

The Role of Ni⁺ Ions in the Activity of NiCaY Zeolite Catalysts for Ethylene Dimerization

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It is shown that thermal reduction at 473 K and photoassisted reduction at 77 K of NiCaY zeolites in hydrogen resulted in formation of Ni⁺ ions, detected by EPR, and in appearance of catalytic activity for the ethylene dimerization reaction at room temperature. Photoreduced catalysts exhibited 5-7 times higher selectivity for production of butenes than the catalysts thermally reduced in H₂. A linear relationship between the rates of ethylene conversion and the Ni⁺ concentrations in the photoactivated catalysts was found. The formation of lower concentrations of Ni⁺ ions was also shown to occur on unreduced NiCaY samples after contact with gaseous ethylene at 300 K. Using EPR spectroscopy the interaction of Ni⁺ ions with olefins was examined, and a reversible poisoning of the dimerization reaction by CO was explained. It is concluded that the catalytic activity of NiCaY zeolites was controlled by the number of Ni⁺ ions, which could be precursors of catalytically active intermediates.

INTRODUCTION

A considerable number of published papers (see, for example, Refs. (1-8)) have been concerned with the problem of nickel-containing oxide and zeolite catalysts for ethylene oligomerization. Since the pioneering work of Hogan *et al.* (1), where the activity of this type of catalyst was considered from the viewpoint of acidic catalysis, our knowledge about the nature of active sites in this reaction has been markedly enlarged.

At the present time there is no doubt that nickel ions directly participate in the formation of catalytically active sites; however, the oxidation and coordination states of the nickel species are still under discussion. For example, Feldbljum (2), by analogy with homogeneous catalysis, proposed the formation of nickel hydrides on the surface of silica-aluminas during the olefin oligomerization reaction, while other authors (3-5) postulated coordinatively unsaturated Ni²⁺ ions on SiO₂-Al₂O₃ surfaces as

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active centers for this reaction. It was also suggested (6) that a highly dispersed Ni⁰-phase in zeolites might be responsible for the catalytic activity. In addition, the possible participation of "low-valent" nickel ions, stabilized in the vicinity of surface acidic centers on silica was also discussed (7, 8). However, the authors of these papers did not give a definite meaning to the term "low-valent" nickel, but just assumed an oxidation state lower than 2+.

Taking into account the results of later publications, it seems logical to identify "low-valent" nickel species with monovalent nickel ions, which can be produced in Ni²⁺-exchanged zeolites (9-11) and in Ni²⁺-silica (12, 13) or Ni²⁺-alumina (13) systems either by mild thermal reduction or by low-temperature photoassisted reduction of Ni²⁺ ions in H₂. This conclusion is supported by the following experimental observations:

(i) The dimerization reaction was found to be poisoned by carbon monoxide (6, 7). This fact can be explained by blocking of catalytically active sites due to formation of Ni⁺(CO)_n complexes with n = 1-3 (9-13);

no indication was found by ir spectroscopy for a strong bonding of CO molecules with Ni²⁺ ions (10).

(ii) The maximum catalytic activity for NiO/SiO₂ and Ni-zeolites was reached after preliminary thermal reduction in H₂ at 570 K (7, 8), that is, under conditions which are favorable for production of Ni⁺ ions.

Further evidence for the participation of Ni ions in catalytic reactions was obtained in our earlier works (13, 14), where the effect of the reducing pretreatment of Ni²⁺/SiO₂ and Ni²⁺/Al₂O₃ on their catalytic activities was studied. It was found that the prerduced catalysts exhibited essentially higher activities for acetylene cyclotrimerization and for ethylene oligomerization at room temperature than the unreduced catalysts. Very recently, Bonneviot *et al.* (11) have observed an analogous effect for ethylene and propylene dimerization reactions over Ni/SiO₂ and NiCaHX catalysts. By means of EPR spectroscopy it was found that Ni⁺ ions were able to form complexes with olefin molecules; their EPR spectra changed as the reaction proceeded.

In the present work the mechanism of ethylene dimerization reaction over NiCaY zeolite catalysts has been studied. The emphasis was placed on a search for a quantitative correlation between the Ni⁺ concentration after catalyst reduction and the rate of the catalytic reaction. It was also hoped that this investigation would shed light on the role of acidic centers and hydride ions in this reaction. NiCaY zeolites were expected to be more suitable objects for a quantitative study than conventional supported systems, since unlike Ni²⁺/SiO₂ and Ni²⁺/Al₂O₃, where different nickel-containing phases exist (nickel oxide, spinels, nickel silicates and aluminates), they contain mainly isolated Ni²⁺ ions localized in the sodalite cages (15).

EXPERIMENTAL

Materials. The starting material, NaY zeolite (SiO₂/Al₂O₃ = 5.7) was successively exchanged with aqueous solutions of CaCl₂

and then Ni(NO₃)₂. After heating at 340 K in air it was outgassed at this temperature at 10⁻⁴ Torr (1 Torr = 133.3 N m⁻²). The nickel content was determined by atomic absorption spectroscopy. The unit cell formula for the zeolite used was Ni_{3.74}Ca_{21.19}Si_{142.13}Al_{49.37}O₃₈₄. The pretreatment of the zeolite samples consisted of outgassing at 370–400 K for 1 h and heating in a flow of dry oxygen (100 Torr), while the temperature was gradually raised (~8 K min⁻¹) to 773 K. Then the samples were kept for 2 h at this temperature. After repeated admissions of oxygen the temperature was decreased to 423 K and the samples were evacuated to 5 × 10⁻⁵ Torr.

Hydrogen and deuterium were purified by diffusion through a red-hot (1100 K) palladium thimble. Carbon monoxide was freed from O₂ and other contaminants by passing through a column with reduced Cr²⁺/SiO₂ adsorbent and several traps cooled with liquid nitrogen. Ethylene from a cylinder was purified by repeated cooling to 77 K and distillation at 143 K. 1-Butene and *cis*-2-butene, manufactured by Fluka (Switzerland), were used without purification.

Catalytic measurements. Catalytic activities of NiCaY in the ethylene oligomerization reaction were measured at room temperature in an evacuable gas-circulating system with greaseless metallic valves, having a total reaction volume of 543 cm³; the amount of catalyst was 0.25–0.32 g. The initial ethylene pressures were 65–70 Torr. In some experiments the products of dimerization and oligomerization reactions were collected in a trap cooled to 140 K. The analysis of reaction mixtures was made by a quadrupole mass spectrometer, using for calibration mixtures of ethylene and butenes of known composition.

Reduction in H₂. Photoreduction of NiCaY catalysts, placed in a quartz reactor, was performed at 77 K under uv-irradiation with a high-pressure mercury lamp, Model DRSh-1000 (1 kW), equipped with a water filter, for 0.5–5 h. The hydrogen pressure

was 2–5 Torr. To provide a more uniform photoreduction the powder samples were shaken during irradiation using an electromagnetic microvibrator. Thermal reduction in H_2 at pressures of 5–10 Torr was carried out at 470 K.

EPR measurements. EPR spectra were recorded at 77 K in the X-band with a Bruker ER-200 D instrument. For EPR measurements a portion of the catalyst could be transferred from the reactor to the sample tubes *in vacuo*.

RESULTS AND DISCUSSION

Catalytic activity of NiCaY. Unreduced samples of NiCaY showed no appreciable activity during the first 10–20 min after admission of ethylene to the catalyst at room temperature. After this "induction period" a rapid decrease in ethylene pressure was observed, indicating the occurrence of the oligomerization reaction (Fig. 1a). Raising the temperature led to shortening of the induction period, and at temperatures higher than 343 K the reaction started immediately after ethylene admission.

Prereduction of the NiCaY catalyst in H_2 , which was shown to be accompanied by the formation of Ni^+ ions (see below), resulted in elimination of the induction period for room-temperature reaction (Figs. 1b–e). It is also seen from Fig. 1 that the initial reaction rates increased with increasing ir-

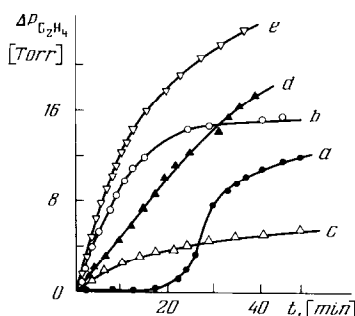


FIG. 1. Rates of decrease of ethylene pressure at room temperature over NiCaY zeolite: (a) unreduced; (b) reduced in H_2 at 473 K for 2 h; photoreduced in H_2 at 77 K for 0.5 h (c), for 2 h (d), and for 5 h (e). $P_{C_2H_4} = 65$ –70 Torr.

TABLE I

Effect of Preliminary Treatments on the Selectivity of NiCaY Zeolite in Production of Butenes

Catalyst pretreatment	Selectivity of butene production in % ^a	
	With a cold trap (140 K) ^b	Without a cold trap
Unreduced	9.3	—
Thermally reduced in H_2 at 420 K, 2 h	12.0	5.2
Photoreduced in H_2 at 77 K, 2 h	62.0	40.5

^a At total ethylene conversion of 15–20%.

^b A cold trap was used to remove products (butenes and higher oligomers) from reaction mixtures.

radiation time in the course of preliminary photoreduction of the catalyst.

As the reaction proceeded, the activity of NiCaY catalysts gradually decreased, probably because the active centers became blocked by oligomers. This phenomenon has been reported before for nickel-containing catalysts in olefin dimerization (3, 8). One can see from Fig. 1 that the rate of ethylene conversion slowed down more rapidly on the thermally reduced sample (curve b) than on the photoreduced ones (curves c–e). The initial activities of these catalysts could be restored by outgassing them at 370–420 K. Desorption of butenes and smaller amounts of hexenes was found to occur during this treatment.

The data on the selectivity of the ethylene dimerization reaction on NiCaY and its dependence on pretreatment conditions are given in Table 1. It is seen that removal of the reaction products (butenes and higher oligomers) in a cold trap led to a marked improvement of the reaction selectivity. It should be also noted that the relative yield of butenes on the photoreduced samples is 5–7 times as high as that on the thermally reduced catalysts.

This effect appears to be associated with the higher rates of secondary reactions of

butenes on the thermally reduced samples. In order to prove this suggestion, the kinetics of 1-butene oligomerization on prereduced NiCaY zeolites were measured (Fig. 2), since 1-butene was found to be the major reaction product of ethylene dimerization (3, 5–7). It follows from Fig. 2, in accordance with our expectations, that the initial rate of 1-butene oligomerization on the thermally reduced catalysts was substantially higher than that on photoreduced samples (curves b and c, respectively). In addition, the thermally reduced samples deactivated more rapidly.

The higher activity of the thermally reduced catalysts in butene conversion is apparently connected with the presence of proton acidic centers on which the olefin oligomerization readily occurs (15, 16). In the course of thermal reduction in hydrogen, not only Ni⁺ ions but also Ni⁰-ferromagnetic clusters are formed. The latter process is accompanied by the appearance of proton acidic centers which are required to maintain the electroneutrality of the zeolite framework (15). Photoreduction is a much more selective process, and no Ni⁰-phase was formed. Therefore butene yields on the photoreduced catalysts remarkably increased.

EPR study of the interaction of Ni⁺ ions with ethylene. The activation procedure of NiCaY samples, described above, led to the formation of Ni⁺ ions, detected by EPR. A representative spectrum of Ni⁺ with $g_{\perp} = 2.092$ and unobservable g_{\parallel} is shown in Fig. 3a. Previously similar spectra were re-

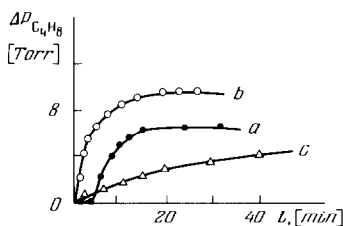


FIG. 2. Rates of decrease of 1-butene pressure at room temperature over NiCaY zeolite: (a) unreduced; (b) reduced in H₂ at 473 K for 2 h; (c) photoreduced in H₂ at 77 K for 1.5 h. $P_{C_4H_8} = 65$ Torr.

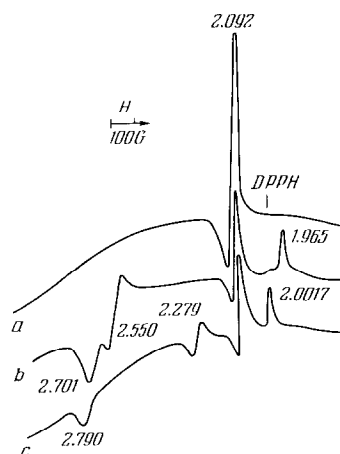


FIG. 3. EPR spectra of photoreduced NiCaY zeolite: (a) photoreduced in H₂ at 77 K for 2 h; (b) after admission of 70 Torr of C₂H₄ at room temperature; (c) after outgassing of sample (b) at 373 K. Spectra were recorded at 77 K.

ported for the Ni-zeolites photo- and thermally reduced in H₂ and were assigned to Ni⁺ ions in S_I or S_{II} positions (9–11).

The amounts of Ni⁺ ions formed by thermal reduction or photoreduction are rather low. The concentration of Ni⁺ ions could be estimated by double graphic integration of the EPR spectra of complexes with CO. Integration of such spectra could be performed more accurately than that of the original broad Ni⁺ spectra with unobservable g_{\parallel} . The maximum Ni⁺ concentration was found to be $3 \times 10^{18} \text{ g}^{-1}$; this value corresponds to only 1–2% of the total number of Ni²⁺ ions in the NiCaY zeolite.

It was of the utmost interest to study the interaction between Ni⁺ ions and olefins since it was thought this might give additional information on the nature of the catalytic activity of reduced samples. After adsorption of relatively small amounts of C₂H₄ ($1 \times 10^{18} \text{ molecules} \cdot \text{g}^{-1}$) on photoreduced NiCaY at 300 K, i.e., when the $N_{C_2H_4} : N_{Ni^+}$ ratio was kept below 0.5, the EPR spectrum of Ni⁺ ($g_{\perp} = 2.092$) did not change. After adsorption of greater amounts of ethylene ($N_{C_2H_4} : N_{Ni^+} = 0.5 \div 3.0$) a gradual decrease of the Ni⁺ EPR signal and appearance of a new signal with g_{\perp}

= 1.965, $g_2 = 2.550$, and $g_3 = 2.701$ were observed (Fig. 3b). The intensity of this spectrum did not change appreciably when increasing the ethylene pressure up to 50–70 Torr.

Identical spectra were obtained when a slightly modified procedure was employed. Ethylene was admitted to the photoreduced and evacuated sample, kept at 77 K. The sample was then removed from the liquid-nitrogen bath and held for a few seconds at ambient temperature. After the frozen ethylene had melted, the sample was immersed again in the liquid-nitrogen bath and EPR spectra were recorded.

It should be noted that the original spectrum of Ni^+ ions with $g_{\perp} = 2.092$ did not disappear completely after ethylene adsorption. This fact may be regarded as evidence for inaccessibility of a certain fraction of the Ni^+ ions for ethylene molecules.

At room temperature the Ni^+ -ethylene complexes are stable for a long time (at least 3 days). Thus, it seems likely that the products of oligomerization reaction (butenes and higher oligomers) are not able to displace ethylene molecules from the coordination sphere of the Ni^+ ions. Outgassing the samples at room temperature did not lead to any change in the intensity or lineshape of the spectrum shown in Fig. 3b, but after heating the sample *in vacuo* at 370 K there was a shift of the g -values and a new spectrum with $g_1 = 2.0017$, $g_2 = 2.28$, and $g_3 = 2.79$ was observed (Fig. 3c). After raising the temperature of evacuation to 520 K the original Ni^+ signal with $g_{\perp} = 2.092$ and with the initial intensity was restored. After such a treatment the zeolites retained their catalytic activity.

It might be thought reasonable to assume that the spectrum shown in Fig. 3b could be assigned to complexes of Ni^+ with the reaction products. However, this suggestion is inconsistent with the following experimental findings:

(1) After 2-butene adsorption at 300 K on prerduced zeolites an EPR spectrum with

different g -values ($g_{\parallel} = 1.957$, $g_{\perp} = 2.66$) was obtained.

(ii) As shown above, identical EPR spectra were recorded either after interaction of excess ethylene with the Ni^+ at low temperature, when the dimerization reaction was quenched, or after adsorption of relatively small amounts of ethylene at 300 K, when the reaction was allowed to proceed.

The spectrum in Fig. 3b is not characteristic of $\text{Ni}^+(d^9)$ ions because one of its g -values (g_1) is substantially less than $g_e = 2.0023$. Earlier we observed similar EPR signals after adsorption of ethylene and propylene on prerduced $\text{Ni}^{2+}/\text{SiO}_2$ and $\text{Ni}^{2+}/\text{Al}_2\text{O}_3$ (13). Recently appearance of EPR spectra with $g_1 < g_e$ and a large g -value anisotropy after adsorption of different olefin molecules on the prerduced NiCaX zeolites has also been reported (11). However, no interpretation of the observed g -values was given so far.

The spectra presented in Fig. 3 (b and c) cannot be explained in terms of simple crystal field theory, which is often applied for interpretation of EPR spectra of transition metal ions and their complexes, since for paramagnetic ions with d^9 -electron configuration this theory predicts all three g -values greater than $g_e = 2.0023$. A large g -value anisotropy in the Ni^+ -olefin spectra can be regarded as an indication that the electronic state of Ni^+ ions is nearly degenerate. Perhaps, the peculiarities in the EPR spectra of such complexes can be attributed to a strong covalent bonding between the d -electrons of Ni^+ ions and the π -electrons of ethylene molecules.

After admission of 60 Torr of C_2H_4 at room temperature on unreduced NiCaY catalysts a weak EPR signal of Ni^+ ions with $g_{\perp} = 2.092$ was developed in 10–15 min. This observation correlates with the existence of the "induction period" for the dimerization reaction, which was described above (Fig. 1). However, in contrast to the prerduced samples, the lines corresponding to the Ni^+ -ethylene complexes could not be seen in this case in the EPR spectra;

this is thought to be due to their low intensity. Carbon monoxide admission (≈ 100 Torr) on the sample with preadsorbed ethylene gave rise to a typical Ni⁺(CO)₃ EPR spectrum (see below); however, its intensity was 3–5 times lower than that in the zeolites prereduced in H₂.

Poisoning catalytic activity by CO. Correlations between activity and the number of Ni⁺ ions. Adsorption of even a small amount of CO (5×10^{18} molecules \cdot g⁻¹) on reduced NiCaY samples completely suppressed their activity in ethylene dimerization. However, this poisoning effect was found to be reversible, because after CO desorption at 420–440 K the samples regained their initial activities.

As shown in Refs. (9–13), Ni⁺ ions can yield complexes with CO molecules, Ni⁺(CO)_{*n*}, in which *n* varies from 1 to 4, depending on the CO pressure. Similar complexes were also detected by EPR in the reduced NiCaY zeolites. The following *g*-values were found: Ni⁺(CO)₃—*g*₁ = 2.013, *g*₂ = 2.118, and *g*₃ = 2.225; Ni⁺(CO)₂—*g*_⊥ = 2.065 and *g*_∥ = 2.212; Ni⁺(CO)—*g*_⊥ = 2.015 and *g*_∥ = 2.39. The Ni⁺(CO)₃ complexes prevailed under CO pressures above 100 Torr; the Ni⁺(CO)₂ complexes were stable when outgassing the zeolite down to residual pressure of 5×10^{-5} Torr at 300 K, while the Ni⁺(CO) species were detected after evacuation of the samples at 350 K. In the last case lines belonging to the Ni⁺(CO)₂ and bare Ni⁺ species were also observed. It should be noted that the thermal stability and the CO pressures required for the formation of Ni⁺(CO)_{*n*} complexes in NiCaY zeolite differ considerably from those characteristic of the corresponding Ni⁺ species in NiCaX zeolites (11).

By measuring the number of CO molecules (*N*_{des.}) desorbed from the samples, pre-outgassed at 300 K, during a temperature rise from 300 K up to 420–440 K, it was possible to estimate the concentration of the Ni⁺ ions. In this way it was found that *N*_{des.} varied from 0.12×10^{18} to 3.5×10^{18}

molecules CO per g catalyst, depending on preliminary irradiation time (0.3–0.5 h). In blank experiments with unreduced samples no CO desorption from the samples, outgassed at 300 K, was observed.

Taking the slopes of the initial portion of the kinetic curves presented in Fig. 1 as a measure of the reaction rates, one can obtain a plot of the activities of the photoreduced NiCaY catalysts versus *N*_{des.}, which is proportional to the Ni⁺ ion concentration produced by photoreduction (Fig. 4). As seen from this figure, there is a linear relationship between *N*_{des.} and the initial dimerization rates over a wide range of the Ni⁺ concentration. This implies that the catalytic activity of the reduced NiCaY zeolites is controlled by the Ni⁺ concentration. Thus it seems reasonable to conclude that Ni⁺ ions take part directly in the formation of the catalytically active sites or are precursors of such sites.

Poisoning the catalytic activity by CO adsorption can be rationalized when considering the corresponding EPR spectra. On the one hand, it was established that at room temperature in the presence of gaseous CO the Ni⁺(C₂H₄)_{*n*} EPR spectra transformed rapidly into the spectra typical of Ni⁺(CO)_{*n*} complexes. This implies that CO molecules behaved as stronger ligands, replacing one or several C₂H₄ molecules from the coordination sphere of the Ni⁺ complexes. On the other hand, even under relatively high pressures of gaseous C₂H₄ (up to 50 Torr), no

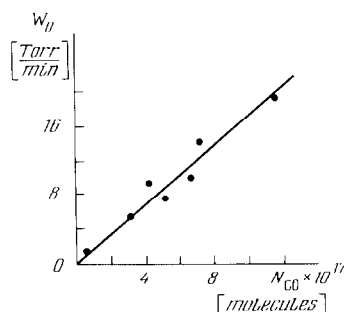
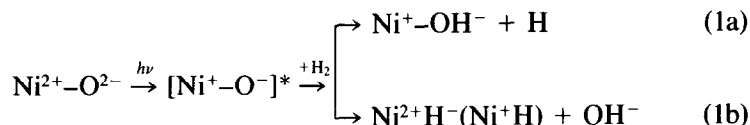


FIG. 4. Dependence of initial rates of ethylene conversion on the number of Ni⁺ ions in photoreduced NiCaY zeolite (sample mass is 0.3102 g).

changes in EPR spectra of the $\text{Ni}^+(\text{CO})_2$ complexes were found to occur at room temperature. Thus it appears from these data that the entering of one or more CO molecules into the coordination sphere of the Ni^+ ions prevents their participation in catalysis.

Formation of hydride ions by photore-



The Ni^{2+}H^- or Ni^+H species formed in reaction (1b) were defined in Ref. (17) as "hydride ions"; they were shown to be the active intermediates in the H_2 - D_2 exchange reaction. On the other hand, Feldbljum (2) assumed that the activity of nickel-containing catalysts in the olefin dimerization reaction could be associated with the formation of a hydride-type bond, $\text{Ni}-\text{H}$. Therefore, it was of interest to investigate the possible role of "hydride ions" in this reaction.

After preliminary uv-irradiation in the presence of 100–200 Torr of H_2 NiCaY samples exhibited a high catalytic activity in H_2 - D_2 exchange at room temperature. This result agrees fairly well with the data of Ref. (17). Heating the photoreduced samples at 390–420 K was accompanied by desorption of 1×10^{18} – 1.5×10^{18} molecules of H_2 per g catalyst and by an increase of the Ni^+ EPR signals to 2×10^{18} – 3×10^{18} spins per g catalyst. In addition, by such a treatment NiCaY samples were completely deactivated in the exchange reaction. This could be explained by the thermal decomposition of the "hydride ions": $\text{Ni}^{2+}\text{H}^- \xrightarrow{400\text{ K}} \text{Ni}^+ + \frac{1}{2}\text{H}_2$.

However, the heat treatment of the photoreduced samples had no noticeable influence on the rates of the ethylene dimerization reaction, so that one may conclude that Ni^{2+}H^- species are not involved in this reaction.

CONCLUSIONS

The results of the present paper clearly

duction of NiCaY and their role in catalysis. In our earlier work (17) which dealt with the study of the low-temperature H_2 - D_2 exchange reaction mechanism on photoreduced NiY zeolites, two parallel reactions were proposed to occur under uv-irradiation:

support the earlier proposed idea about the involvement of "low-valent" nickel ions in the ethylene dimerization reaction. The observed correlations between the concentration of Ni^+ ions in reduced samples, and also the number of CO molecules required for poisoning of the catalysts, and the rates of the dimerization reaction enable us to draw a definite conclusion that the catalytic activity of NiCaY zeolites in ethylene dimerization reaction is determined by the presence of Ni^+ ions. Using EPR spectroscopy, it was possible to clarify the mechanism of the poisoning effect of CO adsorption and to explain why the induction period was observed in the case of unreduced samples. Furthermore, it is shown that the photoactivation of NiCaY catalysts has certain advantages as compared to the thermal reduction procedure, because it gives catalysts with better selectivity for the dimerization process.

Nevertheless, the mechanism of the catalytic action of Ni-containing centers still remains unclear. A more thorough study of the structural and chemical properties of the Ni^+ complexes with olefins detected by EPR, and their further transformations under reaction conditions might give a deeper insight into detailed mechanism of the oligomerization catalysis and may be an object for future investigations.

REFERENCES

- Hogan, J. P., Banks, R. L., Lanning, W. C., and Clark, A., *Ind. Eng. Chem.* **47**, 752 (1955).

2. Feldbljum, V. Sh., "Proceedings, 4th International Congress on Catalysis, Moscow, 1968," Vol. 1, p. 192. Nauka, Moscow, 1970, and Vol. I, p. 222. Akademiai Kiadó, Budapest, 1971.
3. Borovkov, V. Yu., Kaverinsky, V. A., and Kazansky, V. B., in "Proceedings, International Symposium on Related Heterogeneous and Homogeneous Catalytic Phenomena," (B. Delmon and G. Jannes, Eds.), p. 253. Elsevier, Amsterdam, 1975.
4. Wendt, G., Finister, J., Shöllner, R., and Siegel, H., *Stud. Surf. Sci. Catal.* **7**, 978 (1981).
5. Wendt, G., Mörke, W., Schöllner, R., and Siegel, H., *Z. Anorg. Allg. Chem.* **488**, 197 (1982).
6. Yashima, T., Ushida, Y., Ebisawa, M., and Hara, N., *J. Catal.* **36**, 320 (1975).
7. Kimura, K., A-I, H., and Ozaki, A., *J. Catal.* **18**, 271 (1970).
8. Maruja, K., and Ozaki, A., *Bull. Chem. Soc. Jpn.* **46**, 351 (1973).
9. Garbowski, E. D., Mathieu, M.-V., and Primet, M., *Chem. Phys. Lett.* **49**, 247 (1977).
10. Kermarec, M., Olivier, D., Richard, M., and Che, M., *J. Phys. Chem.* **86**, 2818 (1982).
11. Bonneviot, L., Olivier, D., and Che, M., *J. Mol. Catal.* **21**, 415 (1983).
12. Elev, I. V., Shelimov, B. N., and Kazansky, V. B., *Kinet. Katal.* **23**, 936 (1982).
13. Elev, I. V., Shelimov, B. N., and Kazansky, V. B., *J. Mol. Catal.* **21**, 265 (1983).
14. Elev, I. V., Shelimov, B. N., and Kazansky, V. B., *Kinet. Katal.* **24**, 938 (1983).
15. Rabo, J. A., Ed., "Zeolite Chemistry and Catalysis." Amer. Chem. Soc., Washington, D.C., 1976. Mirachev, Kh. M., and Isakov, Ya. I., "Catalytic properties of metal-containing zeolites," p. 555.
16. Jacobs, P. A., "Carboniogenic Activity of Zeolites." Elsevier, Amsterdam, 1977.
17. Shuklov, A. D., Surin, S. A., Shelimov, B. N., and Kazansky, V. B., *Kinet. Katal.* **16**, 468 (1975).