

## Some Aspects of the Bifunctional Action of Nickel-Zeolite Catalysts in the Conversion of Toluene

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The bifunctional action of nickel-zeolite catalysts toward toluene conversion is studied. The additive behavior of both components of the catalysts is confirmed on the basis of the interpretation of their activity from three points of view: bifunctional catalysis, catalysis on the metal, and catalysis on the acidic component. New two-component catalysts of the type NiO/CaNaY<sub>3.2-5.0</sub> (nickel content from 2.5 to 7.5 wt%) are developed. After reduction they are active for the dealkylation of toluene and under certain conditions for the disproportionation of toluene. The catalysts may be used for production of benzene and xylenes from toluene.

### INTRODUCTION

A fundamental problem in bifunctional catalysts is whether their total activity is a combination (MA) of the activity of the metal (M) and the acidic component (A), or is a sum of the activities of both components [(M) + (A)]. Some reactions are interpreted in terms of the first version, e.g., isomerization and cracking of *n*-paraffin hydrocarbons on PtCaY (1). The results obtained agree with the classical theory of bifunctional catalysis (2). Similar data are also obtained for the hydrocracking of *n*-octane on nickel-zeolite catalysts (3, 4). The nickel forms of Y-zeolites exhibit polyfunctional properties toward the alkylation of benzene and other aromatic hydrocarbons with ethylene (5-7) and the dimerization of ethylene (5, 8). However, the study of the cracking of cumene, hydrogenation of benzene, hydrogenolysis of ethane, and isomerization of *n*-hexane on a series of nickel-zeolite catalysts with a wide range of acidities (9) showed no

appreciable dependence between the two catalyst components.

The disproportionation of toluene generally takes place on catalysts of the acidic type. Nickel-zeolite catalysts obtained by ion exchange and subsequent reduction in flowing hydrogen are also active toward this reaction (10). Undoubtedly the metal deposited on the zeolite surface affects the conversion of toluene. It is not clear, however, whether it takes part in the disproportionation process. In order to explain the role of the metallic nickel in the reactions taking place on nickel-zeolite catalysts, a series of catalytic experiments have been carried out. As a result new two-component catalysts of the type nickel oxide-CaY zeolites were developed. After reduction they are active toward the dealkylation of toluene and under certain conditions toward the disproportionation of toluene. The catalysts may be used for production of benzene and xylenes from toluene.

TABLE 1  
Sample Composition<sup>a</sup>

No.	Sample	Nickel content (of abs. dry substance) (mol%)	Pro- cedure No.
1.	NiO/NaX <sub>2.6</sub>	3.2	1
2.	NiO/NaY <sub>3.2</sub>	3.2	1
3.	NiO/NaY <sub>3.8</sub>	3.2	1
4.	NiO/NaY <sub>5.0</sub>	3.2	1
5.	NiO/80CaNaX <sub>2.6</sub>	3.2	1
6.	NiO/80CaNaY <sub>3.2</sub>	3.2	1
7.	NiO/85CaNaY <sub>3.8</sub>	3.2	1
8.	NiO/78CaNaY <sub>5.0</sub>	2.5	1
9.	NiO/78CaNaY <sub>5.0</sub>	3.2	1
10.	NiO/78CaNaY <sub>5.0</sub>	5.0	1
11.	NiO/78CaNaY <sub>5.0</sub>	7.5	1
12.	NiO/Ni78CaNaY <sub>5.0</sub>	5.0	2
13.	NiO/78CaNaY <sub>5.0</sub>	3.2	3
14.	NiO/78CaNaY <sub>5.0</sub>	5.0	3
15.	NiO/78CaNaY <sub>5.0</sub>	7.5	3
16.	NiO/78CaNaY <sub>5.0</sub>	10.0	3
17.	NiO + 78CaNaY <sub>5.0</sub>	3.2	4
18.	NiO + 78CaNaY <sub>5.0</sub>	5.0	4
19.	NiO + 78CaNaY <sub>5.0</sub>	7.5	4
20.	NiO + 78CaNaY <sub>5.0</sub>	10.0	4
21.	NiNaA <sub>1.9</sub> + 78CaNaY <sub>5.0</sub>	3.2	5
22.	NiNaA <sub>1.9</sub> + 78CaNaY <sub>5.0</sub>	5.0	5
23.	NiNaA <sub>1.9</sub> + 78CaNaY <sub>5.0</sub>	7.5	5
24.	NiNaA <sub>1.9</sub> + 78CaNaY <sub>5.0</sub>	10.0	5
25.	Ni78CaNaY <sub>5.0</sub>	5.0	6

<sup>a</sup> The numerals before Ca denote the extent of ion exchange of Na<sup>+</sup> with Ca<sup>2+</sup>; those after the zeolite type denote the molar ratio SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>.

### EXPERIMENTAL

Synthetic X and Y zeolites with SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratios from 2.6 to 5.0 have been used. The calcium form of the zeolites was obtained by ion exchange of Na<sup>+</sup> with Ca<sup>2+</sup> from a 4 N CaCl<sub>2</sub> solution (extent of exchange about 80%). The nickel forms of the zeolites were obtained by the following procedures:

(1) Ni(OH)<sub>2</sub> was precipitated from a 5% solution of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O with a 5% solution of KOH at pH 7 to 8. The zeolite was added, and the mixture was stirred for 15 min. The obtained suspension was

allowed to stand overnight; it was then decanted and washed several times with distilled water. The precipitate was filtered and dried at 110 to 120°C for 3 hr.

(2) Ni(OH)<sub>2</sub> was precipitated in the presence of the calcium form of the zeolite. The subsequent treatment was as in (1) above.

(3) Ni acetylacetonate was dissolved in chloroform and mixed with the calcium form of the zeolite. The solvent was evaporated with continuous stirring. The supported Ni acetylacetonate was decomposed to nickel oxide at 450°C in an air flow for 2 hr.

(4) The zeolite was mixed mechanically with NiO (Merck p.a.) by thorough grinding in an agate mortar for 2 hr.

(5) The calcium form of the zeolite was mixed mechanically with NiNaA<sub>1.9</sub> by thorough grinding in an agate mortar for 2 hr.

(6) Ion exchange was achieved between the calcium form of the zeolite and nickel ions from a 0.1 N solution of Ni(NO<sub>3</sub>)<sub>2</sub>.

The exact composition of the samples, determined by complexometric and atomic absorption analysis of the filtrates, is given in Table 1. The samples were tabletted and crushed, and the screen fraction 0.5 to 0.8 mm was used. The catalytic experiments were carried out in a flow system using a microreactor with a volume of 4 ml. The experiments were made at atmospheric pressure over the temperature range 330 to 470°C, using a hydrogen/toluene or nitrogen/toluene ratio of 10 and a space velocity of 1.1 hr<sup>-1</sup>. The catalysts were pre-treated in a flow of air or hydrogen for 2 hr at 450°C after the temperature had been slowly raised to this value. The composition of the reaction products was determined by gas chromatographic (gc) analysis using a flame ionization detector and a column employing polyethylene glycol adipate at 110°C.

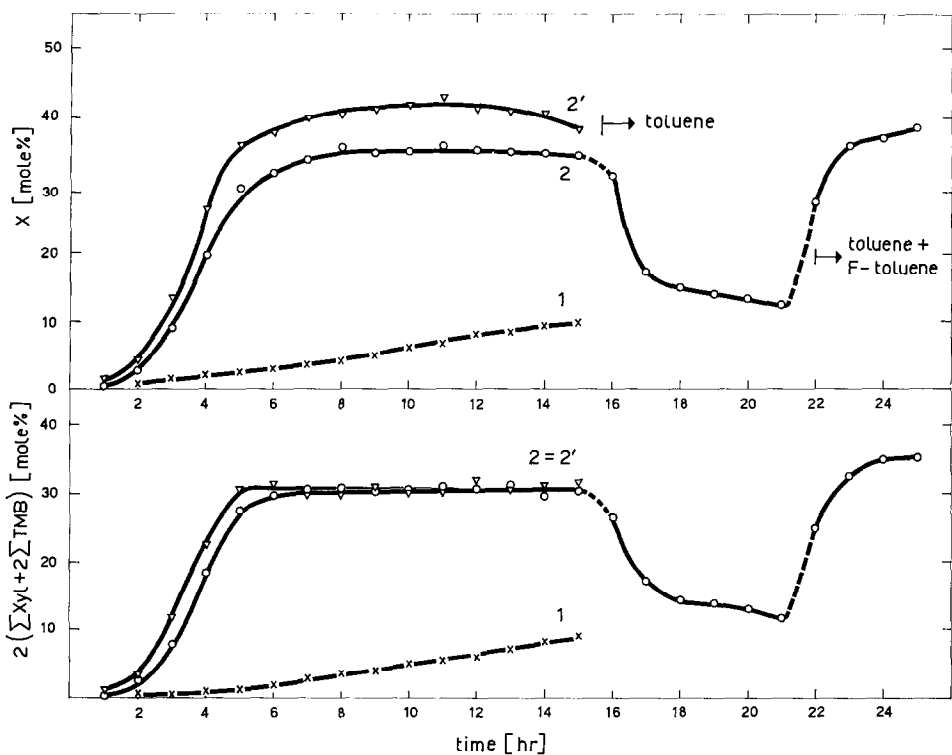


FIG. 1. Total conversion extent  $X$  (mol%) and disproportionation products  $2(\Sigma xyl + 2\Sigma TMB)$  (mol%) as a function of time (hr) for  $83CaNaX_{2.6}$  at  $450^\circ C$  (curve 1) and  $78CaNaY_{5.0}$  at  $450^\circ C$  (curve 2) and  $470^\circ C$  (curve 2'). Promoter fluorotoluene (1.5 wt%).  $\Sigma xyl$  is the sum of *m*-, *p*-, and *o*-xylene;  $\Sigma TMB$  is the sum of mesitylene, pseudocumene, and hemillitene.

## RESULTS AND DISCUSSION

The activity and selectivity of the two-component nickel-zeolite catalysts strongly depends on the pretreatment and composition of the zeolite. No conversion of toluene occurs under the present conditions on  $CaNaX_{2.6}$  and  $CaNaY_{3.2-5.0}$ . Low amounts of fluorotoluene or bromobenzene (about 1 to 2%) added to toluene lead to a slight ( $CaNaX_{2.6}$ ) or significant ( $CaNaY_{3.2-5.0}$ ) activity toward the disproportionation of toluene. This is shown in Fig. 1. The products of disproportionation are benzene, xylenes, and about 1 to 2% of trimethylbenzenes, mainly pseudocumene. The ordinate [ $2(\Sigma xyl + 2\Sigma TMB)$ ] is a measure of the selectivity toward the disproportionation and yields the amount of the products of this reaction in mole percents which are

in a stoichiometric ratio, e.g.,



When nickel oxide is introduced to the calcium form of the zeolite, the only product of toluene conversion is benzene. The optimal nickel content of the catalytic system is 2.5 to 7.5 wt% with respect to benzene yield (see Fig. 2, sample  $NiCaNaY_{5.0}$ ). The catalytic system shows highest activity when nickel oxide is deposited from aqueous solutions (see Fig. 3).

The systems  $Ni/NaA$  and  $Ni/NaX$  are active only toward the dealkylation of toluene. Promoting of the reaction mixture does not induce a catalytic activity for disproportionation. The latter takes place only in the presence of calcium ions (extent of exchange about 80%) in Y-zeolites. The calcium ions stabilize the crystal lattice and

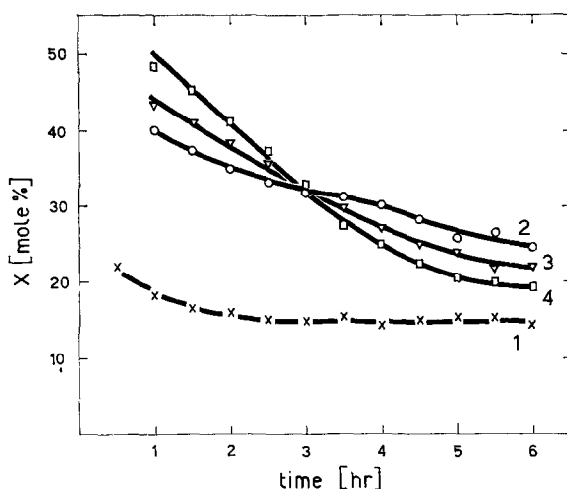


FIG. 2. Total conversion extent  $X$  (mol%) as a function of time (hr) at 330°C for the sample  $\text{NiO}/78\text{CaNaY}_{6.0}$  with different nickel contents (wt%). Curve 1, 2.5 wt% (sample 8); curve 2, 3.2 wt% (sample 9); curve 3, 5.0 wt% (sample 10); and curve 4, 7.5 wt% (sample 11).

affect the proton acidity of the initial zeolites (11, 12). The properties of the catalytic system  $\text{Ni}/\text{CaNaY}$  remain practically the same for molar ratios  $\text{SiO}_2/\text{Al}_2\text{O}_3$  from 3.2 to 5.0.

Comparing the properties of catalysts obtained by ion exchange and by deposition one sees a principal difference in their actions: Those obtained by deposition

catalyze only the dealkylation, whereas the ones obtained by exchange catalyze simultaneously the dealkylation and disproportionation. The two types of catalyst have different acidity and a different state of nickel. Infrared work on the chemisorption of pyridine indicates that the acidity of supported catalysts is considerably lower than that of exchanged ones (5). Catalysts

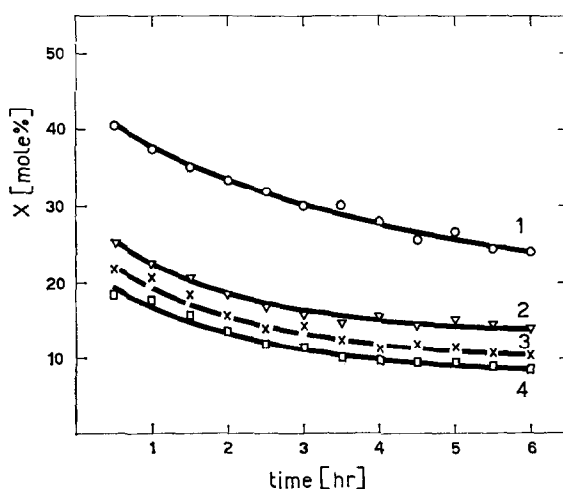


FIG. 3. Total conversion extent  $X$  (mol%) as a function of time (hr) at 330°C for samples containing 3.2 wt% Ni, obtained by different procedures. Curve 1, sample 9; curve 2, sample 13; curve 3, sample 17; and curve 4, sample 21.

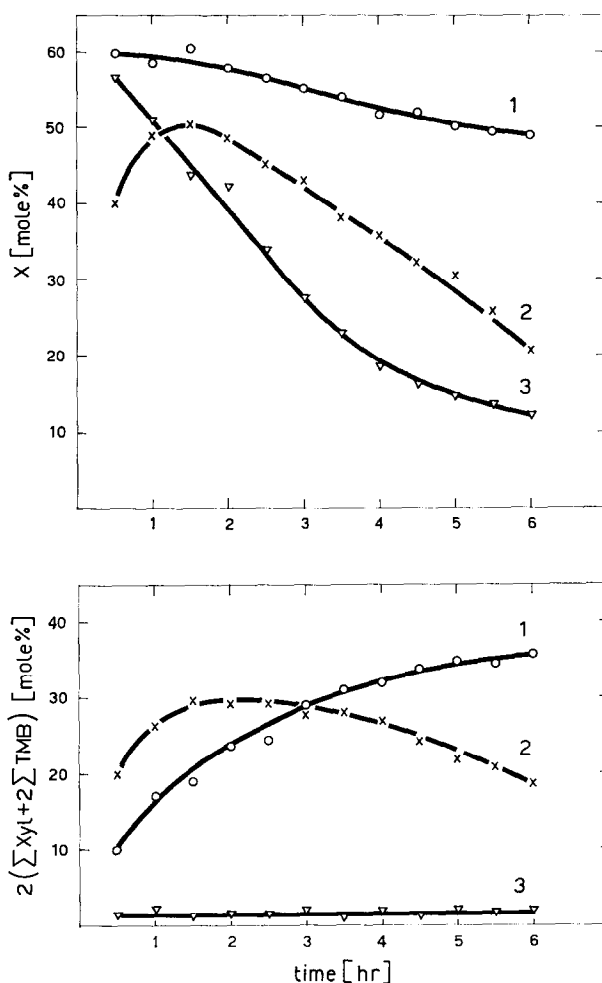
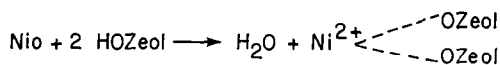


FIG. 4. Total conversion extent  $X$  (mol%) and disproportionation products  $2(\sum X_{yl} + 2\sum TMB)$  (mol%) as a function of time (hr) for samples with equal Ni content, obtained by different methods. Curve 1, coprecipitation (sample 12); curve 2, ion exchange (sample 25); and curve 3, deposition (sample 10).

obtained by precipitation of nickel oxide in the presence of  $\text{CaNaY}_{5.0}$  are highly effective toward the disproportionation of toluene, due to the possibility of partial ion exchange. The catalytic systems thus obtained are more advantageous than those obtained only by ion exchange or deposition (Fig. 4). The study of the catalytic properties of supported and ion-exchanged nickel zeolite samples treated in a flow of hydrogen and air reveals that from the whole variety of nickel species ( $\text{Ni}^0$ ,  $\text{Ni}^{2+}$ ,  $\text{NiO}$ ) only the

nickel ions are active for the disproportionation of toluene. Nickel ions are introduced by ion exchange or are obtained from the decomposition of nickel salts during the thermal treating, e.g.:



In the case of  $\text{NaY}$ , which has no acidic sites, nickel ions are not formed, and these samples are not active for disproportionation. The high activity of  $\text{NiO}/\text{CaNaY}$  and

of the ion exchanged catalysts (13) subjected to thermal treatment in an air flow and tested in nitrogen is interpreted in this way. Their high initial activity, however, drops rapidly because of the intense coking of the surface. The high activity toward the disproportionation of toluene of the reduced nickel-zeolite catalysts obtained by ion exchange is attributed to the fact that more than 30%, in some cases 40 to 50% (8), of the nickel ions remain unreduced, thereby being the main source of proton acidity (14). In the presence of hydrogen the metallic nickel assists the elimination of some unsaturated hydrocarbons, which otherwise would polymerize and block the active sites.

Direct treating of the system NiO/CaY with hydrogen results in a rapid reduction

of nickel oxide and deposition of metallic nickel on the surface. In this case only dealkylation takes place. After the metallic component is deactivated and toluene is 'mixed,' e.g., with 1.5% fluorotoluene, the activity of the zeolite component (in this case CaNaY<sub>5.0</sub>) increases and its acidity achieves a sufficient value for the disproportionation to take place (see Fig. 5). Thus, when NiO is deposited, or when NiO or NiNaA is mechanically mixed with CaNaY, after the deactivation of the metallic component and promoting with F-toluene, the "carrier" is activated to a level as if only CaNaY is present. The introduction of the promoter from the start of the experiment results in enhanced benzene yield: from the dealkylation on the metal and the disproportionation on

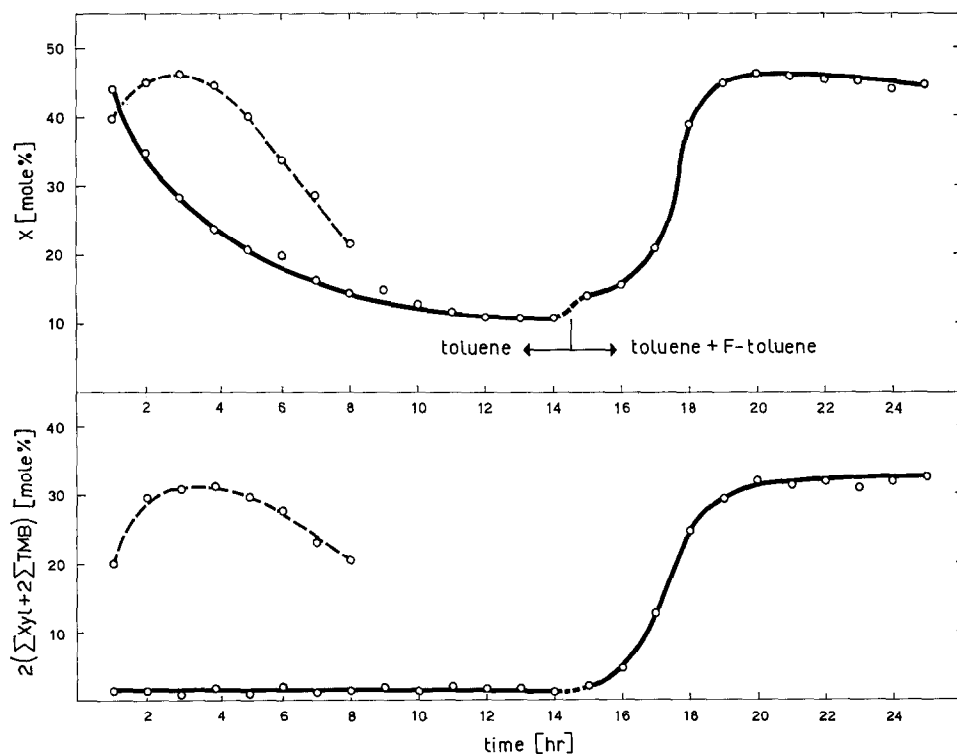


FIG. 5. Total conversion extent  $X$  (mol%) and disproportionation products  $2(\Sigma Xyl + 2\Sigma TMB)$  (mol%) as a function of time (hr) for sample 9. The reaction is carried out with toluene and toluene + 1.5 wt% fluorotoluene. (---) denotes a sample with the same composition obtained by ion exchange.

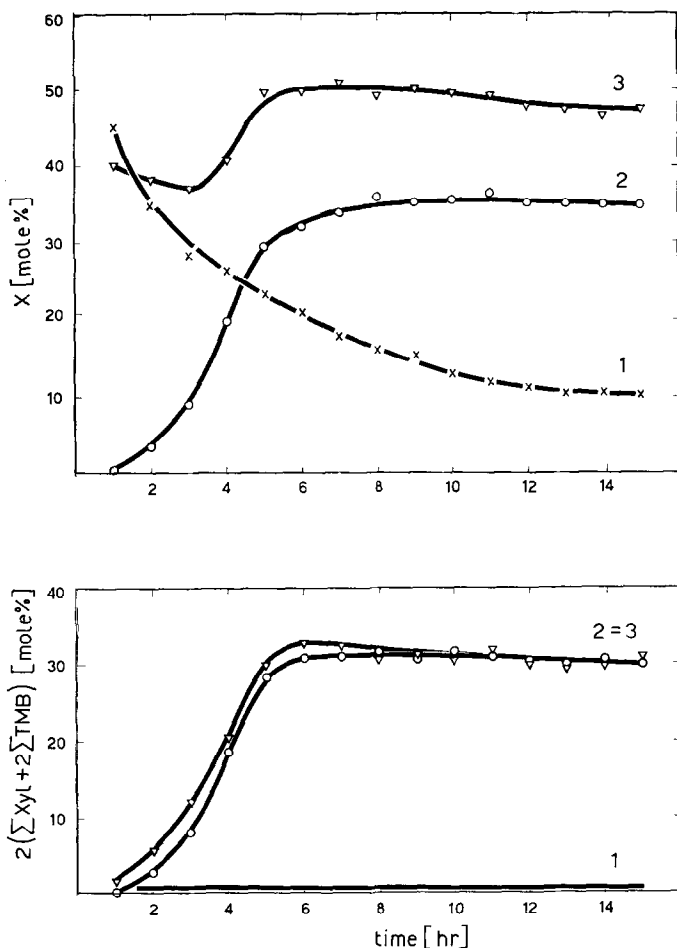


FIG. 6. Total conversion extent  $X$  (mol%) and disproportionation products as a function of time (hr) for sample 9. Curve 1, treating with toluene; curve 3, treating with toluene with 1.5 wt% fluorotoluene. Curve 2, initial sample  $78CaNaY_{6.0}$  treated with the mixture toluene + fluorotoluene.

the activated  $CaNaY$ . These effects are shown in Fig. 6. The results definitely point to an additive action of both components of the bifunctional catalysts. No experimental evidence is found for synergism between the two components.

It may be concluded that the nickel-zeolite catalysts containing only metallic nickel are not active for toluene disproportionation. The active species for this reaction are those which contain nickel ions in the crystal lattice, or nickel oxide on the surface. The effect of the nickel ion may be observed by raising the acidity of  $CaNaY$  by adding low amounts of fluoro-

toluene, bromobenzene, steam, or other promoters. The bifunctional action of the nickel-zeolite catalysts containing metallic nickel on the surface is explained in terms of the observed deactivation of the acidic catalysts during the process caused by coke deposition on their surface. Hydrogen, activated by the metal, promotes hydrogenation and desorption of these high molecular weight products, thus keeping high the activity of the acidic component. The interpretation of the bifunctional action of the nickel-zeolite catalysts given by us should not be considered as an exception, but as a contribution to the

classic explanation of the mechanism of action of the bifunctional catalysts.

Considering the action of the nickel-zeolite catalysts from the three points of view (bifunctional catalysis, catalysis on the metal, and catalysis on the acidic component), which are not mutually exclusive, it may be concluded that their relative effect strongly depends on the working conditions (temperature, carrier gas, concentration of the metal and acidic sites, etc.).

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