# INFLUENCE OF EXCHANGEABLE CATION ON $Ni^{2+}$ REDUCTION AND $Ni^0$ MIGRATION IN X ZEOLITE

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It was shown that $Ni^{2+}$ reducibility and $Ni^0$ particle size obtained by hydrogen reduction are depending on $Ni^{2+}$ location, Lewis centers concentration, nature and concentration of other elements present in its environment, pretreatment and reduction conditions.

It was possible to obtain very small particles of $Ni^0$ (7 Å) stabilized in the zeolitic lattice.

## Introduction

In recent years, the reduction of transition metal ions supported on zeolite has been investigated with the aim of obtaining highly dispersed metallic particles of homogeneous size.

In the present work, we have undertaken a comparative study of the hydrogen reduction of $Ni^{2+}$ ions in an X zeolite by varying factors such as

— the $Ni^0$ concentration by unit cell,
— the initial location of these cations,
— the nature of a second cation present in its environment,
— the acidic degree of the support.

By several methods, we try to determine the $Ni^0$ formation in order to obtain highly dispersed particles stabilized in the lattice.

### Materials

The samples were prepared by exchanging sodium X zeolites (Linde Carbide) with 0.1 N solution of $Ni^{2+}$ and $Me^{x+}$ nitrates ($Me^{x+} = Ca^{2+}$, $K^+$, $Ce^{3+}$, $La^{3+}$) or with ammoniacal solutions of $Pt (NH_3)_4^{2+}$ and $Pd(NH_3)_4^{2+}$ ions.

### Table I

*Initial sample:* $Na_{86}$ $(SiO_2)_{106}$ $(AlO_2)_{86}$ $n$ $H_2O$ *(unreduced samples)*

| Composition | Abreviation |
|---|---|
| $Ni_{31}Na_{24}X$ | $Ni_{31}X$ |
| $Ni_8Na_{64}HX$ | $Ni_8X$ |
| $Ni_{10}H_{66}X$ | $Ni_{10}HX$ |
| $Ni_{24}Pd_{0,3}Na_{12}H_{25}X$ | $Ni_{24}PdX$ |
| $Ni_{12}Pd_6Na_{12}H_{22}X$ | $Ni_{12}Pd_6X$ |
| $Ni_{17}Pt_{0,45}Na_{40}H_{11}X$ | $Ni_{17}PtX$ |
| $Ni_{24}Ce_6Na_{18}X$ | $Ni_{20}CeX$ |
| $Ni_{10,5}Ca_{20}H_{21}Na_{24}X$ | $Ni_{10}CaX$ |
| $Ni_{14}La_{15}Na_9H_4X$ | $Ni_{14}La_{15}X$ |

The $Na^+ H^+ Ni^{2+} X$ samples were prepared by exchanging a partially decationized sample with 0.1 N solutions of $Ni^{2+}$.

The sample composition was determined by chemical analysis (Table I).

All samples were pretreated for 16 hours under vacuum at $10^{-6}$ torr and at 773 K.

### Experimental methods

The $Ni^{2+}$ location was determined by X-ray analysis using GALLEZOT's method [1].

Kinetic analysis was performed by measuring the rate of the hydrogen uptake in a classic volumetric apparatus at constant hydrogen pressure and at various temperatures. In some experiments successive reduction desorption cycles were carried out. The amount of gas desorbed was measured by a Mac Leod gauge and analyzed by mass spectroscopy. Besides some experiments were carried out under dynamic conditions at constant flow of hydrogen and various temperatures.

The magnetization was measured by the Weiss extraction method either in an electromagnet giving 21 K. oe. (measurements at 300 and 77 K) or in a super conductive coil reaching 70 K. oe. (measurements at 4.2 K.)

EPR measurements were made with Varian $E_3$ spectrometer in X band.

The benzene hydrogenation was studied in a differential steady state flow microreactor and the measurements were generally performed at low conversion (normally $\leqq 5\%$).

The initial hydrogen and benzene pressure were 702 and 58 torr respectively. A standard temperature of 383 K was chosen in order to make comparison with data already published [2]. Catalysts weights were generally of the order of 300 mg for a total gas mixture flow of 1.4 $lh^{-1}$. Under these conditions, interdiffusion phenomena were negligible. Reactants and products were analyzed on a 5% Carbowax 20 M on spherical XO B 0.75 column at 353 K.

### Results

### I — Cationic Location

The cationic location was determined by X-ray analysis based on Debye-Scherer diffraction diagram. The results corresponding to the different samples studied are given in the following tables:

Examination of Table II suggests the following comments:

— Crystallographic analysis agrees with chemical analysis if we assume that the excess $Na^+$ located in II (supercages) corresponds to $Ni^{2+}$ ions.

— The $Ni^{2+}$ location is highly depending on the nature of other cations introduced into the lattice and on the $Ni^{2+}$ concentration.

— The results reported in Table III show that $Ni^{2+}$ ions disappear at the same time from sites I (hexagonal prisms) I' (sodalite cavities) and II (supercages). However we know [4] that in Y zeolite $Ni^{2+}$ disappears successively from sites II, I' and I.

The data allowed us to explain kinetic results for the $Ni^{2+}$ reduction in NiNaX and NiNaY.

The study of other samples after reduction is in progress.

*Table II*

*(Reduced samples)*

| Sample | Atom | Number of atoms per unit cell |
|---|---|---|
| $Ni_8Na_{64}X$<br>$a^* = 24.79 \pm 0.02$ Å<br>$R^{**} = 0.097$ | Na(II)<br>Ni(I)<br>Na(I′) | 30.1 (9)<br>5.3 (5)<br>20.4 (3) |
| $Ni_{31}Na_{24}X$<br>$a = 24.47 \pm 0.02$ Å<br>$R = 0.104$ | Na(II)<br>Ni(I)<br>Ni(I′) | 34 (1)<br>11.7 (4)<br>9.6 (5) |
| $Ni_{17}Pt_{0,45}Na_{40}X$<br>$a = 24.54 \pm 0.02$ Å<br>$R = 0.091$ | Na(II)<br>Ni(I)<br>Ni(I′) | 36 (1)<br>11.3 (3)<br>5.8 (3) |
| $Ni_{10}Ca_{20}Na_{24}X$<br>$a = 24.75 \pm 0.02$ Å<br>$R = 0.103$ | Ca(II)<br>Ca(I)<br>Ni(I′) | 20 (1)<br>12.1 (4)<br>7.8 (3) |
| $Ni_{24}Ce_6Na_{18}X$<br>$a = 24.67 \pm 0.02$ Å<br>$R = 0.120$ | Na(II)<br>Ni(I)<br>Ce(I′) | 24 (1)<br>11.7 (4)<br>3.2 (4) |
| Ni La NaX<br>$a = 24.95 \pm 0.02$ Å<br>$R = 0.29$ | Na(II)<br>Ni(I)<br>La(I′) | 30<br>10<br>10 |

    * a: unit cell parameter
    ** $R = \Sigma |F_0 - F_c| / \Sigma |F_0|$ where $F_0$ and $F_c$ are the observed and calculated structure factors (Refinement program ORFLS) [3]
    The figures in parentheses correspond to the standard error on the last significant figure.

*Table III*

| Sample | atom | Number of atom per unit cell |
|---|---|---|
| $Ni_{31}X + H_2$<br>(523 K)<br>$a = 24.42 \pm 0.02$ Å<br>$R = 0.103$ | Na(II)<br>Ni(I)<br><br>Ni(I′) | 32.8 (9)<br>11.9 (7)<br><br>8.8 (9) |
| $Ni_{31}X + H_2$<br>(713 K)<br>$a = 24.42 \pm 0.02$<br>$R = 0.109$ | Na(II)<br>Ni(I)<br>Ni(I′) | 25 (1)<br>9.6 (4)<br>7.6 (6) |

## II — *Kinetic Results*

Kinetic studies have shown that the static hydrogen reduction of $Ni^{2+}$ in X zeolite is depending on the $Ni^{2+}$ concentration and on the nature and percentage of the second cation. We have reported in Fig. 1 and 2 the curves $\alpha = f(t)$ where $\alpha$ is the degree of advancement $[\alpha(t) = NiO/(Ni^{2+} + Ni^0)]$ of the reaction.
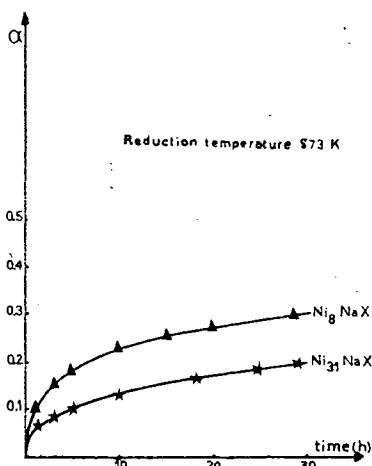


*Fig. 1.* Curves $\alpha = f(t)$ for $Ni^{2+}$ reduction by hydrogen ($P_{H_2} = 50$ torr) in NiNaX.

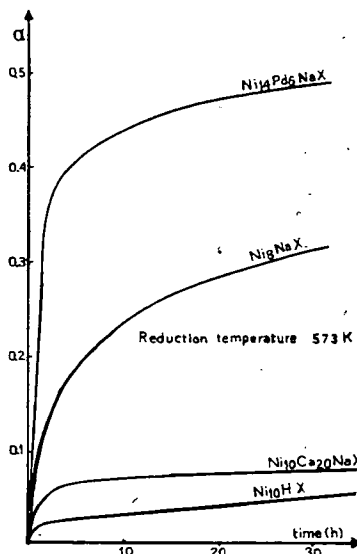*Fig. 2.* Influence of other cations on $Ni^{2+}$ reduction by hydrogen ($P_{H_2} = 50$ torr).

It is observed that for $Ni^{2+}Na^+X$ whatever is the $Ni^{2+}$ concentration the curves are superimposable and the activation energy $E = 28$ Kcal/mol as long as the degree of transformation for whole ranges of temperature and pressures is the same. The reduction under static conditions is limited by hydrogen diffusion towards $Ni^{2+}$ for which location sites are assumed energetically homogeneous.

For the other samples, it is necessary to consider that several competitive steps are involved in the transformation. For example for $La^{3+}Na^+Ni^{2+}X$, $Ce^{3+}Na^+NiX$ activation energy is varying when the degree of transformation increases. It is impossible under these conditions to assume the cationic sites to be energetically homogeneous and to define the rate determining step. However, in all cases, diffusion process takes place and reaction products (particularly OH groups) are inhibiting the reduction. Under static conditions it is difficult to obtain a complete reduction at temperatures lower than 673 K.

It was observed in Fig. 2 that the various cations influence the $Ni^{2+}$ reducibility.

So at a given temperature, the lowest value of $\alpha$ is obtained for $H^+Ni^{2+}X$ sample. The vacuum treatment at 773 K before the reduction reaction leads to the formation

of Lewis acid centres. These centres can behave like oxidizing centres which will therefore favor the redox equilibria towards 2:

$$Ni^{2+} + H_2 \underset{2}{\overset{1}{\rightleftarrows}} Ni^0 + 2H^+ \qquad (1)$$

Under these conditions the reduction of $Ni^{2+}$ is very difficult and requires fairly high activation energies. In presence of $Ca^{2+}$, the $Ni^{2+}$ reduction is difficult and we observe by EPR measurements the presence of $Ni^+$ which is alone in this sample when reduction temperature is lower than 573 K.

Conversely, small quantities of $Pt^0$ or $Pd^0$ in the lattice obtained by preliminary reduction of $Pt^{2+}$/or $Pd^{2+}$ in X zeolite increase the $Ni^{2+}$ reducibility; the higher is the $(Pd^0, Pt^0)$ concentration, the greater will be the reducibility. Besides, it is possible to obtain the complete $Ni^{2+}$ reduction when $Ce^{3+}Ni^{2+}X$ and $(Pt^0, Pd^0)Ni^{2+}X$ are treated by a dynamic flow of hydrogen at 623 K. In all cases, the dynamic conditions for a given temperature increase the degree of advancement $\alpha$.

## III — Particle diameters

a) $Ni^{2+}$ is only with $Na^+$ $(Ni^{2+}Na^+X)$. The results obtained by magnetic measurements at 300 and 77 K on NiX show that for reduction temperatures below or equal to 523 K, both very small particles occluded in the zeolitic cavities and larger particles in the 60—100 Å range located on the outside of the surface (Table IV).

*Table IV*

| Samples | Total metal weight per cent | Reduction temperature | Particle diameter in Angström | Rate at 383 K in mol $(C_6H_6)S^{-1}$ $(gNi^0)^{-1}/10^{-7}$ | Ea Kcal/mol$^{-1}$ |
|---|---|---|---|---|---|
| Ni$_8$X | Ni: 3.54 | 523 K $\alpha = 0.1$ 573 K $\alpha = 0.4$ | $D \sim$ 60 Å $D <$ 15 Å $D \sim$ 150 Å | 38.2 | $14 \pm 0.5$ |
| NiPd$^0$X | | 573 K $\alpha = 0.6$ | $D \sim 30$ Å | | |
| NiPt$^0$X | Ni: 7.34 Pt: 0.65 | 573 K $\alpha = 0.28$ | $D \sim 25$ Å | | |
| NiCeX | Ni: 10.1 | 573 K $\alpha = 0.3$ Dynamic reduction 623 K $\alpha \neq 1$ | 85% $D < 15$ Å 15% $D \sim 30$ Å 85% $D = 7$ Å 15% $D = 30$ Å | 65.7 72 | $13.4 \pm 0.5$ $12 \pm 0.5$ |
| NiPt$^0$X | Ni: 7.34 Pt: 0.65 | Dynamic reduction 623 K $\alpha \neq 1$ | $D \sim 25$ Å | 48.9 | $12—13 \pm 0.5$ |

Reduction desorption cycles were carried out on these samples at the reduction temperature. During the desorption runs it was observed a hydrogen desorption and simultaneously a decrease in the magnetization of the sample considered. This can reasonably be attributed to partial reversal of $Ni^{2+}$ ion reduction according to the equilibrium (1).

At higher temperatures $>573$ K the mean particle diameter increases very rapidly and reaches values greater than 150 Å. Under these conditions the reduction is no longer reversible.

b) When *cations other than Na⁺ are present* with $Ni^{2+}$, the results are not the same.

We can see on Table IV. that in presence of $Pd^0$, $Pt^0$ the $Ni^0$ particle size obtained is very homogeneous (25—30 Å) and does not depend on reduction temperature. Furthermore by carrying out reduction desorption cycles on a given sample $Ni^{2+}_{14} Pd^0_6 X$ between 523—633 K, it is possible to attain almost complete reduction and to obtain $Ni^0$ particles of uniform size about 25 Å.

In the presence of $Ce^{3+}$ magnetic measurements show that the degree of reduction determined by saturation magnetization at 77 K is always very much less than that measured by hydrogen uptake. This suggests that there are very small $Ni^0$ particles ($\bar{D} < 15$ Å). The mean size of particles saturated at 77 and 300 K is 25 Å for samples reduced below 523 K under static conditions.

When the $Ni^{2+} Ce^{3+} X$ is pretreated under oxidizing conditions, static reduction leads to $Ni^0$ particles which are homogeneously distributed but much larger than before ($\bar{D} \sim 60$ Å). Under dynamic reduction at 593 K it was obtained an almost complete reduction ($Ni^0/Ni$ tot$=0.85$) and particle diameters determined at 4.2 K were about 7 Å.

## IV — Catalytic activity

We studied the benzene hydrogenation activity of the metallic nickel particles as a measure of the surface active sites. This reaction is generally considered as a structure insensitive one. The effect of temperature is shown by the Fig. 3. Under our experimental conditions, the plot is linear below 450 K and yields a value for $E_{ap}$ of about 14 Kcal/mol in agreement with the other published results [2, 5]. Nevertheless, we may notice a slight enhancement of our values. Data reproducibility during temperature cycles indicates that no catalysts deactivation occurs. This result may be interpreted like a good thermostability of reduced and unreduced nickel particles.

The appearance of a maximum of activity with $E \neq 0$, at about 473 K, is also very clear. Theorical origin for this maximum has been extensively discussed by COENEN et al. [2].



Fig. 3. Arrhenius plot for benzene hydrogenation. Reaction rate in mol. $C_6H_6 S^{-1}$ $(g Ni^0)^{-1}$
(a: $Ni_8 X$, b: $NiCe_6 X$ static reduction, c: $NiCe_6 X$ dynamic reduction, d: $NiPtX$ dynamic reduction.)

It is interesting to consider now the activity data in relation with the results of the preceeding sections. Primarily we may observe that the order of decreasing is the same as that of reducibility. These observations show that the activity may be considered, in first approximation, as a measure of the superficial metallic nickel. The second point is relative to the effect of static or dynamic reduction treatment. It is also clearly shown that dynamic conditions produce higher rates.

The effect of second element ($Ce^{3+}$, $Pd^0$, $Pt^0$) on activity is perhaps the more drastic one, when considering the data obtained with NiX and NiCe X for instance (Table IV).

As for the reducibility effect of $Pt^0$ and $Ce^{3+}$, the activities of $Ni^0Ce^{3+}X$ and $Ni^0Pt^0X$ are similar.

At last, as it was foreseen, no effect of particle size or of metal location is detected when looking for activity per square meter of metallic nickel. It is noticable that even with various experimental parameters, all catalysts have an activity of the same order of magnitude.

## Conclusion

These results show that both reducibility, of $Ni^{2+}$ ions exchanged in X zeolite, and dispersion of the resulting $Ni^0$ particles, depend greatly on the cation or second metal present in its environment. Besides catalytic activity of the samples for benzene hydrogenation is depending on their reducibility and thermostability. Generally it is observed [6, 7] that the diameter and the stability of metal particles obtained after reduction depend on several factors:

— The acidity or the basicity of the support.
— The eventual existence of redox mechanisms which interact with the energetics of the kinetic process.
— The thermostability of the OH groups formed during the reduction.
— The presence of a modifying element which can interact strongly with the support and with the metal crystallites [8].
— For the samples studied in this work, the above factors influence the reduction process and particle migration.
— For the reduction of $H^+Ni^{2+}X$ which contains a larger number of acidic centres (Lewis sites), it was shown a considerable inhibition to reduction and consequently the formation of large particles. These acidic centres can favor the oxidation process in the redox equilibrium.
— In the presence of $Pd^0$ or $Pt^0$ several factors may be involved: these metal particles highly dispersed inside the cavities interact strongly with the lattice and are also active in the $Ni^{2+}$ reduction process by providing atomic hydrogen. Also $Pt^0$ or $Pd^0$ clusters decrease the surface acidity and may play the role of donors relative to the strongly acid sites of zeolites.
— In the presence of $Ce^{3+}$, the reduction of $Ni^{2+}$ ions leads to a highly dispersed metallic state. Now it may be suggested that $Ce^{3+}$ ions could have an important effect on the thermostability of the OH groups formed during the reduction. $Ce^{3+}$ would be a modifying element. Its role is depending on concentration and pretreatment conditions.

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