formation of a bidisperse nickel distribution /1-3/ and acidic Brønsted or Lewis sites.

It has been shown previously /4/ that during the conversion of toluene at an elevated pressure competitive chemisorption of toluene takes place and that at the chemisorption on the acidic Brønsted sites is dominant. It initiates the disproportionation reaction which occurs via carbonium ions on the Brønsted acid sites. Poisoning of the acidic centers with  $Na^+$  ions leads to a complete change in the pattern of toluene conversion due to the chemisorption of toluene on the metallic centers.

In this work, a more detailed study of the effect of the concentration of acidic sites on the disproportionation and hydrodealkylation activities of NiNaY zeolites was made.

### EXPERIMENTAL

The nickel form of NaY ( $SiO_2/Al_2O_3 = 5.06$ ) was obtained by ion exchange using 0.2 M  $Ni(CH_3COO)_2 \cdot 4H_2O$ . After that the zeolite was dried in air at 390 K and extruded with the addition of 20%  $Al_2O_3$ . The activation was performed in air in the range of 723-823 K and the reduction in a stream of  $H_2$  at 773 K for 4 h.

The acidic centers were poisoned by treating the activated or reduced samples of NiNaY with 0.005–0.1 M NaOH.

The acidity of the catalysts was determined in a Specord 75 IR unit. The intensity of pyridinium ion absorption band at  $1545\text{ cm}^{-1}$  was taken as the measure of Brønsted acidity.

The nickel metal phase was characterized by X-ray diffraction and magnetic method. The number and the size of  $\text{Ni}^0$  particles inside the supercages was measured in a string electromagnet of 100 kOe (measurements at 290 K and 4.2 K).

Toluene conversion was performed in a flow apparatus (FOK/GYEM, type 115/09) in the temperature range of 690–870 K and at a pressure of 4 MPa. The catalyst charge was  $4\text{ cm}^3$ , hydrogen/toluene molar ratio: 6 and space velocity:  $1\text{ h}^{-1}$ .

## RESULTS AND DISCUSSION

The concentration of the acidic Brønsted sites together with the characteristics of the metallic nickel phase are shown in Table 1. All samples of NiNaY zeolite reduced by  $\text{H}_2$  at 773 K give two  $\text{Ni}^0$  species: nickel crystallites on the external surface with diameters of 12–20 nm and nickel clusters inside the supercages with a diameter of about 1 nm.

Table 1

No cat.	Temperature of activation in air (K)	Poisoning by g $\text{Na}^+$ /g zeolite		Concentration of Brønsted sites (mmol/g)	Ni ext. <sup>a</sup> (wt. %)	Ni int. <sup>b</sup> (wt. %)
		before reduction	after reduction			
1.	823	—	—	0.287	3.26	1.90 <sup>c</sup>
2.	823	—	$\text{H}_2\text{O}$	0.187	1.76	—
3.	823	—	0.0014	0.235	1.67	—
4.	823	—	0.0043	0.204	1.64	—
5.	823	—	0.0072	0.187	1.54	—
6.	823	—	0.0115	0.169	1.62	—
7.	823	—	0.0719	0.130	2.16	—
8.	723	0.0719	—	0.088	2.03	—
9.	823	0.0719	—	0.085	2.63	—

<sup>a</sup>Diameter of the external  $\text{Ni}^0$ ,  $D_{\text{ext}} = 12 - 20\text{ nm}$ ;

<sup>b</sup>Diameter of the internal  $\text{Ni}^0$ ,  $D_{\text{int}} = 1\text{ nm}$ ;

<sup>c</sup>Catalysts Nos 1–7 were reduced in the same batch

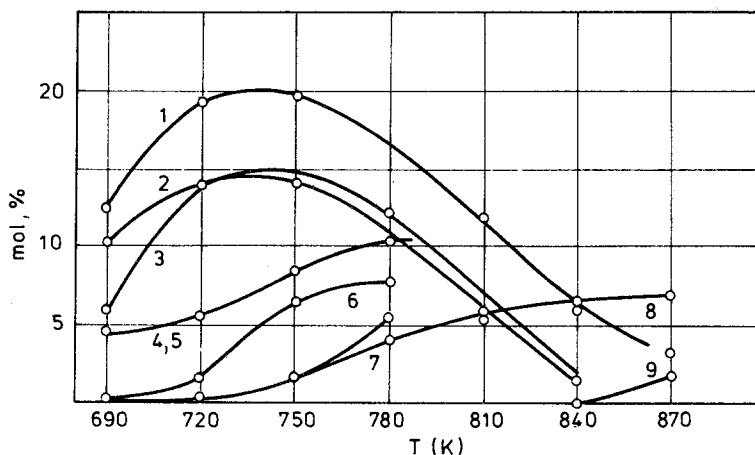


Fig. 1. Disproportionation activity as a function of reaction temperature

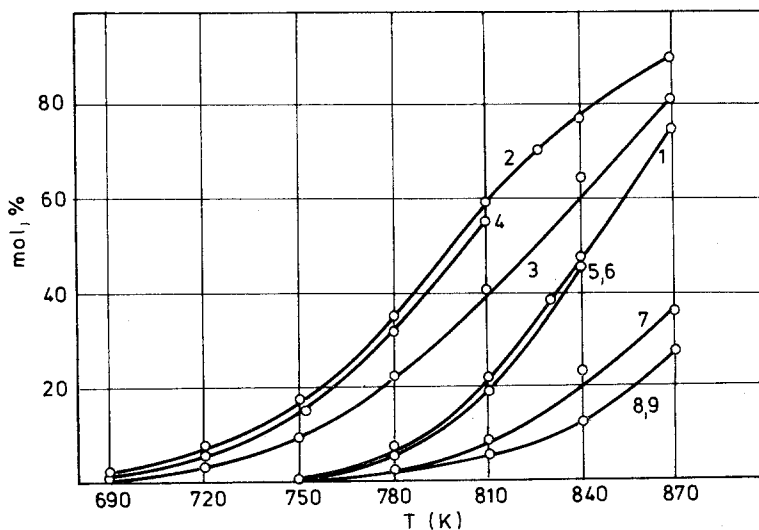


Fig. 2. Hydrodealkylation activity as a function of reaction temperature

The variation in disproportionation activity is plotted against the reaction temperature in Fig. 1. The disproportionation activity reaches a maximum around 750 K in the case of active catalysts. Poisoning of the acidic centers with  $\text{Na}^+$  ions leads to a decrease in the disproportionation activity and to a movement of the activity range to higher temperatures. Simultaneously, hydrodealkylation activity begins to appear at 680–750 K and increases continuously with the reaction temperature; the results are shown in Fig. 2.

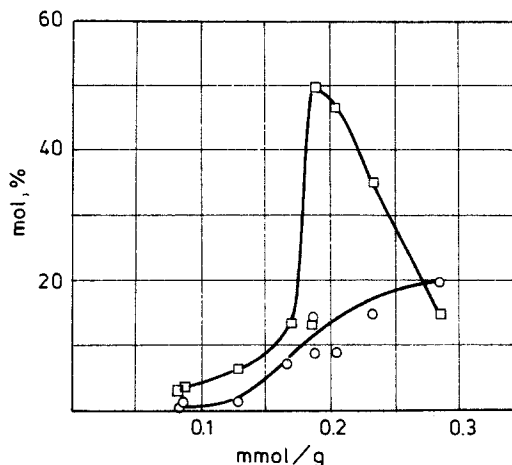


Fig. 3. The disproportionation activity at 750 K ( $\circ$ ) and hydrodealkylation activity at 800 K ( $\square$ ) as a function of the concentration of Brønsted acid sites

Figure 3 shows the effect of the acidic Brønsted site concentration on the disproportionation and hydrodealkylation activities. The disproportionation activity correlates with the number of Brønsted acid sites which confirms their role in this reaction, whereas the hydrodealkylation activity reaches a maximum for a moderate concentration of Brønsted sites. The activity of the catalysts No. 2 (treated with  $H_2O$ ) and Nos. 3–4 (treated with a lower concentration of NaOH solution) increases to nearly 90% mol at 870 K. This can be attributed to a good balance of the acidic and metallic function for the hydrodealkylation of toluene. The total blockage of the acidic centers causes the loss of the activity in the disproportionation as well as in hydrodealkylation reaction.

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