unique feature of the composite copper-alumina catalyst is that it suppresses the formation of side products, notably that of ether on alumina.

ACKNOWLEDGMENTS

Valuable suggestions and critical comments from Professors P. Mars and M. Boudart have led to several improvements in the interpretation of the results reported in this work. The advice of Dr. P. S. Murti during the experimental work is gratefully acknowledged.

REFERENCES

1. Dolgov, B. N., Koton, M. M., and Siderov, N. V., *J. Gen. Chem. USSR* **6,** 1456 (1936); *CA* **31,** 2170 (1937).
2. Dolgov, B. N., and Nizovkina, T. V., *J. Gen. Chem. USSR* **19,** 1119 (1949).
3. Prasad, J., PhD thesis, Andhra University, Waltair, India, 1970.
4. Menon, P. G., and Prasad, J., *J. Catal.* **17,** 238 (1970).
5. Prasad, J., and Murti, P. S., unpublished data.
6. Weisz, P. B., and Swegler, E. W., *Science* **126,** 31 (1957).
7. Hindin, S., Weller, S. W., and Mills, G. A., *J. Phys. Chem.* **62,** 244 (1958).
8. Sinfelt, J. H., *in* "Advances in Chemical Engineering" (T. B. Drew, and J. W. Hoopes, Jr., eds.), Vol. 5, p. 49. Academic Press, New York, 1964.
9. Weisz, P. B., and Prater, C. D., *in* "Advances in Catalysis" (W. G. Frankenberg, V. I. Komarewsky, and E. K. Rideal, eds.), Vol, 9, p. 575. Academic Press, New York, 1957.
10. Menon, P. G, and Prasad, J., *J. Res. Inst. Catal. Hokkaido Univ.* **16,** 629 (1968).
11. Maxted, E. B., *in* "Advances in Catalysis" (W. G. Frankenburg, V. I Komarewsky, and E. K. Rideal, eds.), Vol. 3, p. 37. Academic Press, New York, 1951.

J. Prasad*
P. G. Menon**

Regional Research Laboratory,
Hyderabad—9, India
Received October 4, 1971

---

* Present address: Department of Chemical Engineering, Twente University of Technology, Enschede, The Netherlands.

** Present address: Ketjen N. V., Post Box 15-C, Amsterdam, The Netherlands.

X-Ray Diffraction Study of Nickel Ion Migration in Y-Zeolite

In a previous paper (*1*) it was shown by X-ray crystal structure analysis that cations in copper-exchanged Y-type zeolites may change positions when various reagents were added. In this paper we have studied by the same method the behavior of nickel ions in a $Ni_{14}Na_{23}Y$ zeolite heated at different temperatures or submitted to the action of different reagents (pyridine, NO and NH_3).

The Linde NaY starting material was ion exchanged in the conventional way with a $NiSO_4$ solution. Chemical analysis for Al^{3+}, Ni^{2+} and Na^+ showed the unit cell composition to be Ni_{14} Na_{23} H_5 Al_{56} Si_{136} O_{384}. Samples I–IV were dehydrated respectively at 140, 200, 300 and 600°C, by heating in oxygen for 12 hr and subsequent evacuation (10^{-5} Torr) for the same time. Seven other samples were obtained on addition of reagents to dehydrated samples. The treatment conditions for each sample are given in Table 1.

The experimental techniques and resolution methods used for crystal structure analysis have already been described in previous papers (*1, 2*). Atomic parameters of framework and extra-framework atoms were refined using 232 structure factors corresponding to 126 diffraction lines. No attempt has been made to locate the Ni^{2+} ions and reagent molecules occupying the supercages.

The cubic unit cell constants and nickel population of hexagonal prisms for all samples are given in Table 1.

TABLE 1

Samples	Heat treatment temp (°C)	Nature of the adsorbed reagent and time (hr) of contact (room temp, 100 Torr)	R index[a]	Cubic unit cell constant a (Å) (±0.005)	No. of nickel ions/unit cell in the hexagonal prisms (estimated error ±0.5)
I	140	—	0.083	24.625	3.7
Ia	140	NO 12	0.071	24.665	1.7
II	200	—	0.063	24.615	4.2
IIa	200	C_5H_5N 24	0.100	24.655	1.9
III	300	—	0.057	24.510	10.0
IIIa	300	C_5H_5N 72	0.077	24.525	9.0
IIIb	300	NO 12	0.066	24.575	6.5
IIIc	300	NO 96	0.063	24.620	3.4
IIId	300	NH_3 24	0.067	24.660	2.7
IV	600	—	0.067	24.470	11.9
IVa	600	C_5H_5N 72	0.068	24.475	11.1

[a] R crystallographic index is defined by $R = \Sigma|F_o - KF_c|/\Sigma|F_o|$, where F_o and F_c are the observed and calculated structure factors.

Dehydration

The sites S_I of samples I and II are occupied by 3.7 and 4.2 Ni^{2+} ions, respectively. Further dehydration (sample III and IV) induces an important displacement of Ni^{2+} ions towards the hexagonal prism centers. However, even for the sample heated at 600°C only 12 Ni^{2+} ions out of 14 can occupy S_I sites. According to Dempsey and Olson (*3*) this limit may be due to the fact that statistically in a Y-type zeolite only 12 hexagonal prisms exist which contain at least four aluminum atoms.

Adsorption of Pyridine

Addition of pyridine gives an important decrease of the S_I site population for the sample heated at 200°C. For samples heated at higher temperatures the ability to move out Ni^{2+} from the hexagonal prisms rapidly decreases and for sample IV the S_I population is probably not changed upon pyridine adsorption since the variation observed is within the experimental error.

Adsorption of Nitric Oxide

Nitric oxide adsorption on samples evacuated at 140 and 300°C, respectively, results in a large decrease of the S_I site population. Nitric oxide can penetrate deeply in the zeolite framework close to the hexagonal prisms; however, the reaction with nickel ions seems to be slow, since 3.5 and 6.5 Ni^{2+} ions are extracted from S_I sites after 12 hr (sample IIIb) and 96 hr (sample IIIc) of contact with the gas. By ESR and infrared spectroscopy the formation of a complex Ni^+NO^+ can be shown (*4*). Moreover, X-ray diffraction lines are broadened and their intensities rapidly decrease with increasing Bragg angles. Hence, defects in the alumino-silicate framework are produced upon adsorption of NO.

Adsorption of Ammonia

Ammonia adsorption (sample IIId) produces a large displacement of nickel ions.

Correlation between the S_I Site Population and the Cubic Unit Cell Constant

The number N of Ni^{2+} occupying S_I sites has been plotted for various samples in Fig. 1 as a function of the cubic unit cell constant a. A linear relation appears between N and a values. The decrease of a as S_I sites are progressively filled is due to the contraction of the hexagonal prisms: the six O(3) atoms which coordinate Ni^{2+} (I) are shifted towards the center of the hexagonal prism. This produces not only a lengthening of the T–O(3) bonds but also draws towards the center of hexagonal prisms the two six membered rings of

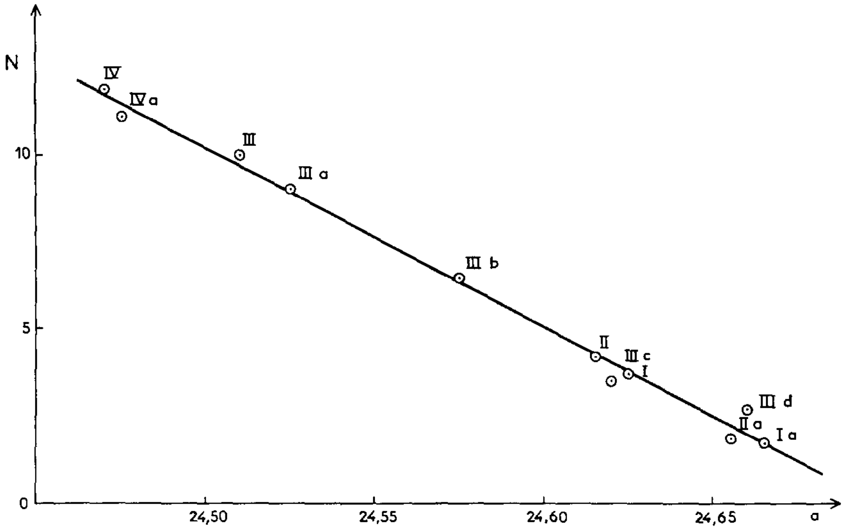

Fig. 1. Number N of Ni^{2+} ions occupying the hexagonal prisms versus the cubic unit cell constant a.

tetrahedra. This linear relationship can be used to obtain the N values with a fair approximation by simple measurements of unit cell constants.

Similar relationships may be established for NiNaY zeolites with other exchange levels.

To sum up, nickel ion location in the porous zeolite framework mainly depends on the nature of adsorbed molecules. Thus nickel ions migrate into the hexagonal prisms on progressive removal of water molecules. On total dehydration nickel ions strongly prefer S_I sites (although their number seems to be limited to 12) where they have an octahedral coordination. A different behavior has been observed for the $Cu_{16}Na_{14}Y$ zeolite (1) in which copper ions in similar conditions are mainly found in $S_{I'}$ sites.

Nickel ions occupying hexagonal prisms are not displaced by pyridine adsorption for completely dehydrated samples. Other large molecules adsorbed in the supercages are probably also unable to displace nickel ions; hence in a catalytic process where the nickel ions are the active centers, the activity of a Ni-Y zeolite having an exchange level lower than 50% would decrease by increasing the heat treatment temperature of the catalyst. Addition of reagents of small molecular size (NO, NH_3) may induce a cation migration from the hexagonal prism to the supercages. However, the effect of nitric oxide appears to be complicated and this problem needs further investigation. The linear relationship observed between the unit cell constant and the S_I site population enables, for any sample of the same exchange level, a quick determination of the number of nickel ions occupying the hexagonal prisms, namely ions which may be inactive because they cannot easily move towards the large molecules of reagents in the supercages.

REFERENCES

1. GALLEZOT, P., BEN TAARIT, Y., AND IMELIK, B., *J. Catal.* **26**, 295 (1972).
2. GALLEZOT, P., AND IMELIK, B., *J. Chim. Phys.* **68**, 816 (1971).
3. DEMPSEY, E., AND OLSON, D. H., *J. Phys. Chem.* **74**, 305 (1970).
4. NACCACHE, C., personal communication.

P. GALLEZOT
Y. BEN TAARIT
B. IMELIK

*Institut de Recherches sur la Catalyse-C.N.R.S.
69-Villeurbanne, France*
Received December 4, 1971