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Fixation of Dinitrogen by Titanium(II) Ions Doped into a Magnesium Chloride Host Lattice

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Titanium compounds have been found to be particularly active in the fixation of nitrogen [1–4]. Usually titanium(IV) or titanium(III) species are reduced *in situ* [2] in the presence of reducing agents such as Grignard reagents, lithium or aluminium alkyls or metal hydrides and to obtain an effective yield of a product such as ammonia or hydrazine, a homogeneous system based on a complex of titanium is usually used [2, 3]. Recently, we have shown that titanium(II) ions can be trapped in an apparently homogeneous manner and in quite high concentrations in magnesium chloride crystals when the crystals are grown from the melt [5]. Since magnesium chloride particles can be reduced to a very small size in a ball mill it seemed possible that many of the titanium(II) ions in the doped lattice could be exposed at the surface and the powder could be used to provide a heterogeneous system which would complex nitrogen without the need for an initial reduction step.

The polycrystalline material was prepared by mixing 42 g of powdered anhydrous magnesium chloride with 20 g of powdered anhydrous zinc chloride and 7.1 g titanium metal crushed sponge under anhydrous conditions in a dry silica ampoule. The ampoule was then sealed under vacuum and heated in a furnace to 800 °C for 24 h to allow the charge to melt and the titanium metal to be oxidized to titanium(II) by the zinc chloride. The furnace was switched off and the sample allowed to cool. No attempt was made to grow single crystals, since this only hinders the milling process which follows but in a separate experiment, crystals were grown by more careful control of the cooling process. The visible spectrum of crystals with low titanium ion concentrations is typical of a d^2 octahedral system [5]. As the titanium ion concentration increases interactions between the titanium ions can be seen, but at the concentrations used here, this system is unique in possessing titanium(II) ions rather than titanium in a formally divalent state. The green polycrystalline material was transferred to a vibrating stainless steel ball mill under nitrogen and milled for 24 h. The product of this reaction was black, suggesting that during the milling process nitrogen had been co-ordinated to the titanium site. On heating to approximately 300 °C under vacuum, a green product was obtained and nitrogen gas corresponding to 1.7% by weight of the sample was given off. This corresponds to one nitrogen per seven titaniums present and indicates both that a very high surface area has been achieved and that most titanium sites exposed are active.

The black ball-milled material was slurried in toluene or decane and lithium aluminium hydride under an argon atmosphere and dilute hydrochloric acid added. On neutralisation with sodium hydroxide, ammonia was given off. It was trapped in concentrated boric acid and titrated with standard hydrochloric acid. Ammonia corresponding to 0.6% by weight of the doped magnesium chloride was found. The mechanism of the reduction process is not known, but a probable overall process might be,

$$\text{surface Ti} \xrightarrow{N_2} \text{Ti}\cdot N_2 \xrightarrow[\text{LiAlH}_4]{6e^-} \text{Ti}\cdot 2N^{3-} \xrightarrow{6H^+} 2NH_3$$

The ball-milling process is well known [6] to produce a sample with a large surface area, which could correspond to up to 1 in 5 of the titanium sites being exposed at some time at the surface. Thus, it seems probable that most sites which become exposed bond one molecule of dinitrogen and, since further reaction to form ammonia is possible, it would appear that the nitrogen is bonded with its axis parallel to the surface. This form of bonding, which has been predicted theoretically [7] for d^2 systems, does not lead to an infrared-active vibration in the co-ordinated nitrogen [3] and no infrared spectra for nitrogen could be observed.

Bercaw [8] reported rather similar behaviour with regard to the absorption of nitrogen using a complex in which the titanium is formally divalent,

$$\underset{\text{green}}{2[\eta\text{-}C_5(CH_3)_5]_2Ti} + N_2 \rightleftharpoons \underset{\text{blue-black}}{[C_5(CH_3)_5]_2TiN_2Ti[C_5(CH_3)_5]_2}$$

The nitrogen incorporated in the above complex cannot be further reduced to ammonia, indicating that this type of Ti–N_2 bond may leave the N_2 just as inert as the free molecule. However, in the ion-doped system nitrogen is further reduced readily, indicating that the bond to the solid surface is of the correct type and strength for further reaction.

These ion-doped systems have potential advantages in studies of nitrogen fixation, since they provide

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a heterogeneous system in which the titanium(II) environment can be modified in a controlled way. For example, by changing the titanium-ion concentration, the relative reactivity of single titanium ions and clusters of titanium ions can be compared. However, the main interest may lie in the fact that the ion-doped systems, considered previously as of use mainly as samples for optical studies, could have a novel chemistry, of which nitrogen fixation is only one example.

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