Evidence of Metal–Support Interaction for an Ni/TiO_2–SiO_2 Catalyst

Edmond I. Ko* and Norman J. Wagner

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

A TiO_2–SiO_2 support, containing approximately one monolayer of TiO_2 on SiO_2, was found to interact with nickel from hydrogen chemisorption and ethane hydrogenolysis studies, but the interaction was not as strong as that exerted by bulk TiO_2.

Murrell and Yates[1] recently showed that, when TiO_2 is deposited in different amounts as a surface phase oxide onto pure SiO_2, the resulting support causes a strong suppression of H_2 and CO chemisorption for ultradispersed rhodium catalysts. Motivated by their work, we have studied the chemical properties of an Ni/TiO_2–SiO_2 catalyst with two objectives in mind. We are interested in determining whether such a surface phase oxide will exert a support effect on catalytic behaviour and, if it does, whether the effect will be comparable with that of a bulk TiO_2 support. We now report results on hydrogen chemisorption and ethane hydrogenolysis relevant to these questions.

The TiO_2–SiO_2 support was prepared by a procedure similar to that described by Murrell and Yates,[1] except in this study a Davison grade 952 silica was used (Brunauer–Emmett–Teller area ~300 m^2/g). The loading of TiO_2 (19.9 wt. %) corresponds to approximately one monolayer of surface phase oxide. *X*-Ray diffraction detected no bulk TiO_2 peaks for the TiO_2–SiO_2 support. In addition, analytical transmission electron microscopy showed a homogeneous

Table 1. Kinetic results for ethane hydrogenolysis over supported nickel catalysts.

Support	Reduction	E_A[a]/kJ mol^{-1}	n[b]	m[b]	Activity at 478 K/ (molecules/s-surface Ni atom)
TiO_2–SiO_2	573 K, 1 h	167	0.9	−1.8	5.6×10^{-5}
TiO_2–SiO_2	773 K, 1 h	168	0.9	−1.6	9.5×10^{-6}
TiO_2[c]	573 K, 1 h	178	1.0	−0.8	1.8×10^{-6}
SiO_2[d]	643 K, overnight	170	1.0	−2.2	9.0×10^{-3}

[a] Determined from the temperature dependence of the rate at ethane and hydrogen partial pressures of 3 and 20 kPa, respectively. [b] Exponents in the experimental power rate law, $kp_E{}^n p_H{}^m$, where p_E and p_H are the partial pressures of ethane and hydrogen, respectively. [c] Calculated from ref. 7. [d] Calculated from ref. 6 for the 10 wt. % sample.

distribution of titanium concentration over the silica substrate.[2] We thus believe that the deposited TiO_2 is well dispersed as a surface phase oxide.

A nickel catalyst was prepared with the TiO_2–SiO_2 support by the incipient wetness impregnation with an aqueous solution of $Ni(NO_3)_2 \cdot 6H_2O$ (Fischer Scientific Company). The metal loading (9% by weight) was confirmed by atomic absorption. The impregnated sample was dried in air at 373 K overnight, then stored in a dessicator. Prior to chemisorption and kinetic studies, the catalyst was reduced at either 573 or 773 K for 1 h in flowing hydrogen (3 l/h). Thermogravimetric measurements, by the procedure described elsewhere,[3] showed that the extent of reduction to metallic nickel was ~50 and 90% for the low- and high-temperature treatment, respectively. The average nickel crystallite size was determined from *X*-ray line broadening to be 3 ± 1 nm. Even with a Mo-K_α radiation source, the crystallite size in this range is near the detection limit of the technique. The value is thus an approximation which serves as an upper limit. In conjunction with the percentage reduction data, the average crystallite size was used to calculate the amount of surface nickel atoms present.

The procedures for hydrogen chemisorption and ethane hydrogenolysis have been described previously.[3,4] After reduction at 573 K, the Ni/TiO_2–SiO_2 catalyst adsorbed a smaller amount of hydrogen at room temperature than an Ni/SiO_2 catalyst. A ratio of adsorbed hydrogen atom/surface nickel atom (H/$Ni_{surface}$) of ~0.3 was found by pulsed chemisorption. This ratio decreased further to ~0.1 when the catalyst was reduced at 773 K. Such a suppression in adsorption is a manifestation of metal–support interaction.[5] It also precludes the use of adsorption data in determining the active metal area. The activity data reported below are calculated on the basis of average crystallite sizes as determined by *X*-ray measurements instead.

Table 1 lists the kinetic data for ethane hydrogenolysis over the Ni/TiO_2–SiO_2 catalyst at the two reduction temperatures used. The experiments were conducted over a temperature range of 500—550 K, a hydrogen partial pressure range of 10—50 kPa, and an ethane partial pressure range of 2—10 kPa. The activities are calculated for 478 K simply to allow a ready comparison with literature data. At both reduction temperatures, the Ni/TiO_2–SiO_2 catalyst shows a significantly lower activity for ethane hydrogenolysis than an Ni/SiO_2 catalyst.[6] Between the two reduction temperatures, the sample reduced at 773 K is less active by a factor of ~5. However, other kinetic parameters, including activation energy and exponents in the experimental rate law, are essentially the same for the two TiO_2–SiO_2 supported samples.

The above results clearly demonstrate a support effect for TiO_2–SiO_2 for hydrogen chemisorption and ethane hydrogenolysis. A basis for comparison must be found to determine if the extent of interaction is comparable to that for bulk TiO_2. It has been shown[7,8] that support effects are dependent on parameters such as crystallite size and reduction temperature. The present results are thus compared with those for a 2% Ni/TiO_2 catalyst, which has an average crystallite size of 3.5 ± 1 nm.[7] As reported elsewhere,[7] the adsorption stoicheiometry (H/$Ni_{surface}$) for the Ni/TiO_2 sample is 0.04 after a reduction at 573 K for 1 h. The suppression in hydrogen chemisorption is thus significantly larger than that for the Ni/TiO_2–SiO_2 sample used in this study.

Another gauge of the extent of interaction is the decrease in ethane hydrogenolysis activity. On extrapolation to the same temperature, the Ni/TiO_2 sample is a factor of ~30 less active than the Ni/TiO_2–SiO_2 sample under the same reduction conditions (Table 1). Another difference between the two supports lies in the experimental rate law. For Ni/SiO_2 catalysts the value of m for the dependence on hydrogen partial pressure is −2.2.[6] A value of −0.8 was reported for the TiO_2-supported sample, whereas in this study values of −1.6 and −1.8 are found. It has been shown[4] that the dependence on hydrogen partial pressure provides a measure of metal–support interaction. The more negative value observed for TiO_2–SiO_2 again indicates a milder support effect, consistent with the smaller suppression in hydrogen adsorption and ethane hydrogenolysis activity.

In summary, we have shown that it is possible to synthesize a surface phase oxide consisting of TiO_2 deposited on SiO_2, which displays a support effect with respect to two chemical probes. The fact that this support is not as interactive as bulk TiO_2 suggests that the extent of metal–support interaction can be controlled by varying the amount of the interacting component.

This research was supported in part by the Center for the Joining of Materials at Carnegie-Mellon University (under an N.S.F.–M.R.L. grant). An equipment grant from Sun Company, Inc. also facilitated the work.

Received, 5th April 1984; Com. 486

References

1 L. L. Murrell and D. J. C. Yates, *Stud. Surf. Sci. Catal.*, 1981, **7**, 1470.

2 E. I. Ko and N. T. Nuhfer, unpublished results.

3 E. I. Ko, J. M. Hupp, F. H. Rogan, and N. J. Wagner, *J. Catal.*, 1983, **84**, 85.

4 E. I. Ko, J. M. Hupp, and N. J. Wagner, *J. Catal.*, 1984, **86**, 315.

5 S. J. Tauster, S. C. Fung, and R. L. Garten, *J. Am. Chem. Soc.*, 1978, **100**, 170.

6 W. F. Taylor, J. H. Sinfelt, and D. J. C. Yates, *J. Phys. Chem.*, 1965, **69**, 3857.

7 E. I. Ko, S. Winston, and C. Woo, *J. Chem. Soc., Chem. Commun.*, 1982, 740.

8 G. L. Haller, D. E. Resasco, and A. J. Rouco, *Faraday Discuss. Chem. Soc.*, 1982, **72**, 109.