

REGULATION OF THE SELECTIVITY AND STABILITY OF ZEOLITE CATALYSTS CONTAINING TRANSITION METALS

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(Received 3th February, 1978)

The mixed forms of synthetic zeolites of Y-type containing Ca, Ni and Cr are tested towards the dealkylation and disproportionation of toluene. The introduction of Cr³⁺ or Cr₂O₃ in the nickel-containing samples results in an increase of selectivity and stability, which is attributed to their effect on the dispersy of the metal particles formed after the reduction of Ni²⁺.

In the search of high-effective catalysts recently much attention is paid to the metal-zeolite catalysts [1]. Their catalytic activity is determined primarily by the type number, amount and state of the transition elements in the zeolite structure [2, 3].

The aim of the present work is to develop catalytic systems based on nickel-zeolite catalysts (obtained by different ways — ion exchange, deposition, mechanical mixing), which should favour the conversion of toluene into benzene, or benzene + xylenes. Furthermore, the possibilities are examined for regulating their selectivity, stability and regenerability by the introduction of chromium (as Cr³⁺ or Cr₂O₃).

Table I
Composition and method for obtaining the test samples

Sample	Ni content wt %	Cr content wt %	Method of preparation
NiO/CaY	2.5—5.0	—	Deposition by precipitation of Ni(OH) ₂
NiO/CaY	3.5—7.5	—	Deposition from Ni-acetylacetonate solution
NiO + CaY	2.5—5.0	—	Mechanical mixing
NiO — CaY	2.5—5.0	—	Precipitation of Ni(OH) ₂ in the presence of CaY
NiCaY	3.1	—	Ion exchange with Ni(NO ₃) ₂ solution
CrCaY	—	0.5—6.0	Ion exchange with Cr(NO ₃) ₃ solution
CrNiCaY	2.7—2.9	0.4—1.2	Ion exchange in NiCaY with Cr(NO ₃) ₃ solution
NiCaY + Cr ₂ O ₃	3.1	1.5—2.1	Mechanical mixing

Experimental part

The experiments are carried out on synthetic zeolites of X and Y-type with molar ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ from 3.2 to 5.0 in calcium form (extent of ion exchange with Ca^{2+} about 80%). The composition and way of obtaining of the Ni-, Cr- and Ni-Cr-containing samples are shown in Table I.

The properties of the catalysts are not noticeably affected by the used amounts of Ni^{2+} and Cr^{3+} . No disturbance of the crystal lattice of the zeolite under these conditions is proved by X-ray analysis.

The catalytic activity of the test samples is determined in a flow system with space velocity of 1.1 h^{-1} at atmospheric pressure in the temperature range 330—470 °C. Ratio hydrogen:toluene = 10. Thermal pretreatment is carried out in hydrogen flow for 2 hours at 450 °C, after the temperature is slowly elevated to this value.

Results and discussion

Recently, catalysts of the type NiO-zeolite are developed [4, 5]. Their activity and selectivity are varied by an appropriate interaction between both components which separately are not active, as in the case of ethylene dimerization [6, 7], or the presence of the second component changes the direction of the conversion, as the alkylation of benzene with ethylene [7, 8].

The catalytic systems NiO/CaY and NiO+CaY used for the conversion of toluene are characterized by the additivity of the activities of the metal and acidic

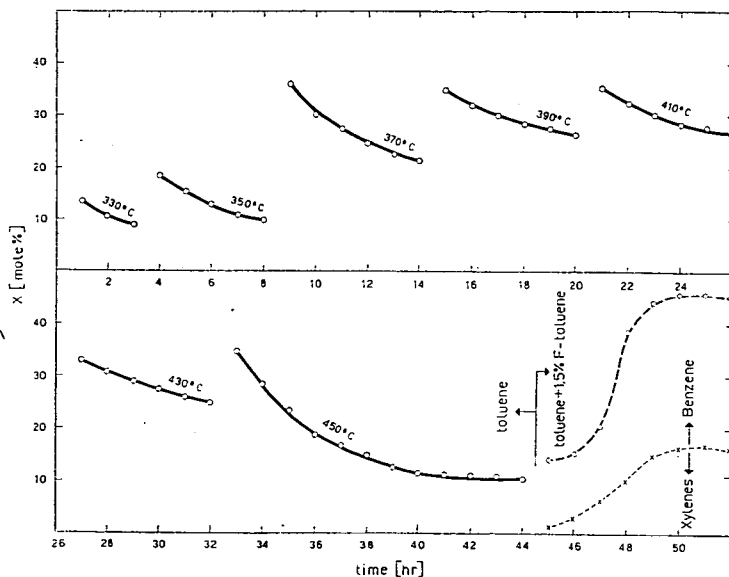


Fig. 1. Consecutive conversion of toluene into benzene and benzene + xylenes on a catalyst NiO/CaY obtained by supporting $\text{Ni}(\text{OH})_2$. Nickel content: 2.5 wt%

component of the two-component catalyst obtained after the reduction of NiO. Initially toluene is converted to benzene on the metal. After the deactivation of the latter, toluene containing about 0.5—1.5% of fluortoluene, bromobenzene, or other halogen-containing substance is passed, *i.e.* under these conditions the "carrier" acts as an independent catalyst. The catalytic activity of the "carrier" is equal to that of the calcium form of the zeolite under the same conditions. The dealkylation of toluene followed by its disproportionation is shown on Fig. 1.

The examined catalytic system provides possibilities for consecutive or simultaneous dealkylation and disproportionation of toluene. It differs from the known similar catalysts by the bifunctional action of the "carrier":

1. The zeolite is used as a carrier. NiO is deposited on it by any of the methods shown on Table I, on which after its reduction, the dealkylation takes place.

2. After the deactivation of the metal, there is a possibility for activating the "carrier" which may act as an independent catalyst for toluene disproportionation.

This catalytic system permits the simultaneous dealkylation and disproportionation of toluene to be performed: Toluene containing 0.5—1.5 wt% of fluortoluene or bromobenzene is passed at temperature of 430—470 °C. Benzene (by both reactions) and xylenes are obtained. When Ni(OH)₂ is precipitated in the presence of CaY, the disproportionation of toluene takes place from the beginning of the process which is probably caused by partial ion exchange. Hence, a new way is shown for obtaining of catalysts for the conversion of toluene to benzene and xylenes, differing essentially from those obtained by ion exchange (see Fig. 2).

The mechanical mixing of Cr₂O₃ to the samples obtained by ion exchange, leads to a significant increase in the selectivity of the catalysts towards disproportionation, their stability and regenerability [9]. This effect is attributed to the influence of Cr₂O₃ on the reduction ability of Ni²⁺ and on the dispersity of the obtained metallic nickel.

In order to elucidate the observed phenomena and to find out new ways for regulating the catalytic properties of the studied catalysts, a series of test samples of CrCaY and CrNiCaY (see Table I) with different Cr³⁺ content are obtained. Under the examined conditions of reduction and reaction, no reduction of Cr³⁺ takes place (at temperatures below 600 °C reduction to metallic state is not observed [3]). The total conversion extent (X) and the sum of the disproportionation products (2/Σ*xy*l + + 2ΣTMB/) as a function of time for a sample of NiCaY with different Cr and Cr₂O₃ content are shown on Fig. 3. The effect of Cr³⁺ on the activity of the nickel-zeolite samples is illustrated by the comparison of the activities of NiCaY (curve 1) and CrNiCaY (curves 2 and 3), taking into consideration that samples containing only chromium (CrNaY and CrCaY) are not active under the examined conditions. For higher Cr³⁺ contents, as well as for the mechanical mixtures with Cr₂O₃ (curves 4 and 5) the maximal activity is reached slower, which is related to the adsorption-desorption processes preceding the catalytic act.

The changes in the selectivity and stability of NiCaY effected by the introduction of Cr³⁺ are related mainly to the influence of the latter on the dispersity of the nickel particles obtained after reduction. Before reduction Ni²⁺ and Cr³⁺ enter the zeolite structure in the form of hexaquo-complexes. Evidence for the latter is given by the reflection spectra in the visible and UV region and by the ESR-spectra of air-dry samples. The method of FMR yielded some data on the size and form of the nickel particles obtained after reduction. It is known that the line width of the FMR signal is sensitive towards the size and texture of the particle. In Table II the parameters

ΔH and the γ -factors for the three most characteristic samples are presented. It is seen that the chromium-containing samples have a considerably smaller line width after reduction, which is a direct indication for the formation of smaller particles of the mixed Ni-Cr-species.

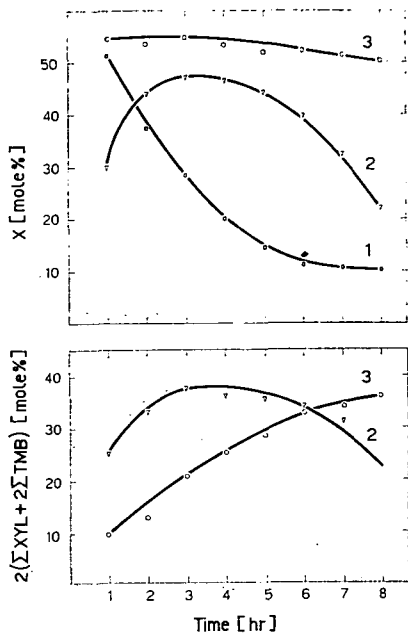


Fig. 2. Total conversion extent and the sum of the disproportionation products ($2/\Sigma_{xyl}+2\Sigma_{TMB}$) as a function of time at 430 °C for samples obtained by:

1. Supporting of $\text{Ni}(\text{OH})_2$ on CaY
2. Ion exchange
3. Precipitation of $\text{Ni}(\text{OH})_2$ in the presence of CaY.

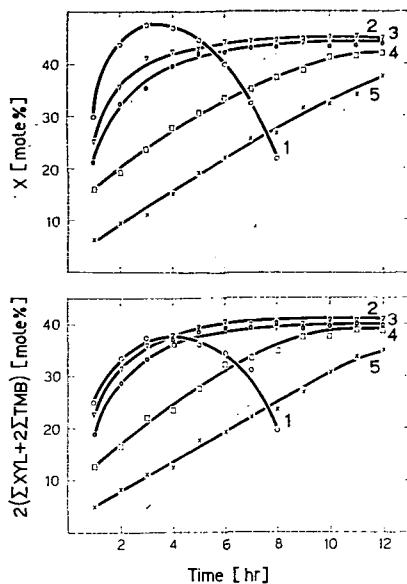


Fig. 3. Total conversion extent and the sum of the disproportionation products ($2/\Sigma_{xyl}+2\Sigma_{TMB}$) as a function of time at 430 °C for a NiCaY sample containing various amount of Cr^{3+} :

1. NiCaY
2. CrNiCaY (0.4 wt % Cr^{3+})
3. CrNiCaY (0.6 wt % Cr^{3+})
4. CrNiCaY (1.2 wt % Cr^{3+})
5. NiCaY + Cr_2O_3 (1.5 wt % Cr)

Table II
Parameters of the FMR spectra for some samples

Sample	Ion content, wt %		ΔH Gauss	ρ
	Ni^{2+}	Cr^{3+}		
NiCaY	3.1	—	820	2.16
CrNiCaY	3.0	0.46	640	2.23
CrNiCaY	2.9	0.67	600	2.23

Furthermore, the nickel particles obtained from Cr^{3+} -containing samples possess an expressed stability towards prolonged treating with toluene at the reaction temperature (the change in ΔH with time is insignificant, which is the most important base for the stable action of these catalysts).

The oxidative treatment during the regeneration leads to an enrichment with Cr^{6+} (proved by the reflection spectra in the visible and UV region), whose strong oxidizing action improves the regenerability of the studied catalysts. Moreover, the obtained Cr_2O_3 is distributed more evenly, thus considerably increasing the selectivity and stability of the regenerated catalysts.

Besides the wide possibilities for regulating the catalytic properties of the studied samples, the obtained results permit to throw light on the important and complicated problem of the mutual interaction between the acidic and metal active sites in the bifunctional zeolite catalysts. In the catalytic systems obtained by mechanical mixing of NiO and CaY (as well as NiNaA and CaY) at different ratios, no experimental support was obtained for a synergism between both functions. The obtaining of more finely dispersed nickel particles in NiCaY by the introduction of Cr^{3+} or Cr_2O_3 contributes to the complete development of the acidic nature of the zeolite, which plays the decisive role for the disproportionation. On the other hand this leads to an enhancement in the hydrogenating capacity of the metal ($\text{Ni}^0 + \text{H}_2$), which results in lower coke-formation.

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