

MAGNETIC STUDY OF ZEOLITE-SUPPORTED NICKEL CATALYSTS

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The magnetic and catalytic properties of Ni supported on LINDE 4A, 5A, 10X, 13X, NaY and NORTON mordenite-type zeolites have been studied. A chemical method has been used to determine the Ni content of ion-exchanged catalysts. The rate of reduction has been investigated at different temperatures by a magnetic method. The reduced catalysts were freed of hydrogen, and their saturation magnetizations and Curie temperatures were determined by thermomagnetic analysis. To compare the activities of the catalysts, they were used for the hydrogenation of benzene. Infrared spectra of zeolites and ion-exchanged and reduced catalysts were recorded. It was found that besides the ion-exchanged Ni the nickel salt too is irreversibly sorbed on the zeolites; the zeolite supported Ni catalysts are reduced only at higher temperature, and even then only partially, and so coarse-grained Ni is formed (characterized by a Curie temperature close to that of compact Ni). On the surface of the A-type molecular sieves finely dispersed Ni is formed; the catalytic activity and hydrogen content of this are higher than the values for X-type supported catalysts.

Introduction

Zeolite-supported nickel catalysts are generally prepared by ion-exchange [1—5] or impregnation [6—7] followed by drying or calcination and finally reduction with hydrogen at 300—600 °C.

The metal content of zeolite-supported Ni catalysts may be anything from a few per thousand to 30—40 w/w%. Depending on the metal content, the catalyst can be suited to various purposes.

The structures of zeolite-supported Ni catalysts were investigated by various methods, first of all by magnetic measurements and X-ray diffraction [8—18].

On the basis of review of the literature dealing with zeolite-supported nickel catalysts it can be stated that these catalysts have been relatively little investigated and there is some contradiction about the reducibility and dispersity of nickel.

Some authors found both large and small nickel particles [12], but others only large nickel crystals [13]. It can be found such a date that nickel has atomic dispersion on the surface of X-type zeolite [9]. The reason of this contradictory results may be that differences in catalyst preparation and in the methods of examination exist and the authors investigated only one of some type of zeolite supported nickel. Therefore it is difficult to compare the results.

Our aim was to study catalysts employed in industrial processes, *i.e.* containing a larger amount of catalytically active metal and supported by different types of

zeolites. Thereby we tried to establish a correlation between special properties of the zeolite supports, the structure of the nickel found on the surface (determined from magnetic measurements), and the catalytic properties.

Investigations were carried out with LINDE 4A, 5A, 10X, 13X, Y and NORTON mordenite zeolite-supported Ni catalysts. The stoichiometric compositions of the supports are listed in Table I. The rate of nickel reduction, the amount of metallic

Table I
Composition of zeolite supports and catalysts

Support	Overall formula + n H ₂ O	Ni (w/w %) theoretical, stoichiometrically exchanged	Ni (w/w %) measured, unreduced	Metallic Ni (w/w %) in reduced catalyst, calcd. from magnetization
LINDE 4A	Na ₂ O·Al ₂ O ₃ ·1.92 SiO ₂	20.1	28.0	5.7
5A	0.25 Na ₂ O·0.75 CaO·Al ₂ O ₃ ·1.92 SiO ₂	20.1	25.8	4.2
10X	0.21 Na ₂ O·0.62 CaO·Al ₂ O ₃ ·2.48 SiO ₂	18.2	25.0	2.6
13X	0.83 Na ₂ O·Al ₂ O ₃ ·2.48 SiO ₂	18.2	23.5	4.2
LINDE Y	Na ₂ O·Al ₂ O ₃ ·5.02 SiO ₂	16.8	20.3 ¹	2.2
LINDE Y			22.7 ²	3.2
NORTON mord.	Na ₂ O·Al ₂ O ₃ ·10.60 SiO ₂	13.4	15.1 ¹	3.2
NORTON mord.			21.9 ²	4.3

¹ Ion exchange at 25 °C.

² Ion exchange at 100 °C.

nickel and its magnetic characteristics were measured with a FARADAY-type magnetic balance [19—20].

The amount of Ni taken up on the zeolite was determined by chemical analysis. The activities of the catalysts were studied in benzene hydrogenation. Infrared spectra were recorded on the pure and ion-exchanged zeolites, and on the reduced catalysts.

Experimental

5 g LINDE 4A, 5A, 10X and 13X zeolites were boiled for 4 hours with 800 ml 0.5 N Ni(NO₃)₂ solution under reflux.

1 g LINDE NaY and NORTON mordenite zeolites were boiled for 1 hour with 400 ml 0.1 N Ni(NO₃)₂ and 0.1 g Na-acetate.

1 g LINDE NaY and NORTON mordenite zeolites were shaken for 10 hours with 200 ml 0.1 N Ni(NO₃)₂ and 0.1 g Na-acetate. The ion-exchanged zeolite was filtered off and washed with distilled water until Ni²⁺ could no longer be detected in the filtrate with dimethylglyoxime. The zeolite thus washed free of unbound nickel ions was dried in vacuum at 100—120 °C and stored in air.

Before the various tests, the samples were dried to constant weight in vacuum at 120 °C, and the dry, impregnated or unimpregnated zeolite was then weighed accurately.

The amount of Ni taken up by ion-exchange was determined gravimetrically. 100 ml 1 N NaCl solution was acidified with 1 drop of concentrated HCl, and about 0.3 g catalyst (with an accuracy of 0.1 mg) was added. The solution was refluxed for 4 hours, filtered, and the support remaining on the filter washed with 3×5 ml 1 N NaCl solution. The Ni²⁺ in the filtrate was determined with dimethyl-glyoxime [21]. The results are given in Table I.

The catalysts were reduced with hydrogen at 375, 400 and 425 °C in the measuring compartment of a FARADAY-type magnetic balance [19]. Following the cooling of the samples to 100 °C from the reduction temperature, the magnetization of the samples was measured as a function of the duration of reduction. The results are listed in Table II.

Table II
Change of magnetization on reduction of the catalysts

Support	Temp. (°C)	Time (hrs)				
		2	4	6	8	
magnetization (emu g ⁻¹ cm ³) ¹						
LINDE	4A	375	0.38	0.70	0.97	1.13
		400	0.77	1.15	1.37	1.48
		425	1.50	1.96	2.25	2.50
	5A	375	0.16	0.42	0.52	0.60
		400	0.33	0.76	1.08	1.15
		425	0.52	1.16	1.45	1.50
	10X	375	0.16	0.24	0.30	0.37
		400	0.20	0.30	0.42	0.52
	13X	425	0.59	0.86	1.19	1.30
		375	0.10	0.17	0.25	0.31
		400	0.33	0.54	0.79	0.95
		425	1.07	1.50	1.95	2.01

¹ 1 emu g⁻¹ cm = 10³/4 Am⁻¹.

Table II (continued)
Change of magnetization on reduction of the catalysts

Support	Temp. (°C)	Time (hrs)								
		0.25	1	2	3	4	5	6	7	8
magnetization (emu g ⁻¹ cm ³) ¹										
Linde Y ²	400	0.20	0.32	0.44	0.57	0.62	0.89	0.96	1.04	1.08
Linde Y ³	400	0.11	0.40	1.08	1.32	1.39	1.41	1.63	1.70	—
Norton mord.	400	1.25	1.49	1.59	1.63	1.64	—	—	—	—
Norton mord.	400	1.88	2.10	2.11	2.16	2.20	2.21	—	—	—

¹ 1 cmu g⁻¹ cm³ = 10³/4 Am⁻¹.

² Ion exchange 25 °C.

³ Ion exchange 100 °C.

The catalysts reduced for 8 hours at 425 °C were degassed for 2 hours in argon at the reduction temperature. The magnetization of the catalysts thus pretreated was measured as a function of temperature and field strength (25–400 °C, 5–10 kOe). The thermomagnetic curves are shown in Figs. 1, 2, 3 and 4.

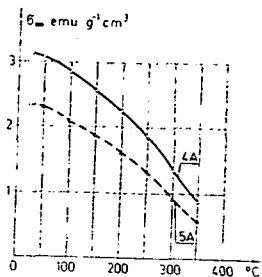


Fig. 1. Thermomagnetic curves of LINDE 4A and 5A-type zeolite-supported Ni catalysts. Saturation magnetization as a function of temperature

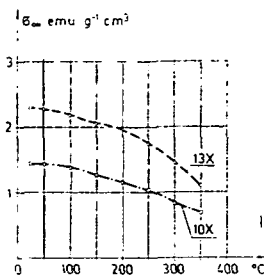


Fig. 2. Thermomagnetic curves of LINDE 10X and 13X-type zeolite-supported Ni catalysts. Saturation magnetization as a function of temperature

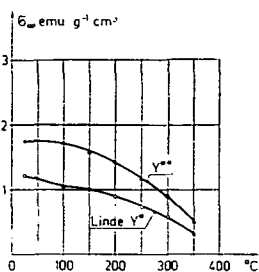


Fig. 3. Thermomagnetic curves of LINDE Y** (ion exchange at 100 °C) and Linde Y* (ion exchange at 25 °C) type zeolite-supported Ni catalysts. Saturation magnetization as a function of temperature

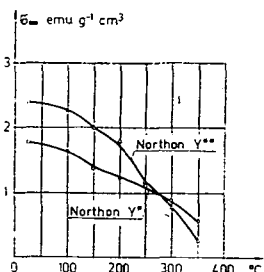


Fig. 4. Thermomagnetic curves of NORTON mordenite** (ion exchange at 100 °C) and NORTON mordenite* (ion exchange at 25 °C) type zeolite-supported Ni catalysts. Saturation magnetization as a function of temperature

The results of the magnetic measurements were evaluated by computer as reported earlier [18], *i.e.* the saturation magnetization (σ_{∞}^0) and CURIE temperature (θ) was determined for the LINDE A and X catalysts (Table III).

The activities of the catalysts were compared in benzene hydrogenation. 5 g granulated zeolite was subjected to ion-exchange as described above, and then placed in a reactor 22 mm of internal diameter and reduced. Hydrogenations were carried out with the activated catalysts at 150, 170 and 190 °C, with a H₂: benzene mol ratio of 6:1, and a benzene feed rate of 0.065 mol/h. The conversion was established by gas-chromatographic analysis of the reaction mixtures (Table III). This measure-

Table III
Magnetic properties and catalytic activities of catalysts

Support	Saturation magnetization (emu g ⁻¹ cm ³)	CURIE temp. (K) ¹	Magnetization change on freeing from hydrogen (%)	Benzene conversion %, 0.065 mol/hr benzene per 5 g catalyst		
				150	170	190
4A	3.28	500	9.8	—	—	—
5A	2.42	566	34.8	90	96	99
10X	1.50	587	6.2	49	72	84
13X	2.42	628	6.3	2	5	10

¹ Curie temperature of compact Ni: 631 K.

ment could not be made with the LINDE 4A zeolite, for in the course of ion-exchange the granulated material disintegrated. This was to be expected, since it is known that the structure of the 4A-type molecular sieve is damaged during Ni ion-exchange.

Infrared spectra of the zeolites and the ion-exchanged and reduced catalysts were recorded in KBr pellets with a Perkin-Elmer 237 spectrophotometer.

Discussion

On ion-exchange under the conditions employed here the exchange is presumably complete (Table I), with, at the same time, a considerable amount of nickel salt and/or hydroxide is irreversibly sorbed, which cannot be removed by washing with distilled water. The Ni(NO₃)₂ decomposes on the reduction of the catalyst, and the NiO formed from it, or possibly already present, and the Ni²⁺ incorporated into the zeolite lattice may be reduced in parallel.

The absorption bands indicative of zeolitic water (1650 cm⁻¹) and also of surface hydroxyls (3500 cm⁻¹) decrease considerably in the infrared spectra after ion-exchange. Together with the results of the determinations of the nickel content, this suggests that a large part of the surface is covered by irreversibly sorbed nickel salt or hydroxide.

The rate of formation of metallic nickel on hydrogen reduction can be measured only above 350 °C, but even at higher temperature it is very low (Table II). Exception is the NORTON mordenite-type catalyst only (reduction time at 400 °C 1 hour). This is surprising, as Al₂O₃ and SiO₂-supported Ni (NiO) catalysts had been found to be reduced at an appreciable rate even at around 300 °C [22].

The chemical determination of the nickel content indicated that NiO was formed from the Ni(NO₃)₂ present at the reduction temperature, and this should be reduced at an appreciable rate. A further surprising result was that only a fraction of the nickel was reduced even after treatment with hydrogen for 8 hours at 425 °C.

This can be explained by the presence of a significant proportion of Ni in the channels and cavities of the zeolites. The metallic nickel formed on the reduction of NiO or Ni²⁺ on the surface blocks this off from access by H₂. In the interior of the aluminosilicate skeleton the inwards diffusion of H₂ and the outwards diffusion of the products of decomposition and reduction of the nickel salt are strongly inhibited.

From the shapes and slopes of the thermomagnetic curves (Figs. 1—4) and from the CURIE temperatures obtained by computer evaluation of the thermomagnetic analysis (Table III) the following sequence of nickel-dispersity on the different zeolites could be concluded:

NORTON mordenite > LINDE 4A, 5A, LINDE Y > NORTON mordenite¹ >
> LINDE 10X, LINDE Y* > LINDE 13X

(¹ ion exchange at 25 °C).

Finely dispersed nickel is found on the NORTON mordenite and LINDE A type zeolites, with coarser grains on the X-type. The thermomagnetic curves and Curie temperatures for the latter more closely resembled those for compact nickel.

There was a significant difference between the dispersity of nickel on Y type zeolites ion exchanged at 100 °C and at 25 °C. In the first case the nickel content was higher and so the irreversibly sorbed nickel content also. We suppose that the reduction of this is easier and gives the finely dispersed metal.

The correlation between the hydrogen content of the Ni catalysts and the difference of the magnetizations of the hydrogen-saturated and hydrogen-free catalysts is almost linear: lesser the amount of sorbed hydrogen, the smaller the difference between the magnetizations of these two states. Thus, the hydrogen content of the catalysts is characterized by the per cent magnetization change shown in column 4 of Table III, which is the results of thermal treatment in argon at 425 °C [17—18]. On this basis the catalysts on the different types of support can be arranged in a sequence. It can be seen that the hydrogen content of the 5A-type molecular sieve-supported Ni is substantially higher than those of the catalysts on X-type supports.

A picture in accord with this is also provided by the measurements on the benzene hydrogenation activity (Table III): the activity of the 5A-supported Ni is higher than those of the 10X and 13X-supported catalysts, though the metallic Ni content of the 10X-supported catalyst is also smaller.

In the course of the magnetic measurements, a study was made of whether the magnetization of the catalysts changes on the action of atmospheric O₂, *i.e.* whether their metallic Ni content is oxidized. In contrast with the Al₂O₃ and SiO₂-supported Ni catalysts already mentioned, the zeolite-supported catalysts cannot be oxidized in air up to 100 °C, *i.e.* their magnetization does not vary in air at 100 °C. This too confirms that the Ni in them is not finely dispersed, and not pyrophoric.

The 4A and 5A and the 10X and 13X-type zeolite supported catalysts have different properties, in spite of the fact that when their cations are exchanged completely for Ni, uniformly NiA or NiX-type materials should be obtained. The probable explanation of the differences is that the Ni salt or Ni hydroxide irreversibly sorbed on the zeolites have different structures, depending on the nature of the cations in the initial zeolites, and thus the properties of the reduced catalysts differ also.

In summary it can be stated that the zeolite-type Ni catalysts examined differ in many respects from the Al₂O₃ and SiO₂-supported Ni catalysts. The Ni²⁺ and NiO in them can be reduced at an appreciable rate only at higher temperatures (400 °C), but even under these conditions only partially, and as a consequence the metallic nickel forms larger particles. This is clearly indicated by the magnetic and catalytic measurements. On the other hand, the Ni formed, which is more stable as a result of the crystalline structure of the zeolite, is less readily oxidized.

References

- [1] Belgian Patent 636 142 (1963).
- [2] Dutch Patent 6 612 371 (1967).
- [3] *Selenina, M., K. Wencke*: Monatsber. Deutsche Akad. Wiss. Berlin **8**, 886 (1966).
- [4] U. S. Patent 3 379 640 (1969).
- [5] *Gioia, F., G. Greco, E. Drioli*: Chim. Ind. (Milan) **51**, 457 (1969).
- [6] Japanese Patent 336 (1955).
- [7] French Patent I 451 019 (1966).
- [8] *Bredikhina, T. N., V. B. Evdokimov*: Zh. Fiz. Khim. **41**, 2975 (1967).
- [9] *Bredikhina, T. N., V. B. Evdokimov*: Vest. Mosko. Univ. Khim. **23**, 36 (1968).
- [10] *Lawson, J. D.*: Ind. Eng. Chem. Res. Develop. **9**, 317 (1970).
- [11] *Rubinstein, A. M., K. M. Minachev, A. A. Shlinkin, V. I. Garamin, G. A. Ashavskaya*: Izv. Akad. Nauk SSSR, Ser. Khim. 786 (1968).
- [12] *Brooks, C. S., G. L. M. Christopher*: J. Catal. **10**, 211 (1968).
- [13] *Reman, W. G., A. M. Ali, C. C. A. Schuit*: J. Catal. **20**, 374 (1971).
- [14] *Richardson, J. T.*: J. Catal. **21**, 122 (1971).
- [15] *Tsutsumi, K., S. Fuji, H. Takhosi*: J. Catal. **24**, 8 (1972).
- [16] *Rudham, R., M. K. Saunders*: J. Catal. **27**, 287 (1972).
- [17] *Romanowski, W.*: Z. anorg. allgem. Chem. **351**, 180 (1967).
- [18] *Egerton, T. A., A. Vickerman*: J. Chem. Soc. Faraday Trans. I **69**, 39 (1973).
- [19] *Tungler, A., J. Petró, T. Máthé, Z. Csűrös*: Magy. Kém. Folyóirat **78**, 434 (1972).
- [20] *Tungler, A., J. Petró, T. Máthé, Z. Csűrös, K. Lugosi*: Acta Chim. Acad. Sci. Hung. **79**, 290 (1973).
- [21] *Erdey, L.*: Gravimetric methods of chemical analysis. Vol. II. (in Hungarian). Tankönyvkiadó, Budapest, 1960, p. 383.
- [22] *Tungler, A., J. Petró, T. Máthé, Z. Csűrös*: Magy. Kém. Lapja **29**, 332 (1974).