Nitrogen Chemisorption on Reduced Titania and Titania-supported Nickel Catalysts

By ROBERT BURCH* and ANTHONY R. FLAMBARD

(*Department of Chemistry, The University, Whiteknights, Reading* RG6 2AD)

Summary Data are presented which show that reduced titania can adsorb quite large amounts of nitrogen, a fact which must be taken into account when assessing the possible existence of strong metal–support interactions in titania-supported catalysts.

IT has been reported[1–7] that titania-supported metal catalysts exhibit anomalous chemisorption and catalytic properties owing to the occurrence of strong metal–support interactions. In the particular case of Ni/TiO_2 catalysts we have shown recently[8,9] that more careful account needs to be taken of the involvement of the reduced titania itself as an *active* component of the catalyst system.

A recent report that Rh supported on titania can adsorb large amounts of nitrogen has also attributed the result to strong metal–support effects.[10] While it is possible that the support may influence the properties of very highly dispersed metal particles, we wish to draw attention to the fact, hitherto ignored, that reduced titania can by itself adsorb nitrogen.

Catalysts containing 1 and 5 wt.% Ni on SiO_2 and TiO_2 were prepared by impregnation of the supports (Degussa P25 fumed titania, surface area 51·8 m^2 g^{-1}, and Grace silica, surface area 286 m^2 g^{-1}) with solutions of nickel nitrate. The catalysts were reduced (following the method of ref. 3) by heating the dried but uncalcined samples at 723 K in hydrogen for 1 h. Evidence that reduction of the titania occurs under these conditions comes both from the colour of the samples (reduced titania is blue) and from separate temperature-programmed reduction experiments which show that reduction commences at about 600 K. Hydrogen chemisorption isotherms were measured in an all-glass static apparatus and the Ni surface area determined by the point B method assuming each H atom occupies 6·5 Å^2.

Nitrogen isotherms were determined at 273 K on each of the catalysts and on the titania support after the standard reduction treatment. The unreduced titania was also examined, but no measurable nitrogen adsorption could be detected. This is important because in addition to showing that reduction of the titania is a prerequisite for the adsorption of nitrogen (see below), it also indicates that there are

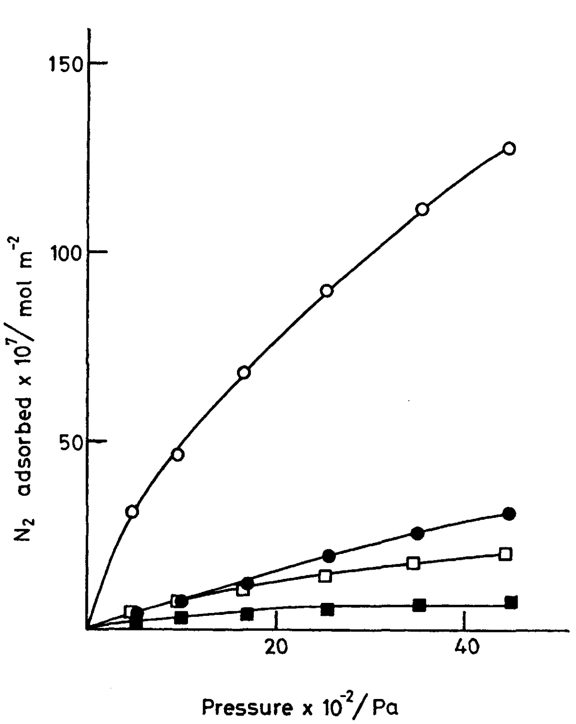

FIGURE 1. Nitrogen adsorption isotherms, calculated on a unit area of metal basis: ●, 1% Ni/SiO_2; ○, 1% Ni/TiO_2; ■, 5% Ni/SiO_2; □, 5% Ni/TiO_2. Metal surface areas obtained from hydrogen chemisorption experiments in m^2 g^{-1} were, respectively, 79, 39, 104, 47.

no significant systematic errors present in the experiments. Dead-space corrections were evaluated in each experiment using helium.

Figure 1 compares the results calculated per unit area of Ni in each sample (*i.e.* amount of nitrogen adsorbed divided by the total amount of hydrogen adsorbed at point B on the hydrogen isotherm). For each metal loading there appears to be an increase in the amount of nitrogen adsorbed by the Ni particles supported on titania. However, the results also show that the 1% Ni/SiO_2 catalyst adsorbs more nitrogen than the 5% Ni/TiO_2 catalyst.

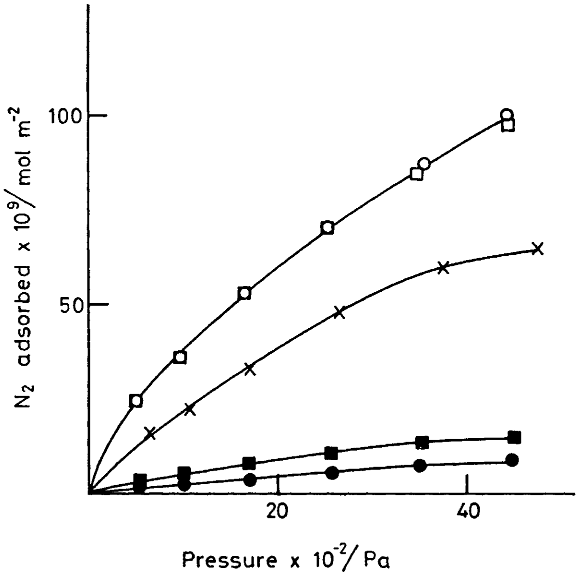

FIGURE 2. Nitrogen adsorption isotherms, calculated on a unit area of support basis: ●, 1% Ni/SiO_2; ○, 1% Ni/TiO_2; ■, 5% Ni/SiO_2; □, 5% Ni/SiO_2; ×, reduced TiO_2.

When the results are recalculated to give the amount of nitrogen adsorbed per unit area of support a very different picture emerges. Figure 2 shows that on this basis the titania-supported samples adsorb much more nitrogen. However, Figure 2 also shows that the blank *reduced* titania adsorbs a large amount of nitrogen. Consequently, most of the nitrogen adsorption measured for the Ni/TiO_2 catalysts is due to adsorption on the support.

The Ni/TiO_2 catalysts adsorb more nitrogen than the reduced titania alone (see Figure 2). However, since the two Ni/titania catalysts adsorb identical amounts of nitrogen, even though the Ni content differs by a factor of 5, it would appear that the effect of adding Ni to titania is to increase the adsorptive capacity of the titania rather than *vice versa*. The nature of the adsorption sites on the titania is uncertain. However, the fact that adsorption does not occur on unreduced titania would indicate that the nitrogen is most probably bound to Ti^{3+} sites adjacent to oxygen vacancies in the surface. We have shown in separate experiments that Ni catalyses further reduction of titania, so the most probable explanation for the additional adsorption when Ni is present is that more adsorption sites are created on the titania.

We conclude that the enhancement of nitrogen adsorption observed for titania-supported catalysts is not due to an increase in the ability of the Ni to adsorb nitrogen but rather because the reduced titania by itself can adsorb nitrogen at 273 K. This unexpected result has obvious implications for any discussion of strong metal–support interactions in titania, supported catalysts.

R. B. thanks AMAX Inc. and A. R. F. thanks the States of the Island of Jersey for financial support.

(*Received*, 18*th May* 1981; *Com.* 586.)

[1] S. J. Tauster, S. C. Fung, and R. L. Garten, *J. Am. Chem. Soc.*, 1978, **100**, 170.
[2] S. J. Tauster and S. C. Fung, *J. Catal.*, 1978, **55**, 28.
[3] M. A. Vannice and R. L. Garten, *J. Catal.*, 1979, **56**, 236.
[4] R. T. K. Baker, E. B. Prestridge, and R. L. Garten, *J. Catal.*, 1979, **56**, 390.
[5] R. T. K. Baker, E. B. Prestridge, and R. L. Garten, *J. Catal.*, 1979, **59**, 293.
[6] M. A. Vannice and R. L. Garten, *J. Catal.*, 1980, **66**, 242.
[7] D. G. Mustard and C. H. Bartholomew, *J. Catal.*, 1981, **67**, 186.
[8] R. Burch and A. R. Flambard, *J. Chem. Soc., Chem. Commun.*, 1980, 123.
[9] R. Burch and A. R. Flambard, *React. Kinet. Catal. Lett.*, accepted for publication.
[10] D. Resasco and G. L. Haller, *J. Chem. Soc., Chem. Commun.*, 1980, 1151.