

## The Effect of Crystallite Size on the Onset of Metal-Support Interactions for Titania-supported Nickel Catalysts

Edmond I. Ko,\* Scott Winston, and Christy Woo

Department of Chemical Engineering, Carnegie-Mellon University, Pittsburgh, PA 15213, U.S.A.

For titania-supported nickel catalysts more severe reduction conditions were found necessary to induce strong metal-support interactions in larger nickel crystallites.

The anomalous chemisorption behaviour recently observed for titania-supported metal catalysts has been ascribed to strong metal-support interactions.<sup>1</sup> Although the exact nature of such interactions is still not well understood, it has been suggested<sup>2</sup> that the extent of interaction may be related to the size of the metal crystallite. We now report that the results of chemisorption and catalytic studies confirm a crystallite size effect.

Two catalysts containing 2 and 10 wt % nickel on titania (Degussa P-25, Brunauer-Emmett-Teller surface area = 50 m<sup>2</sup>/g) were prepared by the method of incipient wetness impregnation using nickel nitrate hexahydrate as the metal salt. Prior to reduction in hydrogen the catalysts were dried overnight in an air oven at 400 K. The reduction was carried out in flowing hydrogen (50 ml/min) and the catalyst was heated with a linear increase of temperature with time from room temperature to the final reduction temperature in about 1 h. X-Ray diffraction measurements after reduction at 573 K for 1 h showed that the average crystallite size for the 2 and 10 wt % samples was 3.5(±1) and 8.0(±1) nm, respectively. These values were in good agreement with those reported by Smith *et al.*<sup>3</sup> The use of a molybdenum X-radiation source allowed a direct measurement of the smaller crystallite size in this study.

The chemisorption study followed the procedure described previously.<sup>4</sup> After reduction at 573 K for 1 h, the 2% Ni-TiO<sub>2</sub> catalyst chemisorbed a negligible amount of hydrogen, a characteristic of strong metal-support interactions. The 10% Ni-TiO<sub>2</sub> catalyst, on the other hand, chemisorbed a normal amount of hydrogen following identical reduction treatment. This normal behaviour was further shown by the excellent agreement found among crystallite sizes determined from chemisorption, X-ray diffraction, and electron microscopy studies (Table 1). Furthermore, subjecting the 10% Ni-TiO<sub>2</sub> catalyst to reduction at 773 K for 1 h resulted in a significant decrease in its hydrogen uptake. This decrease was reflected in an unexpectedly large crystallite size as would be calculated on the basis of chemisorption results. At the same time, X-ray diffraction and electron microscopy studies showed no evidence of metal agglomeration.

These results clearly indicated that a more severe reduction

Table 1. Crystallite size for 10 wt % titania-supported nickel catalysts.

Reduction treatment in hydrogen	Size/nm		
	Chemisorption	X-Ray diffraction	TEM <sup>a</sup>
573 K, 1 h	10	8	8-11
773 K, 1 h	>40	8	8-11

<sup>a</sup> TEM = transmission electron microscopy.

treatment was necessary to induce strong metal-support interactions in a 10% Ni-TiO<sub>2</sub> catalyst. More significant was the finding that the same catalyst could be made to behave in a chemically similar manner to a non-interacting system under appropriate reduction treatment. In other words, the onset of metal-support interactions could be studied on the same catalyst as a function of reduction temperature.

It should be noted that the low hydrogen chemisorption uptake was not due to incomplete reduction of the catalyst. Smith *et al.*<sup>3</sup> examined a 12.3% Ni-TiO<sub>2</sub> catalyst by oxygen chemisorption, and reported almost 90% reduction after similar treatment. In addition, thermogravimetric data indicated that the catalyst experienced no further weight change when the reduction temperature was raised from 573 to 773 K.<sup>5</sup> Therefore it appeared unlikely that the observed difference in chemisorption behaviour was due to varying degrees of reduction of the metal salt.

To confirm our observations ethane hydrogenolysis was studied on the same two catalysts. Ko and Garten<sup>6</sup> showed previously that this reaction is a sensitive chemical probe for metal-support interactions. In particular for titania-supported nickel catalysts, a weaker dependence of the reaction rate on hydrogen partial pressure is found, indicative of a less hydrogen-deficient surface intermediate (C<sub>2</sub>H<sub>2</sub>). The reaction was carried out as reported earlier<sup>6</sup> and the results obtained are shown in Table 2. A C<sub>2</sub>H<sub>2</sub> surface intermediate was identified for the 10% Ni-TiO<sub>2</sub> catalyst after reduction at 573 K for 1 h. Since the same surface intermediate was found for silica-supported nickel, there appeared to be no interaction for this

**Table 2.** Chemisorption and catalytic properties of titania-supported nickel catalysts.

Wt loading/%	Reduction treatment in hydrogen	Amount of hydrogen chemisorbed/ml g <sup>-1</sup> Ni	Specific activity for ethane hydrogenolysis at 525 K mol m <sup>-2</sup> Ni h <sup>-1</sup>	Surface intermediate in ethane hydrogenolysis (power rate law)
2	573 K, 1 h	2	$9 \times 10^{-6}$	C <sub>2</sub> H <sub>4</sub> (rate = $k p_E^{1.0} p_H^{-0.8}$ )
10	573 K, 1 h	16	$5 \times 10^{-5}$	C <sub>2</sub> H <sub>2</sub> (rate = $k p_E^{0.9} p_H^{-1.7}$ )
10	773 K, 1 h	3	$1 \times 10^{-5}$	C <sub>2</sub> H <sub>4</sub> (rate = $k p_E^{1.0} p_H^{-1.2}$ )

sample. However, a C<sub>2</sub>H<sub>4</sub> surface intermediate was identified for both the 10% Ni-TiO<sub>2</sub> catalyst reduced at 773 K for 1 h, and the 2% Ni-TiO<sub>2</sub> catalyst reduced at 573 K for 1 h. In addition, the fact that these two catalysts had comparable specific activities (Table 2) suggested that the observed low chemisorption uptake of the 2% Ni-TiO<sub>2</sub> catalyst was not caused by incomplete reduction. A separate run using an oven-dried but unreduced 2% Ni-TiO<sub>2</sub> catalyst showed *no* ethane hydrogenolysis activity at the same temperature.

The excellent agreement between chemisorption and ethane hydrogenolysis results, as shown in Table 2, provides direct evidence for a crystallite size effect on the onset of metal-support interactions.

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