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Evidence of a Strong Metal–Support Interaction and of Ni–Si Alloy Formation in Silica-Supported Nickel Catalysts

The behavior of Pt/TiO_2 catalysts is unusual (*1–6*). When reduced by H_2 at a low temperature (473 K), they chemisorb a significant amount of H_2 and are normally active in the hydrogenation of benzene. Their reduction at a higher temperature (800 K) results in a sharp decrease of both catalytic activity and H_2 uptake. These variations cannot be accounted for by metal sintering or encapsulation. However, subsequent oxygen treatments followed by low-temperature reductions restore most of the normal properties of Pt/TiO_2. The low activity of the catalyst after its reduction at high temperatures has been attributed to strong metal–support interaction (SMSI) which would be destroyed by a subsequent O_2 treatment. The exact nature of this interaction, however, still remains obscure.

It has also been shown that Pt/SiO_2, Ni/TiO_2, and Ni/SiO_2 catalysts demonstrate a similar behavior (*7–9*). However, the reduction temperature which lowers the catalyst activity is higher for silica-supported metals than for titania-supported ones, thus suggesting that the low-activity state may be related to the reduction of supports.

This note reports results on Ni/SiO_2 which demonstrate that a Ni–Si alloy is probably formed when the catalyst is in the SMSI state.

The catalyst precursor, 20 wt% Ni, was prepared by reacting silica from Degussa (200 m^2/g) with a nickel nitrate hexammine solution (*10*). Samples were reduced by flowing hydrogen in a quartz cell by linearly raising the temperature from 300 K to the desired temperature at one of two selected heating rates, 2 and 20°C/min. The restoration treatment of catalysts reduced at high temperatures consisted of an oxidation in flowing O_2 at 800 K and of a subsequent reduction in flowing H_2 at the same temperature for 1 h. Magnetization of the outgassed samples was measured in an electromagnet providing moderate fields (21 kOe) at various temperatures. The specific saturation magnetization (per gram of total nickel), M_s was obtained by plotting magnetization against the reciprocal field strength, $1/H$, and by extrapolating to zero value. Most of the studied samples were shown to be superparamagnetic (no remanence and coincidence of the M vs H/T plots for two different temperatures), allowing the determination of the average (surface) diameter, D_s, of nickel particles (*10*). Catalytic activity measurements were performed in a differential flow reactor at atmospheric pressure (*7–9*).

We shall describe and discuss our results in the following order: (i) influence of the heating rate during the reduction process on the chemisorptive and catalytic properties of Ni/SiO_2 catalysts, (ii) influence of the heating rate on the morphological properties of the same samples.

In Table 1 are presented the hydrogen uptakes, q_H, and catalytic activities in benzene hydrogenation, r, of samples reduced under various conditions and subsequently restored. With regard to both catalytic and chemisorptive properties, the behavior of Ni/SiO_2 catalysts prepared at either heating rate is qualitatively similar to that of Pt/TiO_2: namely, reduction at high temperatures results in decreases of q_H and r, and subsequent O_2 treatments followed by H_2 reduction at a moderate temperature partially restore the properties of the system.

Table 2 shows the nickel particle sizes,

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TABLE 1

Quantities of Adsorbed Hydrogen and Catalytic Activities in Benzene Hydrogenation of Ni/SiO_2 Catalysts

	Reduction temperature (K)	Samples	q_H 10 Torr, 300 K (ml NTP/g of total Ni)	$r \times 10^{-18}$ (molecules/s/g of total nickel)[a]
High heating rate	920	I	22.5	1.1
	1120	II	7.8	0.056
	Restored	III	9.1	0.33
Low heating rate	920	IV	41.5	1.4
	1180	V	5.7	0.04
	Restored	VI	6.8	0.21

[a] H_2 pressure = 600 Torr (1 Torr = 133.3 N m^{-2}); benzene pressure = 4 Torr; T = 303 K; total gas flow = 120 ml/min.

D_s, and the specific saturation magnetization, M_s, of the Ni/SiO_2 catalysts. An examination of this table reveals that, whatever the heating rate, an increase of the reduction temperature results in a moderate increase of D_s, and that the restoring treatment does not change the dispersion of nickel. Thus, the variations of q_H and r reported in Table 1 cannot be accounted for by D_s variations, as for the case of Pt/TiO_2 catalysts.

Reduction at high heating rates leads to Ni/SiO_2 catalysts with specific saturation magnetization near to that of pure, bulk nickel (samples I and II in Table 2). This suggests that (i) the nickel phase in the catalysts is completely reduced, (ii) the reduction of the silica support with the subsequent formation of a bulk Ni–Si alloy is improbable, since addition of small amounts of Si into Ni would have drastically decreased saturation magnetization (*11*). This conclusion agrees with that reached from magnetic measurements at 4.2 K (*12*). However, the existence of a surface Ni–Si alloy is not precluded. After the restoring treatment, the saturation magnetization of the samples is somewhat smaller than that of samples I and II. This probably means that the restored sample is reduced but partially.

TABLE 2

Ni Particle Size and Saturation Magnetization of Ni/SiO_2 Catalysts

	Reduction temperature (K)	Sample	D_s (nm)	M_s at 300 K (emu cgs/g of total Ni)
High heating rate	920	I	6.5	53
	1120	II	12.3	52.2
	Restored	III	12.8	41
Low heating rate	920	IV	3.9	51.4
	1180	V	10.9[a]	0
	Restored	VI	9.3	38
		Bulk nickel		54.4

[a] Measured at 77 K.

When reduction is performed at low heating rates, the specific saturation magnetization measured at 300 K of the Ni/SiO_2 catalyst reduced at moderate temperatures (sample IV) is nearly equal to that of bulk nickel. In contrast, the specific saturation magnetization drops to zero when the final reduction temperature is 1180 K (sample V). However, the sample reduced at 1180 K becomes ferromagnetic at 77 K and M_s then increases to 16.2 emu cgs. This sample probably contains a Ni–Si alloy, the Curie point of which lies between 77 and 300 K (*11*). The silicon atomic percentage in the bulk Ni–Si alloy displaying the same M_s is 11.5 (*11*). Its Curie point is 190 K. It may be assumed that the metal phase in the catalyst reduced at 1180 K at low heating rate (sample V) has the same silicon concentration. Indeed, this approximately corresponds to the limit of solubility of Si in Ni. The subsequent restoration treatment probably achieves a complete reoxidation of the Ni–Si alloy into the separate NiO and SiO_2 phases and the further reduction more or less completely converts NiO into pure nickel.

The formation of a bulk Ni–Si alloy at low heating rates and high reduction temperatures is probably due to a better elimination of water, which is suspected to play an inhibiting effect in the silica reduction.

The low catalytic activity of sample V, obtained by reduction at 1180 K at low heating rate, can be tentatively ascribed to a Ni–Si alloying effect. We are indeed led to assume that a Ni–Si alloy is also formed to account for the low catalytic activity of sample II, reduced at 1120 K at high heating rates. However, as the hypothesis of a bulk alloy formation is ruled out for this case on the basis of M_s measurements, we must assume that in sample II alloying is limited to the outermost layers of the nickel particles. It should be noted that similar alloying effects have been already invoked by Den Otter and Dautzenberg (*13*) to account for the loss of H_2 uptake which is observed when Pt/Al_2O_3 catalysts are reduced at relatively high temperatures.

The present results confirm that the behavior of Ni/SiO_2 is similar to that of Pt/TiO_2. The reason for the SMSI effect has been traced in the present case to the existence of bulk or surface Ni–Si alloys. This explanation of the SMSI may not be restricted to Ni but could also be valid for the case of other metal-supported catalysts.

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