

## EVIDENCE FOR A WEAK METAL-SUPPORT INTERACTION IN ALUMINA-SUPPORTED NICKEL CATALYSTS

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The reduction of Ni/Al<sub>2</sub>O<sub>3</sub> at high temperatures does not result in a decrease of the H<sub>2</sub> uptake and catalytic activity towards C<sub>2</sub>H<sub>6</sub> hydrogenolysis per metal surface atoms. This is typical of a weak metal-support interaction. Moreover, no Ni-Al alloy formation has been detected by magnetism. This behavior, at variance with that of Ni/SiO<sub>2</sub>, confirms that the occurrence of the strong metal-support interaction is probably related to support reduction with alloy formation.

Восстановление Ni/Al<sub>2</sub>O<sub>3</sub> при высоких температурах не приводит к уменьшению адсорбции H<sub>2</sub> и каталитической активности в гидрогенолизе C<sub>2</sub>H<sub>6</sub>, отнесенной к поверхностным атомам металла. Это является типичным для слабых взаимодействий металла с носителем. Это поведение, в противоположность поведению Ni-SiO<sub>2</sub>, подтверждает то, что проявление сильного взаимодействия металла с носителем, вероятно, связано с восстановлением носителя и образованием сплава.

The behavior of some supported metal catalysts is unusual. When reduced at moderate temperatures their chemisorption and catalytic properties are normal. Their reduction at higher temperatures is accompanied by a decrease of both catalytic activities toward hydrocarbon conversions and H<sub>2</sub> uptakes which cannot be accounted for by metal sintering or encapsulation. Subsequent O<sub>2</sub> treatments followed by low temperature reductions restore most of the normal properties. This phenomenon has been attributed to the occurrence of some strong metal-support interaction (SMSI) which would be destroyed by O<sub>2</sub> treatment. In this respect, Pt/TiO<sub>2</sub> can be considered as an archetype /1-6/. Other supported catalysts, however, demonstrate the very same behavior. This is the case for other precious metals supported on TiO<sub>2</sub> /6/, Ni/TiO<sub>2</sub> /7/, Pt/SiO<sub>2</sub> /8/ and Ni/SiO<sub>2</sub> /9/. In the latter system, the reason for the SMSI effect has been traced to the existence of a Ni-Si alloy /9/. Pt/Al<sub>2</sub>O<sub>3</sub> catalysts probably exhibit a similar behavior /10-11/.

This note reports on preliminary results obtained on Ni/Al<sub>2</sub>O<sub>3</sub>, which demonstrate that the strong metal-support interaction does not occur and that a Ni-Al alloy does not form.

## EXPERIMENTAL

The precursor (21.1 wt. % Ni) was obtained by reacting aluminum oxide C from Degussa (100 m<sup>2</sup>/g) with a hexammine nickel nitrate solution /12/. Reduction was performed in flowing hydrogen (5 or 10 l/h) for 15 h by linearly raising the temperature from 300 K to the desired temperature at one of the two selected heating rates, 16 and 1 °C/min. The quantity of adsorbed hydrogen was measured after outgassing at 623 K for 2 h at 10<sup>-6</sup> Torr in a volumetric apparatus equipped with a precision gauge ("Texas Instruments"). The magnetization of the outgassed samples was measured in an electromagnet providing 21 kOe at various temperatures. The specific saturation magnetization, M<sub>s</sub>, was obtained by plotting magnetization, M, against the reciprocal field strength, 1/H, and extrapolating to zero value. The average (surface) diameter, D<sub>s</sub>, was calculated from low and high field data /13/. The catalytic activity toward ethane hydrogenolysis was measured in a quasi-differential flow reactor with a fixed bed at atmospheric pressure.

## RESULTS AND DISCUSSION

The influence of the activation conditions on nickel particle size and saturation magnetization is illustrated in Table 1. An increase of the reduction temperature results in an increase of nickel particle size due to sintering. Whatever the heating rate, the observed saturation magnetization is nearly equal to that of the bulk nickel (54.4 emu cgs/g Ni), indicating that at the reaction temperatures considered the reduction is almost complete. M<sub>s</sub> is not altered when the final reduction temperature is high (1073 K) and when the precursor is pretreated in vacuum at 973 K. This behavior is in contrast to that observed for Ni/SiO<sub>2</sub> catalysts: the reduction of the latter catalyst at low heating rates and high temperatures resulted in a drop of M<sub>s</sub> due to the SiO<sub>2</sub> reduction and to Ni-Si alloy formation /9/. The results reported in Table 1 show unambiguously that no Ni-Al alloy is formed since the addition of small amounts of Al into Ni is known to decrease drastically the saturation magnetization /14/.

The influence of the reduction temperature on the catalytic activity and on the volume of adsorbed hydrogen is shown in Table 2. When the reduction temperature

Table 1  
Influence of activation conditions on Ni particle size and saturation magnetization

Heating rates (K/min)	Reduction temperature (K)	H <sub>2</sub> flow (l/h)	D <sub>s</sub> (nm)	M <sub>s</sub> at 300 K (emu cgs/g of total Ni)
16	773	5	6.0	51.2
16	1073	5	8.3	53.8
1	873	10		53.1
1	1173 <sup>a</sup>	10		54.4
bulk nickel				54.4

<sup>a</sup>Pretreated at 973 K in vacuum.

Table 2  
Hydrogen uptake and catalytic activity of the solids  
in ethane hydrogenolysis

Reduction temperature (K)	D <sub>s</sub> (nm)	V <sub>H<sub>2</sub></sub> 300 K, 10 Torr (STP ml)	r <sup>a</sup> molecules [s/cm <sup>2</sup> Ni]
573	4.1	60	0.098 x 10 <sup>12</sup>
773	6.0	25.2	0.156 x 10 <sup>12</sup>
1073	8.1	16.6	0.085 x 10 <sup>12</sup>
"restoration" treatment <sup>b</sup>			
	8.0	14.5	0.06 x 10 <sup>12</sup>

<sup>a</sup>Measured at 483 K, H<sub>2</sub> pressure = 160 Torr, ethane pressure = 6 Torr.

<sup>b</sup>Consisting in an O<sub>2</sub> treatment at 773 K for 1 h followed by a reduction in flowing hydrogen at 773 K for 1 h.

increases from 573 to 1073 K, the observed hydrogen uptake decrease can be accounted for by the nickel particle size increase. The catalytic activity is not altered by high reduction temperature. Moreover, subsequent O<sub>2</sub> treatment at 773 K followed by H<sub>2</sub> reduction at the same temperature of the sample reduced at high temperature, does not change the hydrogen uptake and decreases the catalytic activity. This behavior is at variance with that previously observed for Ni/SiO<sub>2</sub>, showing that Ni/Al<sub>2</sub>O<sub>3</sub> does not exhibit the strong metal-support interaction already observed in a number of supported catalysts.

## TURLIER, MARTIN: METAL-SUPPORT INTERACTION

A comparison of the behavior of Ni/SiO<sub>2</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> shows that the SMSI effect parallels that of the alloying effect, thus confirming that both phenomena are probably related.

It can also be noted that different metals (Pt and Ni) supported on the very same support (Al<sub>2</sub>O<sub>3</sub>) give rise to different metal-support interactions /10, 11/. So far, we have no satisfying explanation and further work is needed to make this point clear.

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