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HYDROGEN RELEASE FROM Ni/FAUJASITE CATALYSTS

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Mono- and multimetallic Ni/NaY samples have been studied by static and dynamic techniques. The reducibility of Ni is dramatically enhanced by Pt clusters in supercages and by Mn ions blocking small zeolite cages. No H_2 is trapped by NaY, but for Ni/NaY, NiPt/NaY, or NiPtMn/NaY more H_2 is released in temperature programmed "desorption" (TPD) than can be adsorbed at 25 °C. Two phenomena are responsible for the apparent discrepancy between ad- and desorption: (1) Ni inside small cages can ad- and desorb hydrogen only when cage windows are widened by thermal vibration to permit passage of H_2. (2) Above 500 °C the original reduction process $Ni^{2+} + H_2 = Ni^0 + 2H^+$ is reversed, i.e. Ni atoms are oxidized by hydroxyl groups. This is confirmed by the H_2 consumption in subsequent reduction. The high-temperature TPD feature can be used to estimate the amount of reduced Ni that is located in small cages.

1. Introduction

In the temperature programmed desorption (TPD) of reduced Ni/NaY catalysts, a characteristic high temperature peak (e.g. near 550 °C) is observed. Such high temperature peaks were reported before by several authors for a variety of transition metal/zeolite catalysts, e.g. Ni/X [1], Ni/Mordenite [2], Ru/NaY [3], Pt/NaY [4,5] and Ag/NaY [6]. Different explanations have been proposed for this remarkable phenomenon, including the following: (1) very strong hydrogen adsorption on the Ni surface [1]; (2) subsurface hydrogen sorption of Ru particles [3]; (3) steric restriction for molecular hydrogen release through narrow sodalite cage windows [4]; and (4) reoxidation of metal atoms or particles by lattice hydroxyl groups [2,5,6].

In this paper we present results which help to discriminate among the above models for the case of Ni/NaY. Our strategy is to compare hydrogen adsorption, measured by a volumetric method, with hydrogen release data from TPD. In addition, we measured the hydrogen consumption in reducing the samples before and after registering a TPD profile, in order to check the reoxidation concept (4). Furthermore, use is made of three recent discoveries:

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1. If the calcination temperature is kept below 360 ° C after ion exchange of platinum, all Pt ions remain in the supercages of the Y zeolites. Subsequent reduction results in small Pt particles located in the supercages, the Pt dispersion being near 100% [7,8].
2. The reducibility of nickel in NaY can be markedly increased by first exchanging Mn ions into the zeolite, and then transporting them to the small cages by a thermal treatment so that these cages become less accessible to Ni ions. The Mn ions do not become oxidized or reduced when the zeolite is calcined in oxygen at 500 ° C, or reduced in hydrogen at 760 ° C, until all the nickel is reduced [8].
3. The presence of platinum in NiPt/NaY or NiPtMn/NaY strongly catalyzes the reduction of Ni, i.e. Ni is reduced at a lower temperature and to a much higher extent than in the absence of Pt [9]. For samples containing Pt and reduced above 300 ° C it may be safely assumed that Pt is completely reduced. The metal dispersion determined from the strong chemisorption of hydrogen is then defined by: $disp. = 100\ H_{ads}/(Ni + Pt)_{red}$.

2. Experimental

a. MATERIALS

The zeolite used was Linde LZ-Y52 with an average particle size of 1 micron. The preparation procedures and metal loadings of four catalysts used in this work are given below. The X-ray diffraction profiles of these samples showed that no significant zeolite structure decomposition occurred during preparation, nor in any of the pretreatments used in this study.

Mn/NaY: A 0.005 N $Mn(NO_3)_2$ solution was added slowly to a constantly stirred NaY zeolite/deionized water slurry (1 g/100 ml), which had been acidified to a pH of 4.0 with dilute HNO_3. After undergoing ion exchange for 6 hr at room temperature, the zeolite was filtered, then washed successively with deionized water, NaOH solution at a pH of 9.0, and again with deionized water. Finally, the zeolite was dehydrated in vacuum, while heating from room temperature to 500 ° C with a slow heating rate (10 ° C/hr) and then held at 500 ° C for 6 hr. The Mn load of the sample was 2.32 wt%.

Ni/NaY: A 0.005 N $NiCl_2$ solution was introduced into a zeolite slurry, which was acidified to a pH of 6.0 with HCl. The catalyst was prepared as above, without the pre-dehydration step, and the time period for ion exchange was 24 hr. The Ni load of the sample was 4.58 wt%.

NiMn/NaY: The same procedure was used here as for Ni/NaY, with Mn/NaY substituted for NaY. The Ni load of the sample was 2.51 wt%.

NiPt/NaY: Ni/NaY was first heated in vacuum up to 500 ° C. After cooling and adding deionized water a Ni/NaY slurry was formed to which a 0.01 N

$Pt(NH_3)_4Cl_2$ solution was added. After filtering, the sample was washed until no chloride ions were detectable. The Pt load of the sample was 3.18 wt%.

NiPtMn / NaY: The same procedure was used as for NiPt/NaY, but Ni/NaY was replaced by NiMn/NaY. The Pt load of the sample was 2.18 wt%.

b. PRETREATMENT CONDITIONS

Pt-containing samples: The catalyst (0.15 g) was heated from 25 ° C to 300 ° C at a heating rate of 0.5 ° C/min in an O_2 flow of 150 ml/min, and kept at 300 ° C for 2 hr. After purging with Ar at 360 ° C, temperature programmed reduction (TPR) and "degree of reduction" experiments were performed. For TPD experiments, the sample was reduced by $5\%H_2/Ar$ flow at 300 ° C for 8 hr, then cooled in a $5\%H_2/Ar$ flow to room temperature.

Pt-free samples: The catalyst (0.15 g) was calcined in Ar from 25 ° C to 500 ° C with a constant heating rate of 0.5 ° C/min, held at 500 ° C for 6 hr, then the extent of reduction was determined at constant temperature. For the TPD experiment, the catalyst was reduced by $5\%H_2/Ar$ flow at 425 ° C for 2 hr, then cooled in a $5\%H_2/Ar$ flow to room temperature.

c. DETERMINATION OF EXTENT OF Ni REDUCTION AND DISPERSION

The "extent of Ni reduction" was calculated from the H_2 consumption at $P_{H2} = 55$ torr and constant temperature (see table 1) in a recirculation reactor with a Datametric pressure transducer whose reference side was evacuated at 10^{-5} torr. For hydrogen chemisorption measurements the reduced sample was evacuated in vacuum at 500 ° C for 15 min; after cooling to 25 ° C, H_2 was admitted, its pressure increasing from 35 to 180 torr. After determining the

Table 1
Extent of Ni reduction and metal dispersion

Sample	Reduction		%Ni reduced	Metal dispersion[1]			%Ni reox.
	$T/°C$;	t/hr		from ads.	from low temp. TPD	from tot. TPD	
		2	7.1	9.8	8.9	18.1	4.6
Ni/NaY	425	8	10.2	9.2	–	–	–
		16	11.7	6.5	–	–	–
		2	45.7	29.5	–	–	–
NiPtMn/NaY	300	8	92.0	26.0	27.6	115.3	56.0
		16	105.8	25.5	–	–	–
		2	42.2	37.2	–	–	–
NiPt/NaY	300	8	52.5	34.5	50.4	175.2	86.0

[1] Metal dispersion $= 100\ H_{ads}/(Ni+Pt)_{red}$.

isotherm for total adsorption, the sample was evacuated at 25 ° C, and a second adsorption isotherm was measured. The difference between both adsorption measurements, extrapolated to zero pressure, was assumed to represent strong hydrogen chemisorption. The ratio of the number of strongly adsorbed H atoms to the number of *reduced* metal atoms is conventionally called "dispersion".

d. TEMPERATURE PROGRAMMED "DESORPTION"

A conventional TPD apparatus was used. The sample was heated in a tubular quartz reactor, typically from −80 to 760 ° C at a constant heating rate of 8 ° C/min. The carrier gas was Ar with a flow rate of 25 ml/min.

3. Results and discussion

Figure 1 shows the TPD profiles of Ni/NaY, NiPtMn/NaY and NaY. For Ni/NaY, that was pre-reduced in a 5%H_2/Ar flow at 425 ° C for 2 hr, there are two main hydrogen desorption peaks. By applying the same treatment to metalfree NaY, no hydrogen desorption is observed. For NiPtMn/NaY three TPD peaks are observed, with the high temperature peak near 550 ° C being the most pronounced. In table 1 the extent of Ni reduction is given for Ni/NaY, NiPtMn/NaY and NiPt/NaY after reduction at different temperatures. As mentioned, the presence of platinum significantly lowers the temperature of Ni

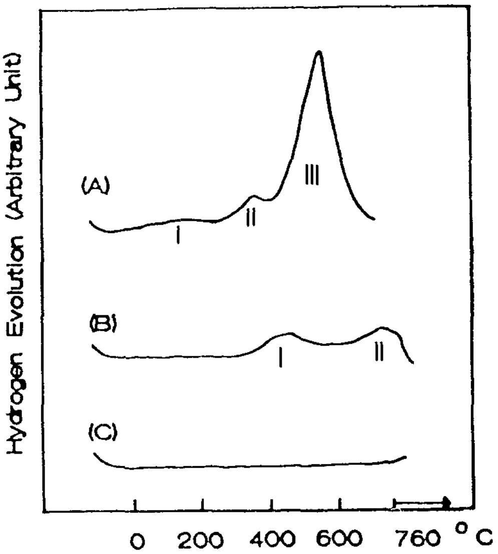

Fig. 1. TPD results of (A) NiPtMn/NaY pre-reduced by 5%H_2/Ar gas flow at 300 ° C for 8 hr, (B) Ni/NaY pre-reduced at 425 ° C for 2 hr and (C) NaY pretreated by 5%H_2/Ar at 425 ° C for 2 hr, then cooled in the 5%H_2/Ar.

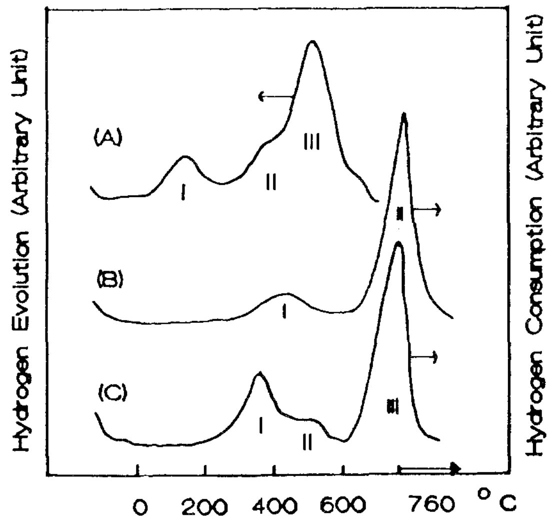

Fig. 2. (A) TPD of NiPt/NaY pre-reduced by $5\%H_2/Ar$ at 300 °C for 8 hr, (B) TPR of NiPt/NaY after TPD run, (C) TPR of NiPt/NaY pre-calcined at 300 °C by O_2 at 300 °C for 2 hr.

reduction, and increases the extent of Ni reduction. It is also clear that Mn addition to the zeolite increases the extent of Ni reduction, as we had reported earlier [8]. These effects are, however, not the main objective of the present paper and will be discussed elsewhere [9].

In table 1 the dispersion, calculated from volumetric adsorption of hydrogen at 25 °C, is compared with (a) the value calculated from integrating the total TPD spectrum, and (b) with the value calculated from the low temperature TPD peaks, i.e. peaks I and II in traces (A) of figs. 1 and 2, but peak I in trace (B) of fig. 1. It should be mentioned that all dispersion data refer to the reduced portion of the metal, as determined from the hydrogen consumption in the recirculation reactor. It is assumed that the extent of reduction is the same for samples reduced in a $5\%H_2/Ar$ gas flow at the same temperature and for the same duration, although the partial pressure of hydrogen (38 torr) was not exactly equal to that used in the recirculation apparatus (55 torr).

All samples show a strong difference between adsorption and desorption data, if the large high temperature peak is included in the latter; the amount of hydrogen released is always larger than the adsorbed amount. For the bimetal and trimetal samples the integrated TPD spectrum results in completely unreasonable dispersions exceeding 100%. This is our first strong indication that the high temperature TPD peak does not represent a true desorption of adsorbed hydrogen.

If only the low temperature TPD peaks are considered, agreement with the adsorption data is fair for Ni/NaY and NiPtMn/NaY. This suggests that the low temperature TPD peaks I + II in fig. 1, (A) for NiPtMn/NaY and the desorption peak I in fig. 1, (B) for Ni/NaY represent true desorptions of adsorbed hydrogen and may be used to calculate the metal dispersion. This is consistent with results reported by Galinskii et al. [10] for Ni/NaY prepared by $Ni(CO)_4$ decomposition. In that case it was shown that Ni particles are located in the supercages, and the two main hydrogen desorption peaks were indeed found at low temperatures, viz. at 155 ° C and 330 ° C.

For NiPt/NaY, however, even the low temperature desorption peak is higher than expected on the basis of volumetric hydrogen adsorption (see table 1). As the "dispersion" calculated from the total amount of hydrogen released in the TPD run, significantly exceeds 100%, it is obvious that a large fraction of this hydrogen must be due to a process different from ordinary desorption.

In discussing the nature of this hydrogen release process, the location of the metal in the zeolite is of importance. Earlier, we had found for Pt/NaY [5] that hydrogen was formed at elevated temperature by reoxidation of Pt, but only for atoms located in sodalite cages. For Ni in NaY it is certain that after calcination the majority of the ions are located in small cages, i.e. sodalite cages or hexagonal prisms. In the present work the reduction temperature (300 ° C) is very low, so that the Ni atoms will remain inside the zeolite cages, and most of them in these small cages. We therefore assume that the hydrogen released at high temperature, possibly also part of the low temperature TPD peak for NiPt/NaY, is due to a process involving metal atoms located in the small cages of the zeolite, i.e. sodalite cages or hexagonal prisms. We propose that the hydrogen evolution at elevated temperature is due to reaction of zeolite hydroxyl groups with Ni atoms in small cages, i.e. a reversal of the reduction of ion exchanged Ni ions with dihydrogen:

$$2\,ZO^- + Ni^{2+} + H_2 \leftrightharpoons Ni^0 + 2\,Z\text{-}OH. \tag{1}$$

The hydroxyl groups in zeolite Y are known to be strong acids; reaction (1), read from right to left, reflects the known chemistry of nickel, which is dissolved in acids. The reaction should be reversible; i.e. reduction of Ni^{2+} ions takes place at a hydrogen pressure near 1 atm., but the reverse reaction is favored at low hydrogen pressure and high temperature, i.e. under the conditions prevailing for the high temperature TPD peak.

Upon assuming that the hydrogen desorption peak at high temperatures, (peak III in traces (A) of figs. 1 and 2, and peak II in trace (B) of fig. 1) is due to reoxidation of nickel, it follows that 4.6% of the reduced Ni is reoxidized with Ni/NaY, 56% with NiPtMn/NaY, and 86% with NiPt/NaY (see table 1).

In order to verify the hypothesis that hydrogen evolution at high temperature is due to reoxidation of Ni by the hydroxyl groups of the support, we decided to measure the extent of this reoxidation by TPR after completion of a TPD run. We used 45 mg NiPt/NaY which had been pre-reduced in an $5\%H_2/Ar$ flow at 300 ° C for 8 hr. This sample was first characterized by TPD (fig. 2, (A)), then a TPR run was performed, using the same temperature program, viz. 8 ° C/min, in $5\%H_2/Ar$ gas flow. The result is shown in fig. 2 (B). For comparison, the TPR profile of a fresh NiPt/NaY (45 mg) sample that had been calcined in oxygen is included in fig. 2 as trace (C).

The results show, that after the TPD run, the Ni containing catalyst consumes a significant quantity of hydrogen, and has a similar reduction characteristic as if calcined in oxygen. The positions and the intensities of the relevant peaks in fig. 2 (B) and (C) are very similar. We conclude that at high temperature a significant portion of the Ni^0 is reoxidized to Ni^{2+} ions. These Ni ions are located in the small cages of the zeolite and indistinguishable from Ni ions which have been brought there by ion exchange, followed by calcination.

The conclusion that metal atoms inside small zeolite cages are reoxidized more easily than metal clusters in supercages or larger metal particles at the external surface is also valid for other metals. Recently the same effect was found for Pt in small cages in zeolite Y [5].

Assuming that under the conditions used in the present paper, platinum is located in supercages and thus not reoxidized by hydroxyl groups, we calculate from the integrated TPR spectrum after the TPD run, that 80% of the nickel is reoxidized. This is consistent with the value of 86% calculated above from the high temperature TPD peak and shown in table 1.

It is also interesting to compare the values for NiPt/NaY with those for NiPtMn/NaY. In a previous paper we had presented evidence [8] that the beneficial action of Mn to enhance the reducibility of Ni is due to site blocking, i.e. Mn ions occupy sodalite cages and hexagonal prisms, rendering these small cages less accessible to Ni ions. The present data are in good agreement with this conclusion. As small cages are occupied by Mn ions, more Ni ions stay in supercages. After reduction the concentration of Ni atoms in small cages is, consequently, lower. As we argued above that the Ni atoms in the smaller cages are more prone to becoming reoxidized by hydroxyl groups at high temperatures, it follows that site blocking by Mn ions should lower the amount of reoxidizable nickel. Indeed, the percentage of reoxidation is 56% for NiPtMn/NaY, but 86% for NiPt/NaY (see table 1). Also the difference between Ni/NaY and the bi- and trimetallic samples can be rationalized. Ni/NaY is reduced at 425 ° C whereas the platinum containing samples are reduced at 300 ° C. It is known that at the higher reduction temperature Ni atoms leave the small cages, migrating to supercages or the external surface, where they will not be reoxidized. Accordingly, a much lower reoxidation percentage, viz. 4.6% was obtained.

Using the same line of reasoning it is expected that the highest concentration of reduced Ni atoms in small cages is realized for NiPt/NaY. These Ni atoms might adsorb hydrogen during the cooling period after reduction, when vibrational motion of the zeolite lattice permits passage of H_2 molecules through the narrow windows, but not at 25 ° C, when passage of a 2.8 Å molecule through a 2.2 Å aperture will be impossible. It is therefore quite likely that the discrepancy between hydrogen adsorption at 25 ° C and desorption of samples that were cooled in hydrogen and then heated in Ar to 400 ° C, is due to this hydrogen adsorption by Ni atoms in the small cages. The first two peaks of the TPD profile of NiPt/NaY are then a more reliable measure of the true metal dispersion than hydrogen adsorption at 25 ° C.

The present conclusions are in line with findings by other groups. Bonneviet et al. [11] reported for small Ni particles (< 2 nm) supported on silica, that about 40% of the particles are reoxidized by heating in vacuum to 300 ° C. Such oxidation of Ni was also observed by Bjorklund and Burwell [12] on alumina and interpreted as a reaction of the Ni particles with the surface hydroxyl groups. For Ag/NaY and Ag/MOR, Jacobs et al. [6] reported that H_2 is formed by "oxidative thermal desorption" from zeolites containing highly dispersed silver; at the same time lattice hydroxyl groups disappear. For Ni/MOR, Suzuki et al. [2] also found a TPD peak at 550 ° C and tentatively attributed it to the oxidation of reduced Ni by zeolite protons.

4. Conclusions

The conclusions of this study are summarized as follows:

1. Hydrogen release at high temperature from Ni-containing Y-type zeolites is due to the reoxidation by hydroxyl groups of Ni atoms in sodalite cages and hexagonal prisms.
2. High temperature TPD peaks can be used to estimate the fraction of Ni atoms located in small cages; TPD peaks at lower temperatures may be used to calculate the metal dispersion.
3. As H_2 molecules cannot pass through 2.2 Å apertures at low temperatures, a determination of true metal dispersion, that includes reduced atoms in small cavities, requires vibrational opening of apertures in measurements of ad- and desorption.

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