# POISONING WITH SODIUM OF THE ACID SITE ACTIVITY OF A BIFUNCTIONAL Ni°HNaY TYPE ZEOLITE CATALYST

By

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The hydrogenation and oligomerization (followed by cracking) reactions of propylene have been investigated over bifunctional Ni°HNaY zeolite catalysts. It could be ascertained that within certain limits changes in ion exchange and reduction conditions result in different catalyst selectivities. The carboniogenic activity of the bifunctional catalysts could be reduced or eliminated completely by using selective poisoning with sodium vapour, rendering separate study of the two functions possible.

Transition metal exchange cations in zeolites can be reduced to finely dispersed metals using agents such as hydroxylamine [1], hydrazine [2], sodium vapour [3], or solutions of metallic sodium in various solvents (ammonia, hexamethyl phosphoric acid diamide, etc.). When dihydrogen is used for this purpose between 470 and 770 K, besides metal atoms (or clusters) $H^+$ ions are also produced stoichiometrically, leading to bifunctional activity. Several excellent reviews and monographs have recently been published on the possibilities of testing bifunctional catalysts [4—7].

Hydrogenation and oligomerization of propylene over the metallic and acidic sites of zeolites are the most widely used test reactions for investigation of the two functions. Whereas the absolute concentrations of the active sites can be influenced by the degrees of exchange and reduction, respectively, their relative amounts do not change considerably (in the case of $Ni^{2+}$ ions the intermediate valence state $Ni^+$ exhibits some stability [8]). In order to test these functions in other proportions than those predetermined by stoichiometry, selective poisoning should be applied for either the hydrogenation-dehydrogenation or the carboniogenic activity.

The acidic centres can be exchanged for inactive ions (e. g. [9]), desactivated by chemisorption of nitrogen bases [10], or eliminated by the use of alkali metal vapour [11]. While most poisons influence both functions more or less, sodium can be regarded as a selective agent for the poisoning of acid site activity, leaving the hydrogenation-dehydrogenation activity and even the degree of reduction intact (see later).

The main objective of this paper was to investigate the influence of selective poisoning by sodium on the selectivity of hydrogenation and oligomerization reactions of propylene over Ni°HNaY type zeolite catalysts.

*Experimental*

a) *Preparation of catalysts*

The NiNaY zeolite was prepared by ion exchange from a NaY sample synthetized by L. I. PIGUZOVA (Moscow). The degree of exchange was measured by complexometric titration after dissolution of the zeolite structure in hydrochloric acid. The unit cell compositions of the original NaY sample and the exchanged specimens are given in Table I. The exchanged zeolite powder was pilled, crushed and sieved. For the experiments, $3.10^{-4}$ kg exsiccator-dry zeolite catalyst, having a grain size between 0.2 and 0.4 mm, was packed into the reactor.

Dihydrogen was used for reduction of the exchange transition metal ions at different temperatures. The reduction was monitored *via* the dihydrogen pressure in a reactor with intensive gas circulation. Reduction was considered "finished" when no more dihydrogen consumption could be observed. The degree of reduction was determined in separate experiments by the procedure published by BREMER and CO-WORKERS (12). It consists in a redox titration, where the amount of $Cr_2O_7^{2-}$ ions consumed for the oxidation of Ni° and Ni⁺ ions is measured.

For study of the effect of selective poisoning by sodium of the carboniogenic activity in zeolites, catalyst sample No. 2 was used with additions of solid $NaN_3$ in varying amounts (see Table I.). Apart from this, the procedure was the same as described previously.

It is worthwhile to mention that the decomposition temperature of $NaN_3$ is lowered considerably in the presence of heavy metal ions (being near 623 K for pure $NaN_3$ samples). Therefore, as a compromise, reduction was carried out at 600 K with dihydrogen. This procedure was preceded by heat treatment and evacuation (residual pressure $10^{-2}$ Pa) at 600 K for 2 hr. After reduction, the catalyst temperature was slowly raised to 723 K to bring the $NaN_3$ decomposition to Na and $N_2$ to completion, and held there for a further 1 hr. Depending on the duration of contact, the sodium vapour released on decomposition of $NaN_3$ diminished the number of

*Table I*

*Unit cell compositions of the zeolite samples used*

| No. | Components | | | | |
|-----|------|------|------|------|------|
|     | Na   | Ni   | Al   | Si   | O    |
| 1   | 58.1 | —    | 60.7 | 131.3 | 384 |
| 2   | 39.4 | 9.6  | 60.7 | 131.3 | 384 |
| 3   | 48.9 | 4.9  | 60.7 | 131.3 | 384 |

*Sodium azide contents of the modified NiNaY (No. 2) zeolite samples*

| No. | 4 | 5 | 6 | 7 | 8 |
|-----|------|------|------|------|------|
| mol $NaN_3$ / mol $Ni^{2+}$ | 0.21 | 0.86 | 2.14 | 4.3 | 23.8 |

acid sites, or even eliminated them completely. As could be inferred from analysis of the Ni° content and catalytic behaviour of samples, the very short duration of contact (seconds or less) of the sodium vapour with the zeolite did not lead to further reduction of $Ni^{2+}$ ions.   –

The reactions taking place in propylene — dihydrogen mixtures in the presence of the catalysts mentioned were followed by g.c. product analysis*.

The experiments could be reproduced quite well. The standard deviation of the kinetic data was less than 2% in parallel runs.

b) *Method for the evaluation of experimental data*

The reaction products obtained from propylene — dihydrogen mixtures of different compositions between 573 and 723 K over Hi°NHaY zeolite catalysts reveal a set of very complex primary, secondary, *etc.* reactions. Among them, the hydrogenation of propylene, its oligomerization (on the basis of the cracking products formed), and the hydroisomerization and hydrocracking of the paraffinic components are clearly discernible. At about 500 K (and below) the rates of these last two types of reactions are negligible, rendering study of the hydrogenation and oligomerization possible.

The product distribution obtained from a 1:1 propylene — dihydrogen mixture at 473 K over a Ni°HNaY zeolite (No. 2) catalyst is to be seen in Fig. 1 as a function of the reaction time.
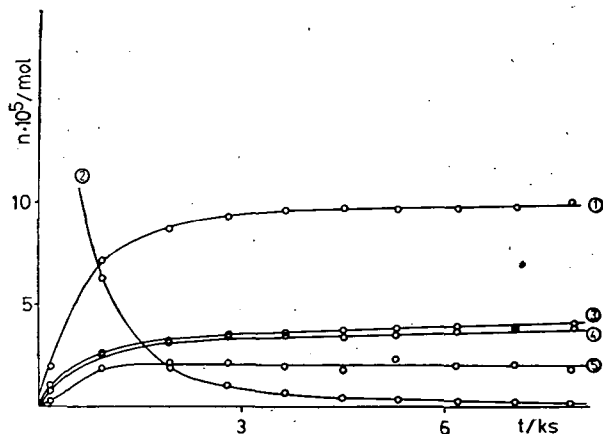


*Fig. 1.* Products obtained by the bifunctional action of the Ni°HNaY zeolite catalyst (No. 2) from 1:1 propylene-dihydrogen mixture as a function of reaction time (reaction temperature: 473 K; reactor volume: $65 \cdot 10^{-6}$ m³; volume of the whole system: $221.9 \cdot 10^{-6}$ m³; initial amount of propylene: $584.4 \cdot 10^{-6}$ mol; products: ①propane: ②propylene: ③*iso*-butane: ④*iso*-pentane; ⑤2-methylpentane).

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Over HY zeolite under otherwise identical experimental conditions, only the characteristic oligomerization — isomerization — cracking (for the sake of brevity: oic) reactions can be observed. The main products of these reactions are paraffinic hydrocarbons (propane, 2-methylpropane, 2-methylbutane, 2-methylpentane) produced from higher oligomeric carbonium ions *via* cracking, followed by $H^-$ ion transfer. Traces of olefins (*iso*-butene and *iso*-pentenes) originate from the respective carbonium ions *via* deprotonation reactions [13]. A similar product pattern results if propylene reacts over $Ni^0HNaY$ in the absence of dihydrogen.

It is worthwhile to draw attention to the interesting observation that $C_1$ and $C_2$ hydrocarbons are produced in surprisingly low amounts.

At present, the experimental data do not seem to justify a detailed interpretation, and we shall simply enumerate the hydrogenation (dehydrogenation) and oic reactions (each characterized by the extents of reaction) leading to the observed products:
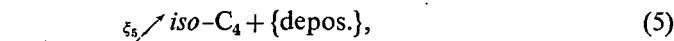
Hydrogenation of propylene:

$$C_3^= + H_2 \xrightarrow{\xi_1} C_3. \tag{1}$$

Production of propyl carbonium ion:

$$C_3^= + H^+ \xrightarrow{\xi_2} \{C_3^+\}. \tag{2}$$
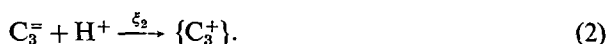
Hydride ion transfer (from an appropriate hydrocarbon species):

$$\{C_3^+\} + H^- \xrightarrow{\xi_3} C_3. \tag{3}$$

Propylene oligomerization:

$$C_3^= + \{C_3^+\} \xrightarrow{\xi_4} \{iso\text{-}C_6^+\}. \tag{4}$$

$\beta$-cleavage of the 2-methylpentyl carbonium ion:

$$\{iso\text{-}C_6^+\} \begin{cases} \xrightarrow{\xi_5} iso\text{-}C_4 + \{depos.\}, & (5) \\ \xrightarrow{\xi_6} iso\text{-}C_5 + \{depos.\}. & (6) \end{cases}$$

Hydride ion transfer:

$$\{iso\text{-}C_6^+\} + H^- \xrightarrow{\xi_7} iso\text{-}C_6. \tag{7}$$
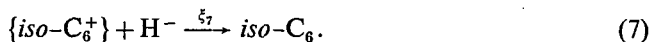
The suggested pathway is certainly oversimplified, because
(i) reaction (4) does not stop at the dimeric species; higher oligomers too are formed, though how far this oligomerization actually proceeds in the cavities of the zeolites has never been clearly established;
(ii) (5) and (6) are merely an indication that *iso*-butane and *iso*-pentane are formed from higher oligomers *via* cracking (leading to lower olefins) and $H^-$ ion transfer to the olefinic fragments; the interpretation of this very complex reaction sequence is still lacking*.

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* The parent carbonium ion is probably not the dimer, but the trimer, because the production of $C_1^+$ and $C_2^+$ carbonium ions is not favoured from a thermodynamic point of view. This agrees well with the observation that methane and ethane are practically absent from the reaction products, on the other hand, the product pattern is too simple for it to be derived easily from the trimer.

Despite the shortcomings indicated, the above model was resorted to in an effort to distinguish between the two main types of reactions, *i.e.* the hydrogenation and the oic reactions of propylene, and to facilitate interpretation of the experimental results.

If the steady-state amounts of carbonium ions in the zeolitic framework are neglected then the extents $\xi_1$ of the hydrogenation reaction (1) and $\xi_2$ of the oic reactions (characterized by step (2)) can be expressed in accordance with Bodenstein's principle by the experimentally observable quantities:

$$\xi_1 = n_{H_2}^0 - n_{H_2} \tag{8}$$

and

$$\xi_2 = n_{C_3} + n_{iso-C_4} + n_{iso-C_5} + n_{iso-C_6} + n_{H_2}^0 - n_{H_2} \tag{9}$$

where the $n_i$-s are the amounts of the respective species in the tank reactor.

The selectivity for the hydrogenation and oic reactions, respectively, is defined by the corresponding rates:

$$S = \frac{d\xi_1/dt}{d\xi_2/dt} = d\xi_1/d\xi_2. \tag{10}$$

Accordingly, the selectivity can be deduced from the slopes of the $\xi_1$ vs. $\xi_2$ curves.

## c) *Activity of the Ni°HNaY zeolitic catalysts as a function of the temperature of reduction*

Transition metal ions occupy different exchange positions in the zeolitic framework, depending on the degree of exchange and the pretreatment conditions (which influence the degree of ion hydration and hence their size and mobility). Therefore, it is not surprising that reduction with dihydrogen does not follow uniform kinetics [14, 15]. From the point of view of catalytic activity, it would be necessary to know not only the degree of reduction, but the distribution of the metal clusters produced as well. Changes in their size and topological availability (which influence the catalytic activity dramatically) cause interesting selectivity phenomena.

As mentioned in the introduction, the ratio $Ni°:H^+$ in the framework is governed by the stoichiometry of reduction and leads to figures near 0.5 (provided $Ni^+$ ions are formed in negligible quantity). From this it follows, as a first guess, that the selectivity toward hydrogenation and oic reactions should remain constant irrespective of the absolute numbers of the relevant active centres. This conclusion turns out to be completely wrong, as illustrated in Figs. 2 and 3.

Figure 2 shows that selectivity towards hydrogenation at 473 K increases with increasing temperature of reduction (curve A). The degree of reduction changes similarly (curve B). At the highest temperature applied (723 K), a proportion of the acid centres are lost by dehydroxylation.

The picture is more complex if the initial concentration of the exchange transition metal ions is different, as shown in its effects in Fig. 3. Samples No. 2 and No. 3 contained 4.2 and 2.1 mass% $Ni^{2+}$ initially. After reduction at 723 K with dihydrogen, the degrees of reduction were 0.328 and 0.425, respectively. This means that the $Ni°$ and $H^+$ content of sample No. 3 was only about 65% that of sample No. 2, and, in

spite of this the selectivity of sample No. 2 towards hydrogenation exceeded that of No. 3 by a factor greater than 3.

These experimental results are explained by the strange behaviour of the metallic phase (migration of atoms to form clusters) and by the fact that processes of lower kinetic order are preferred in the case of parallel reactions. In addition hydrogenation is one of the fastest catalytic transformations.
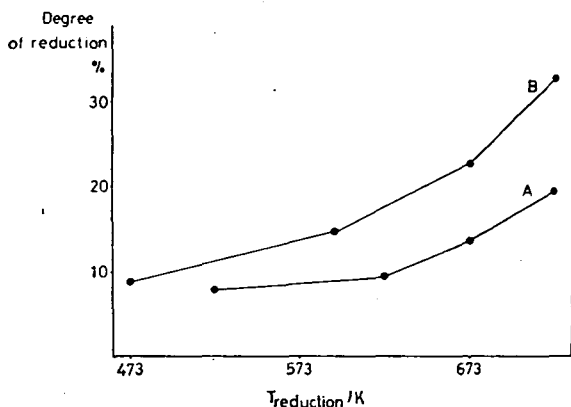


Fig. 2. Change of the selectivity (curve A) and the degree of reduction (curve B) as a function of reduction temperature (other parameters are the same as at Fig. 1.).
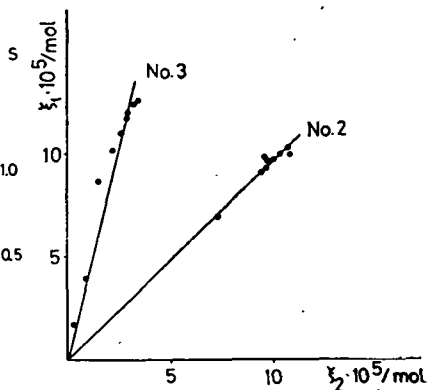
Fig. 3. The affect of the initial $Ni^{2+}$ ion concentration of zeolites on the selectivity (reaction circumstances are the same as at Fig. 1).

d) *Effect of the reaction temperature*

The product distributions of two characteristic runs are shown in Figs. 4 and 5. In 1:1 propylene-dihydrogen mixtures, hydrogenation predominates at 423 K. Products from the oic reactions appear in minor quantities only. At 623 K the contribution of the oic reactions to the products is significant (2-methylpentane and 2-methylbutane are unstable at this relatively high temperature and undergo secondary cracking reactions).

Data on the changes in selectivity at different temperatures are listed in Table II. On increase of the temperature to 523 K the oic reactions steadily gain in importance. At about 523 K the amount of propane among the products starts to increase, which can be accounted for by secondary cracking and H-transfer reactions of the paraffinic hydrocarbons produced in the oic reactions.

*Table II*

*Effect of the reaction temperature on the selectivity*

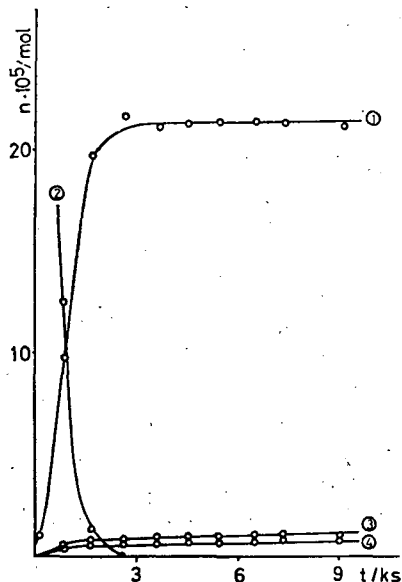| Reaction temperature [K] | 423 | 473 | 523 | 573 | 623 |
|---|---|---|---|---|---|
| Selectivity (S) | 11.8 | 0.98 | 0.39 | 0.46 | 0.81 |

Fig. 4. Product distribution obtained by the action of the Ni°HNaY zeolite catalyst (No. 2) from 1:1 propylene-dihydrogen mixture at 423 K as a function of reaction time (reactor volume: 70.5 · 10⁻⁶ m³; volume of the whole system: 227.4 · 10⁻⁶ m³; initial amount of propylene: 584.4 · 10⁻⁶ mol; products: ① propane; ② propylene; ③ iso-butane; ④ iso-pentane).
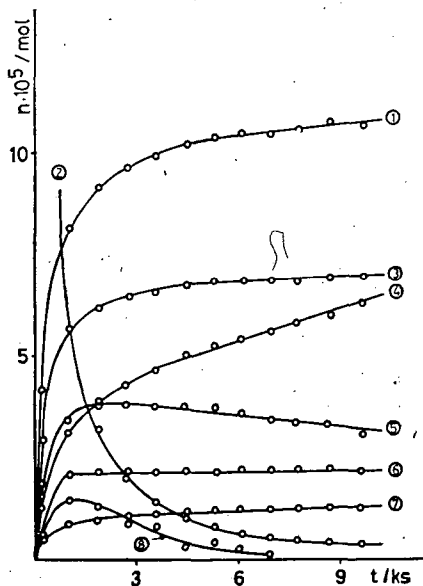
Fig. 5. Product distribution obtained by the action of the Ni°HNAY zeolite catalyst (No. 2) from 1:1 propylene-dihydrogen mixture at 623 K as a function of reaction time (reactor volume: 54.5 · 10⁻⁶ m³; volume of the whole system: 211.4 · 10⁻⁶ m³; initial amount of propylene: 584.4 · 10⁻⁶ mol; products: ① propane; ② propylene; ③ iso-butane; ④ methane; ⑤ iso-pentane; ⑥ ethane; ⑦ butane; ⑧ 2-methylpentane).

This behaviour reflects a very complicated temperature-dependence, where the displacement of the hydrogenation equilibrium, the increase of the rate of oligomerization, and the appearance of reactions with higher activation energies (cracking) are clearly discernible.

It could be concluded from these investigations that separate study of the hydrogenation and oic reactions in propylene-dihydrogen mixtures over Ni°HNaY zeolites can most conveniently be carried out at around 473 K.

e) *Effect of changing the propylene: dihydrogen ratio*

As expected, the selectivity of Ni°HNaY zeolite catalysts depends on the initial composition of the propylene-dihydrogen mixtures. The data in Table III demonstrate convincingly that at compositions poor in dihydrogen the oic reactions take over; on the other hand, in mixtures rich in dihydrogen hydrogenation is the predominant reaction.

*Table III*

*Effect of the propylene: dihydrogen ratio on the selectivity*

| Propylene:dihydrogen ratio | 4:1 | 1:1 | 1:4 |
|---|---|---|---|
| Selectivity (S) | 0.59 | 0.67 | 0.79 |

## f). *Effect of poisoning by sodium on the selectivity of bifunctional Ni°HNaY catalysts*

For selective poisoning of the acid site activity in Ni°HNaY zeolite catalysts, sample No. 2 was used with added $NaN_3$. (Compositions are given in Table I.)

The changes caused in the selectivity by varying additions of $NaN_3$ are seen in Fig. 6. The experimental data reveal that even small amounts of $NaN_3$ (0.21 mol $NaN_3$/mol $Ni^{2+}$) are able to influence the selectivity in favour of hydrogenation by poisoning the acid site activity. From an azide content of 2.14 mol $NaN_3$/mol $Ni^{2+}$ on, only hydrogenation takes place over the catalysts, as shown in Fig. 7. Here the sum of the oligomeric products observed at a preselected time (100 min) is plotted against the degree of poisoning (which is measured as the amount of added $NaN_3/Ni^{2+}$). It is to be seen that the oligomerization activity (*i.e.* catalyst acidity) is reduced to a great extent, and is finally eliminated completely, due mainly to the
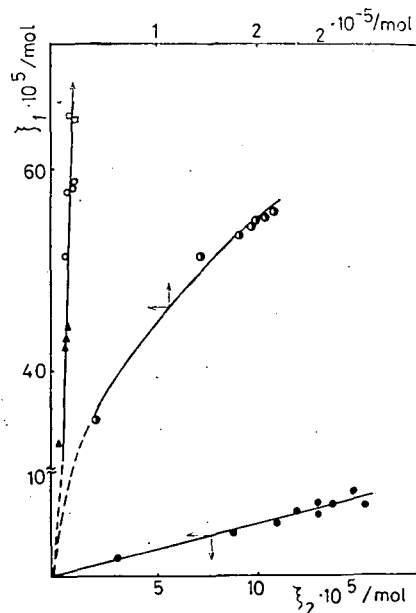
*Fig. 6.* Change of the selectivity caused by added $NaN_3$ (reaction circumstances are the same as at Fig. 1; catalysts: ● No. 2; ◀ No. 4; ▲ No. 5; ○ No. 6; ▣ No. 7)
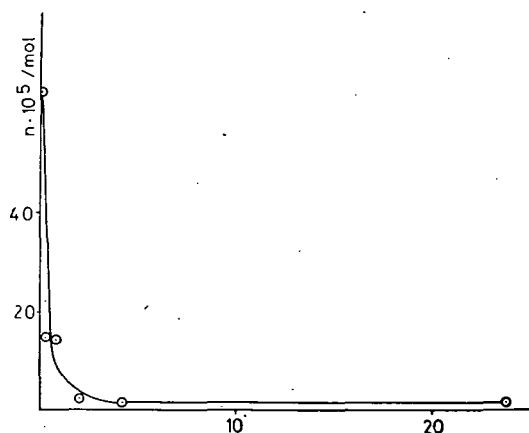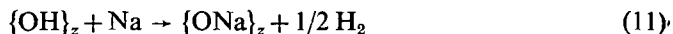
*Fig. 7.* The sum of the oligomeric products observed at 100 min as a function of the amount of added $NaN_3$ (reaction circumstances are the same as at Fig. 1).

reaction:

$$\{OH\}_z + Na \rightarrow \{ONa\}_z + 1/2 \, H_2 \tag{11}$$

(where $\{OH\}_z$ stands for the Brönsted acid site concentration in the zeolite). The simple neutralization reaction between acidic centres and NaOH (from traces of water and sodium):

$$HOH + Na \longrightarrow NaOH + 1/2 \, H_2 \tag{12}$$

$$NaOH + \{OH\}_z \rightarrow \{ONa\}_z + HOH \tag{13}$$
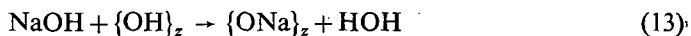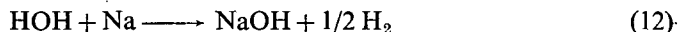
can not be excluded as a possible cause of poisoning either.

Direct IR investigations on the reduction of HF and LF OH band intensities as caused by poisoning with sodium vapour corroborate the results of kinetic investigations [16]. This experience is in complete agreement with what has been observed in cyclopropane isomerization over zeolites and its poisoning with sodium [11].

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## ДЕЗАКТИВАЦИЯ КИСЛОТНЫХ АКТИВНЫХ ЦЕНТРОВ БИФУНКЦУОНАЛЬНЫХ ЦЕОЛИТНЫХ КАТАЛИЗАТОРОВ ТИПА Ni°HNaY НАТРИЕМ

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Исследованы реакции гидрогенизации и олигомеризации (последующие за крекингом) пропилена на бифункциональных цеолитных катализаторах типа Ni°HNaY. Можно установить, что в определенных пределах ионного обмена и условиях восстановления происходит изменение селективности каталитических свйств. Карбоногеническая активность бифункциональных катализаторов может быть уменьшен или исключен полностью с применением селективного отравления парами натрия, одновременно представляя возможность раздельного изучения различных активных центров.