

## An Electron Spectroscopic Study of the Adsorption of Nitrogen on a Ni/TiO<sub>2</sub> Catalyst prepared *in situ* in the Spectrometer: Evidence for Dissociative Adsorption in the Strong-metal-support-interaction (SMSI) State†

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Nitrogen is dissociatively adsorbed on an annealed Ni/TiO<sub>2</sub> surface just as on a Ti–Ni alloy surface while it is molecularly adsorbed on a Ni/Al<sub>2</sub>O<sub>3</sub> surface.

Strong-metal-support-interaction (SMSI) catalysts such as Ni/TiO<sub>2</sub> and Rh/TiO<sub>2</sub> have attracted considerable attention.<sup>1</sup> EXAFS studies of such catalysts have shown the evidence for bonding between the dispersed metal atoms and the metal of the oxide support.<sup>2,3</sup> These catalysts exhibit unusual adsorption behaviour of CO and H<sub>2</sub> in the SMSI state. Thus, in the SMSI state they do not chemisorb CO.<sup>4</sup> It has been shown recently that nitrogen adsorbs in large quantities on Ni/TiO<sub>2</sub> and Rh/TiO<sub>2</sub> surfaces,<sup>5,6</sup> but the nature of the adsorbed nitrogen species is not known. We have carried out a comparative study of N<sub>2</sub> adsorption on Ni/TiO<sub>2</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalyst surfaces prepared *in situ* in the electron spectrometer. For this purpose, we have exploited the diagnostic value of the N(1s) core-level spectra which show features characteristic<sup>7,8</sup> of physisorbed (~403 eV), molecularly chemisorbed (401 and/or 405 eV) and dissociatively adsorbed (397 eV) nitrogen species. In addition, we have made use of the Ti(2p) and Ni(2p) core-level spectra and the valence band spectra to characterize the catalyst surfaces. We have also employed the HeII spectra to further confirm the nature of the adsorbed species. The present study has revealed that N<sub>2</sub> adsorption is partly dissociative on an annealed Ni/TiO<sub>2</sub> catalyst surface where the SMSI is expected; this adsorption behaviour is similar to that found on a Ni–Ti alloy surface. In contrast, we observed only molecular adsorption on a Ni/Al<sub>2</sub>O<sub>3</sub> surface.

Ni/TiO<sub>2</sub> and Ni/Al<sub>2</sub>O<sub>3</sub> catalyst surfaces were prepared in the sample preparation chamber of a VG ESCA 3 MkII spectrometer by oxidising a clean Al or Ti surface, followed by the controlled deposition of Ni on the oxidised surface as described earlier.<sup>9</sup> The thickness of the oxide layer was around 30 Å and the coverage of Ni was in the region of 1.2–4 × 10<sup>15</sup> atoms cm<sup>-2</sup>. In the case of the Ni/TiO<sub>2</sub> catalyst, we have studied the adsorption of N<sub>2</sub> after depositing Ni on a freshly prepared TiO<sub>2</sub> surface without any subsequent heat treatment. Adsorption was also studied on a Ni/TiO<sub>2</sub> surface annealed in UHV at 770 K which gave rise to a decreased Ni concentration and a considerable proportion of Ti<sup>3+</sup> on the surface as shown by the Ti(2p) and Ni(2p) core-level spectra as

well as the valence band spectra. For purpose of comparison, we have investigated the adsorption of N<sub>2</sub> on a Ni–Ti alloy

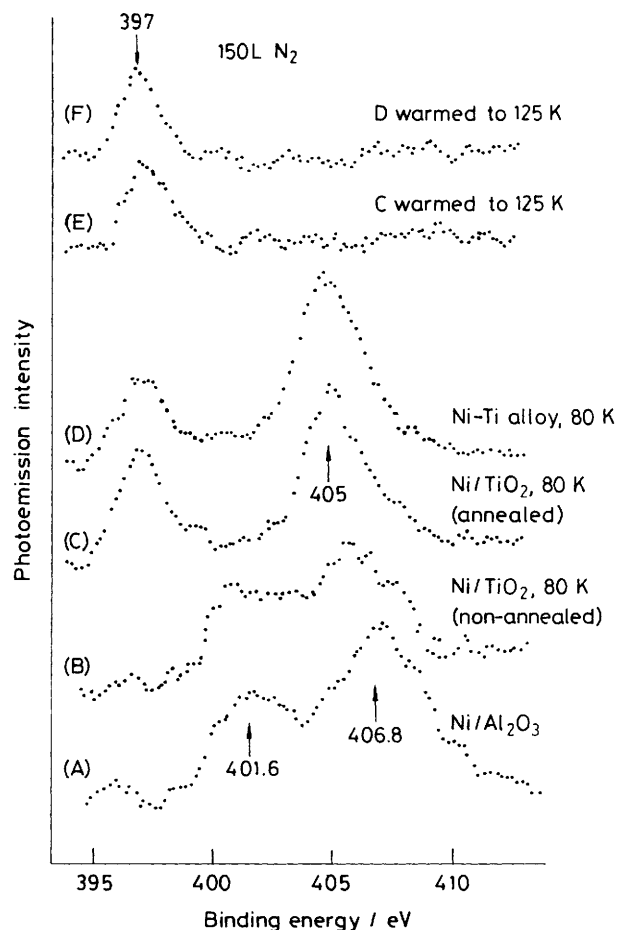


Figure 1. N(1s) core-level spectra of N<sub>2</sub> adsorbed on different simulated catalyst surfaces.

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surface prepared by depositing Ni on a clean Ti surface and then annealing it at 750 K. The alloy surface gave a valence band spectrum similar to that reported for Ni–Ti alloys.<sup>10</sup>

On the Ni/Al<sub>2</sub>O<sub>3</sub> surface, N<sub>2</sub> adsorbs molecularly at 80 K with features at 401 and 407 eV [Figure 1, spectrum (A)] due to the screened and the unscreened final states. The HeII spectrum shows two characteristic peaks at 9.4 and 13.2 eV due to the (1 $\pi_u$  + 3 $\sigma_g$ ) and the 2 $\sigma_u$  orbitals, respectively, of the chemisorbed molecular nitrogen. This adsorption behaviour is not unlike that found on a polycrystalline Ni surface.<sup>11</sup> On a TiO<sub>2</sub> surface, however, nitrogen physisorbs at 80 K with a characteristic N(1s) feature around 403.5 eV and a three-peak HeII spectrum (8.8, 10.8, and 13.6 eV) similar to that of gaseous nitrogen.

On the non-annealed Ni/TiO<sub>2</sub> surface, we observe molecular chemisorption with N(1s) features at 401 and 405 eV, just as on the Ni/Al<sub>2</sub>O<sub>3</sub> surface [Figure 1, spectrum (B)]; the HeII spectrum is also similar. On the annealed Ni/TiO<sub>2</sub> surface, however, adsorbed N<sub>2</sub> gives two features at 397 and 405 eV, the former due to dissociated nitrogen and the latter, due to weakly chemisorbed molecular nitrogen [Figure 1, spectrum (C)]. The HeII spectrum shows two peaks (8.8 and 13.0 eV) due to the molecularly adsorbed species and a feature around 5.6 eV due to the atomic species. On warming the surface, the weakly chemisorbed species desorbs leaving dissociative nitrogen at 125 K [Figure 1, spectrum (E)]. Significantly, on the Ni–Ti alloy surface also, we see weak molecular chemisorption and dissociative adsorption at 80 K [Figure 1, spectrum (D)], with only the dissociated species remaining above 125 K [Figure 1, spectrum (F)]. These results bring out the similarity between the surfaces of the annealed

Ni/TiO<sub>2</sub> catalyst and the Ni–Ti alloy. It seems that the annealed Ni/TiO<sub>2</sub> catalyst surface corresponds to the SMSI state.

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