

## Ni REDOX EQUILIBRIUM IN MORDENITES AT VARIOUS HYDROGEN PRESSURES

C. MIRODATOS

Institut de Recherches sur la Catalyse, Villeurbanne

and

D. BARTHOMEUF

Laboratoire de Chimie des Solides, Université Paris VI

### ABSTRACT

The extent of the reduction of nickel supported on sodium, hydrogen and steamed mordenites is different for the bulk and for the surface of the particles. Equilibrium constants for the redox reaction are estimated for both processes. The nickel dispersion, the extent of bulk and surface reductions depend on the balance between the number of sites of suitable acid strength and the reduction hydrogen pressure. The enhanced catalytic properties of steamed mordenites are related to the specific occurrence of Ni metal on the outer surface of the particles under high hydrogen pressure.

### INTRODUCTION

Applied research has shown the high catalytic performances in acidic catalysis of metal loaded zeolites. Thus, mordenites partly exchanged with transition metals are used in aromatic conversion under specific conditions of activation and reaction (1-3). The specific role played by the metal phase, besides the acid active phase, is not clear, probably in line with the changes in the metal state according to the type of support and pretreatment (4). In this work we have studied among various activation procedures the role and the effect of hydrogen pressure on mordenite supported nickel in close relation with toluene disproportionation data reported in (5).

Besides the interest for catalysis it is also of importance to understand the reduction process of the transition metals supported on acidic carriers in order to control this process (6). Both the gas and the solid phases (reducible ion and support) are involved in the mechanism. The present study is an attempt to point out the respective influence of those parameters.

### EXPERIMENTAL

Material. The protonic mordenite catalysts referred to as HM (Si/Al = 5) and

HMD when dealuminated ( $\text{Si}/\text{Al} = 9$ ) have been already described in (1,7,8). The sodium-form, Na-M ( $\text{Si}/\text{Al} = 5$ ) was provided by Norton (Zeolon 900). Nickel was exchanged in the sodium (1.3 wt % Ni) or decationated (1.45 wt % Ni) forms with 0.5 M nickel nitrate solutions at room temperature to give NiNaM, NiHM and NiHMD zeolites. Each of the Ni samples has been either treated in flowing air (treatment (1)) or steamed (2) prior reduction at 773 K.

Magnetic measurements. The nickel phase was studied by means of magnetic methods as described in (4,9) giving the degree of nickel reduction and the average nickel particles diameters. Magnetic measurements under high  $\text{H}_2$  pressure (up to 1.2 MPa) were carried out in a stainless steel cell allowing both a reduction under flowing hydrogen and magnetic measurements using the Weiss extraction method. A typical experiment consists of reducing the sample at 773 K under a flow of hydrogen at the desired pressure (0.1-1.2 MPa), then cooling it down to room temperature without changing  $\text{H}_2$  pressure or flow conditions. The cell is then disconnected and isolated from the flow system and the sample internally transferred into the magnetic part of the cell. The magnetic isotherm can be recorded 1) under the reduction pressure (in this case, outer metal atoms with chemisorbed hydrogen do not participate in the collective ferromagnetism), ii) after evacuation - or helium flush - of the cell at 673 K for 1h (in this case all the nickel atoms bulk or surface, which remain in their metallic state in vacuum or neutral atmosphere are taken into account). The comparison between i) and ii) magnetic isotherms allows to determine the amount of stable metallic surface onto the nickel particles. This is also evaluated from the amount of hydrogen chemisorbed onto the sample (volumetry) after its evacuation (or the flush) at 673 K.

Electron microscopy. Electron micrographs were obtained using a JEM 100 CX transmission electron microscope.

## RESULTS

Table 1 presents data from magnetic, volumetric and electron microscopy measurements. Let us note first that magnetic and electron microscopy informations are quite consistent, although the former are obtained "in situ" and the latter in the open air. The main features of these data are : i) the bulk degree of nickel reduction at 773 K is lower than unity whatever be the reduction procedure for the hydrogen forms of mordenite and very close to unity for the sodium forms. The increase in bulk reduction as a function of temperature (fig. 1) strongly depends on the zeolite, the sodium and steamed forms being the more easily reducible samples. ii) The fraction of nickel metal for hydrogen mordenite is significantly improved when the reduction is carried out at high  $\text{H}_2$  pressure (1.2 MPa) instead of atmospheric pres-

Table 1

Magnetic, volumetric and electron microscopy (E.M.) data after reduction at 0.1 (I) and 1.2 MPa (II) hydrogen pressure

Catalysts	Bulk degree of reduction (a)		Average particle diameter (nm)				Size heterogeneity				Fraction % of surface with Ni metal (from H <sub>2</sub> adsorption)			
			Magnetic		E.M.		Magnetic <sup>(b)</sup>		E.M. <sup>(c)</sup>		Magnetic <sup>(d)</sup>		Volumetric <sup>(e)</sup>	
	I	II	I	II	I	II	I	II	I	II	I	II	I	II
NiHM (1)	0.85	0.93	20	20	35	*	0.5	*	1.4	*	0	0	0	0
NiHM (2)	0.9	0.91	14.4	10.4	25	10.0	0.5	0.13	1.0	0.6	0	11	0	4
NiHMD (1)	0.65	0.89	20	20	*	*	0.7	0.5	*	*	0	0	*	*
NiHMD (2)	0.82	0.94	18.0	13.0	*	*	0.6	0.5	*	*	0	5	*	*
NiNaM	1.00	0.98	12.4	10.8	*	*	0.5	0.45	*	*	9	12	10	11

(a) Calculated after outgassing at 673 K the samples reduced at 773 K.

(b) Ratio of the difference between low and high field diameters to the average particle diameter (9).

(c) Ratio of the difference between the highest and the lowest particle size to the average size of the whole distribution.

(d) Ratio of the metallic nickel able to chemisorb hydrogen to the total content of metallic nickel.

(e) Calculated from the adsorption capacity extrapolated at full surface coverage and from average particle diameter (H/Ni = 1 is assumed).

\* not determined

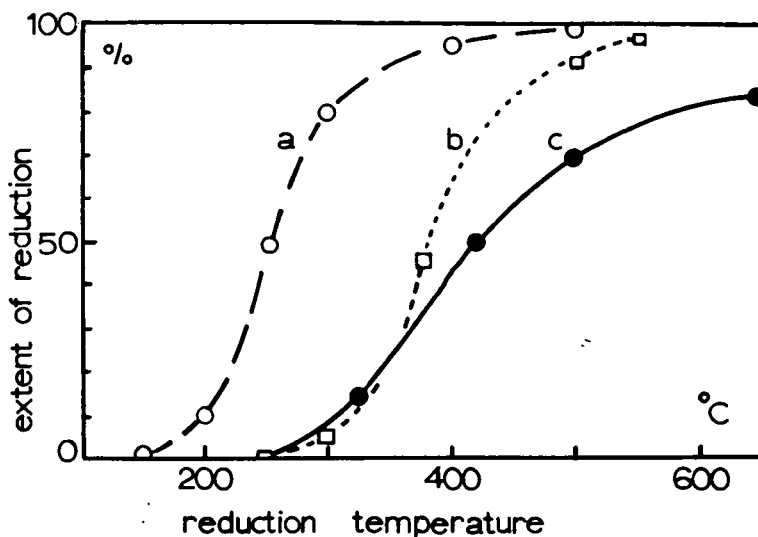


Fig. 1. Change in the degree of reduction at  $P_{H_2} = 0.1$  MPa as a function of reduction temperature. a : NiNaH, b : NiHM (2), c : NiHM (1).

sure. The same holds for nickel dispersion: average particle diameter, particle size distribution and size heterogeneity are shifted towards lower values (Table 1). It can be noted that the average diameter of nickel particles are for any sample larger than the mordenite channels ( $\approx 0.7$  nm). The nickel particles are then located either outside the framework of the zeolite or entrapped in locally destroyed parts of the framework. iii) Only the sodium nickel samples (NiNaM) and the steamed nickel hydrogen mordenite (NiHM (2) and NiHMD (2)) are able to chemisorb hydrogen, i.e. display particles with metallic surface after evacuation. This coincides with the best nickel dispersion in electron microscope studies. iv) There is no specific effect of mordenite dealumination (i.e. Si/Al ratio) on the state of nickel for hydrogen mordenite material: similar relations between  $H_2$  pressure, steaming treatment, nickel reduction and dispersion are observed, the samples being dealuminated or not.

Catalytic performances. From refs. 5 and 7, table 2 reports some data concerning the effect of pressure in toluene disproportionation carried out on similar H-mordenite samples, exchanged or not with nickel.

The kinetics of the reaction (partial orders vs  $H_2$  or toluene) has been discussed in details in (2,5). It will only be emphasized from Table 2 that the best catalytic performances (activity and selectivity) are obtained at high  $H_2$  pressure with a nickel loaded sample which has been initially steamed (NiHM (2)). In all other cases (dry air pretreated and/or low pressure catalysis), the nickel phase does not play any clear role in the disproportionation process.

Table 2

Catalytic activity in toluene disproportionation at 723 K,  $P_{H_2}/P_{Toluene} = 4$  after 5h on stream (5,7)

Catalyst	$r(10^{-4} \text{ mole h}^{-1} \text{ g}_{\text{Zeol.}}^{-1})$	
	I	II
HM (1)	8	20
NiHM (1)	2	15
HM (2)	2	55
NiHM (2)	5	85

I : Total pressure = 0.1 MPa

II: " " = 1.5 MPa

In order to get more information on the state of nickel in catalytic course, some experiments have been performed with the present series of nickel mordenite in CO/H<sub>2</sub> methanation considered as a probe reaction for metallic nickel. Corresponding data are reported in table 3.

Table 3

Catalytic activity in CO/3H<sub>2</sub>, methanation (P = 0.1 MPa, T = 593 K, microdifferential reactor flow)

Catalysts	CO conversion ( $10^{-3} \text{ mole h}^{-1} \text{ g}_{\text{Ni}}^{-1}$ )		Fraction of Ni metal accessible (b) (%)	
	I (a)	II	I	II
NiNaM (1)	9	28	9	12
NiHM (1)	0	8	0	0
NiHM (2)	0	34	0	11

(a) I : activated in flowing H<sub>2</sub>,  $P_{H_2} = 0.1 \text{ MPa}$

II : activated in flowing H<sub>2</sub>,  $P_{H_2} = 1.2 \text{ MPa}$

(b) From table 1

For all samples yielding significant amounts of methane, the apparent activation energy was found around 20 kcal/mole in the 573-623 K range and methane selectivity higher than 90 % which is quite consistent with the values reported for usual supported nickel catalysts (e.g. Ni/SiO<sub>2</sub> (10)). Only nickel loaded on sodium mordenite or on steamed hydrogen mordenite activated under high H<sub>2</sub> pressure is reactive

towards CO/H<sub>2</sub> mixture and so behaves as usual supported metal. The good coincidence noted in table 3 between the CO/H<sub>2</sub> activity and the occurrence of stabilized surface metal atoms after evacuation (or the flush) at 673 K for given activation and reduction conditions strongly suggests that the information in table 1 obtained by magnetic and volumetric methods at room temperature (degree of reduction, dispersion, metal/oxide surface) will reflect the state of the nickel phase even when further experimental conditions (T,P) are different from those used for reduction. The reduction step primarily determines the nickel behavior.

## DISCUSSION

Correlations with catalytic activity. The toluene disproportionation reaction has been shown to proceed on the Brønsted acid sites of the mordenite, whether hydrogen or nitrogen atmosphere is used (5,7). Yet, a kinetic inhibiting effect of hydrogen pressure has been put forward on the basis of the formation-decomposition equilibrium of the benzylic carbocation, proposed as an intermediate species in the disproportionation mechanism (7). The present study shows an obvious correlation between H<sub>2</sub> pressure activation, good catalytic activity and stability in toluene disproportionation and the occurrence of a metallic surface. The latter is ascertained either from physico chemical characterization (volumetry and magnetism) or from CO/H<sub>2</sub> probe. It is reasonable to admit that this specific property to display a metallic surface under reaction conditions (steamed H-mordenite activated at high H<sub>2</sub> pressure) over-compensates the above mentioned inhibiting effect of H<sub>2</sub> pressure. This role of metallic nickel is very probably in line with coke formation and pore fouling (5). The schematic process would be : hydrogen activation on the Ni particles, then hydrogenation of coke precursor avoiding the very fast deactivation which is noted in (5) for samples reacting at atmospheric pressure. In such a process the migration of activated species from the particles of nickel to the coke deposits is likely to occur. This is consistent with the evidences of hydrogen spillover in partially reduced nickel catalysts provided in (11).

Thermodynamics of reduction. Besides the correlation observed between the improved catalytic properties and the presence of nickel metal, the results allow to obtain detailed information on the parameters of importance for nickel reduction. The will be discussed in terms of effect of the OH groups acidity, of hydrogen pressure, of temperature, of steaming and of dealumination. Sample NiNaM does not show any acidity. A Ni-SiO<sub>2</sub> sample studied previously (4) and added here for comparison show a large number very weak sites. The steamed NiHM (2) and NiHM (2) mordenites have a small number of strong acid sites and the two samples pretreated in an air flow, NiHM (1) and NiHMD (1), a large number of strong sites (8). For those various samp

rising the hydrogen pressure increases the degree of bulk reduction and decreases the particle size and size heterogeneity. It also gives nickel particles with metal nickel on the outside only when the number of strongly acidic hydroxyls is small (NiNaM, NiSiO<sub>2</sub>, NiHM (2) and NiHMD (2)). Raising the reduction temperature increases the bulk reduction (fig. 1). Steaming modifies the acidity (decrease in the number of acid sites but not of their strength (8)). It also leads to smaller particles and interestingly gives particles with an outer surface of nickel metal only at high hydrogen pressure. By contrast, dealumination alone does not give any specific effect on nickel reduction. This is very likely related to the only small changes in mordenite acidity it produces (8,12).

Average bulk reduction. The increase in bulk reduction with hydrogen pressure, temperature and decrease in strong acid sites concentration is in agreement with the known equilibrium (4,13-15).



For instance fig. 1 evidences that the extent of reduction at any given temperature higher than about 650 K and at  $P_{\text{H}_2} = 0.1 \text{ MPa}$  increases from NiHM (1) to NiHM (2) and then NiNaM following the order of decreasing number of strong acid sites. Except for NiNaM none of the other mordenites reaches the complete reduction even at  $P_{\text{H}_2} = 1.2 \text{ MPa}$ . A higher hydrogen pressure is necessary.

The importance of zeolite acidity has been already shown for NiX and Y zeolites at atmospheric pressure (14).

Surface reduction. Uncomplete average bulk reduction may result in heterogeneous particles. It was already shown that for instance a NiHM (1) sample reduced at 773 K and low  $P_{\text{H}_2}$  (0.1 MPa) consists of nickel particles with a core of metal and a shell of nickel oxide. Other Ni supported oxides such as the Ni-SiO<sub>2</sub> sample are uncompletely reduced in the same conditions but display a metal character at the outer surface of some particles (4). This suggests a heterogeneous distribution of oxide and of the metal particles. The nickel mordenites considered here give results depending on the reduction conditions. Table 4 summarizes the occurrence of nickel metal on the particles surface. It can be easily seen that the surface reduction is also governed by the reaction (1) (influence of acidity - number and strength of sites and of hydrogen pressure). Nevertheless the conditions required for the complete nickel reduction at the surface differ from those in the bulk. For instance the steamed samples (2) show metal on the surface under high hydrogen pressure while the particles average bulk reduction is only 91-94 %. This arises probably from the relative distribution of Ni ions and strong acidic OH groups and from the formation mechanism of the nickel particles, which may give heterogeneity in the phases distribution.

Table 4

Changes in nickel surface state as a function of hydrogen pressure and acidity (number and strength of sites)

Catalyst	Acid sites	Metal nickel on surface particle (a)		$K_p = P_{H_2}^{(a)}$
		$P_{H_2} = 0.1 \text{ MPa}$	$P_{H_2} = 1.2 \text{ MPa}$	
NiNaM	no	yes	yes	$K_p < 0.1$
NiSiO <sub>2</sub>	large number very weak	yes	yes	$K_p < 0.1$
NiHM (2)	small number strong	no	yes	$0.1 < K_p < 1.2$
NiHMD (2)	small number strong	no	yes	$0.1 < K_p < 1.2$
NiHM (1)	large number strong	no	no	$K_p > 1.2$
NiHMD (1)	large number strong	no	no	$K_p > 1.2$

(a) Reduction temperature 773 K

(1) Mordenites pretreated in dry air

(2) Steamed mordenites

Equilibrium constant. An attempt can be made to estimate the equilibrium constant of the reaction (1). It has to be noted that in the experimental conditions used all the water evolved from the zeolite is continuously removed by the hydrogen flow. At equilibrium the only vapor phase left in the system is hydrogen. It is also the only gas phase involved in reaction (1). The equilibrium constant can then be easily expressed as  $K_p = P_{H_2}$ . For the surface reduction at 773 K the values estimated from the shift of the equilibrium (1) to the left or to the right are given in table 4.

For the average bulk reduction at 773 K,  $K_p$  would be less than 0.1 MPa for the non acidic NiNaM sample and higher than 1.2 MPa for the other mordenites.

Nickel dispersion. The smaller particle sizes (10 to 13 nm) and better homogeneous size distribution are obtained for those samples which have particles with nickel metal on their surface (NiNaM, Ni-SiO<sub>2</sub> (4) and steamed mordenites). The three properties are very likely related to a good balance between the rate of nickel reduction and that of particle growing. The nickel transfer from its initial cationic sites inside the mordenite framework (16) to its final structure of metal particles probably occurs during the reduction treatments via a process of ionic species migration (4,16). No or little particle motion is effectively expected at 773 K (17). The Ni<sup>2+</sup> migration from one cationic site to another one should be high when the



number of protonic sites, weak or strong is high i.e. for NiSiO<sub>2</sub> and NiHM (1), NiHMD (1) mordenites. If the nickel reduction is faster than the migration, i.e. for small number of protonic sites, weak or strong, the final dispersion is high. This occurs already at low hydrogen pressure for NiNaM and Ni SiO<sub>2</sub> (weak acidity) and only at high hydrogen pressure for the steamed mordenites (strong acidity).

#### CONCLUSION

This study relates the high catalytic activity of some Ni mordenites under high hydrogen pressure to the presence of nickel metal on the outer surface of the particles. This arises from the conjunction of steaming which reduces the concentration of strong protonic sites and the reduction under high pressure. The stabilized metal able to activate hydrogen, associated with a low concentration of strong protons plays a major rôle in the catalyst life time, limiting the deactivating coke deposition.

The study of nickel reduction under two different hydrogen pressures allows an estimation of the equilibrium constant of the redox reaction to be made. Different behaviors regarding bulk and surface reduction are observed. The final nickel state (dispersion, bulk reduction, occurrence of Ni metal on the outer surface of the particles) depends on the relative rates of the migration and of the reduction of nickel ions. A high number of hydroxyls seems to favor the migration rate over the reduction rate while a small number would do the opposite. In addition, for similar OH groups concentration and hydrogen pressure, the higher the acid strength, the lower the reduction degree seems to be. As a consequence the balance between the number of acid sites of suitable strength and the hydrogen pressure determines the nickel particles characteristics.

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