

Fixation of Molecular Nitrogen on a Rhodium/Titanium Dioxide SMSI (Strong Metal-Support Interaction) Catalyst

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The presence of Ti^{3+} and its increase in surface concentration during high temperature reduction are responsible for the large amounts of nitrogen chemisorption on a titania-supported Rh system at room temperature.

It is known that rhodium itself is unable to chemisorb nitrogen and only decomposes ammonia at high temperature. However, when supported on activated carbon or alumina and promoted by potassium, rhodium has been shown to chemisorb nitrogen¹ and to have a stable activity for ammonia synthesis comparable to that of iron.² It has been reported that Rh supported on titania can adsorb large amounts of nitrogen and the possibility of a strong metal-support interaction (SMSI) has been invoked.³ Also, it has been shown that reduced titania itself can adsorb nitrogen and the effect of adding metal to titania is only to increase the adsorptive capacity of titania.⁴ The nature of the adsorption sites on titania is uncertain. However, the fact that nitrogen is not adsorbed on unreduced titania indicates that nitrogen may probably be bound to Ti^{3+} sites. It is now shown that the presence of a Ti^{3+} species and its surface concentration on Rh/ TiO_2 , reduced at high temperature, facilitate the activation of molecular nitrogen.

The catalyst Rh (1 wt. %)/ TiO_2 was prepared from $RhCl_3 \cdot 3H_2O$ and TiO_2 by the incipient wetness method and dried overnight at 393 K. The product was calcined at 573 K for 3 h and subjected to low temperature reduction at 473 K for 8 h. Adsorption measurements of CO and N_2 were carried out at room temperature on pre-reduced samples using a conventional volumetric apparatus. In each case, before the commencement of adsorption studies at room temperature, the samples were pre-reduced in hydrogen at various temperatures and then evacuated at that particular temperature for 2 h.

The samples of Rh/ TiO_2 reduced at various temperatures gave rise to two e.s.r. signals (Figure 1, inset). For reduction temperatures of 573 K and above, there appeared a signal which was a singlet at $g = 2.001 \pm 0.001$ at room temperature,

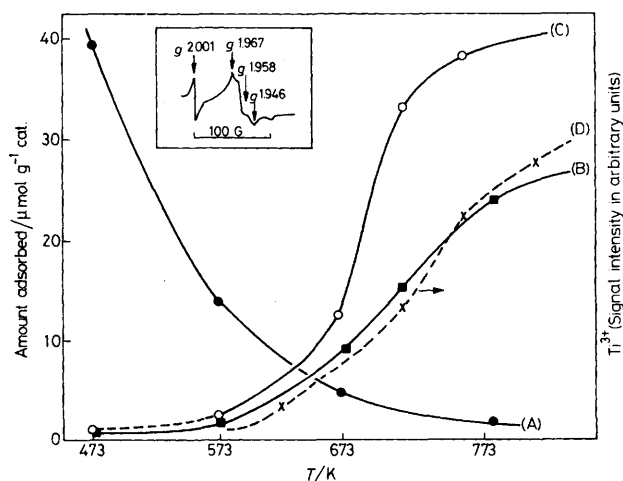
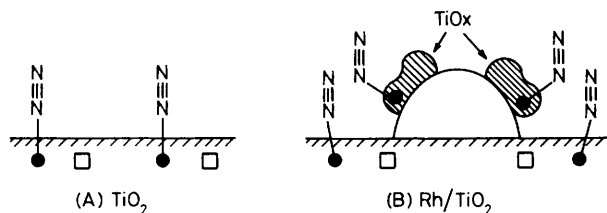


Figure 1. Adsorption of (A) CO on Rh/ TiO_2 ; (B) N_2 on TiO_2 ; (C) N_2 on Rh/ TiO_2 . Curve (D) shows the increase in signal intensity of Ti^{3+} with reduction temperature on Rh/ TiO_2 . Inset represents the e.s.r. spectrum of the singlet and the triplet observed at room temperature and at 78 K, respectively ($G = 10^{-4}$ T).



Scheme 1. Schematic representation of nitrogen on (A) reduced TiO_2 ; and (B) reduced Rh/TiO_2 in the SMSI state. ●, Ti^{3+} ; □, oxygen vacancy.

and a triplet $g_1 = 1.967$, $g_2 = 1.958$, $g_3 = 1.946 \pm 0.001$ observable only at 78K. The triplet appeared for a reduction temperature of 620 K, and progressively increased in intensity with increase in reduction temperature (Figure 1, curve D). A similar signal was observed in reduced titania and has been ascribed to Ti^{3+} species.⁵

The adsorption of CO and N_2 with increase in the reduction temperature is shown in Figure 1. The decrease in CO adsorption on pre-reduced samples between 473 and 773 K (curve A) confirms that the system under consideration attains a SMSI state after high temperature reduction. The amounts of nitrogen adsorbed appeared to be similar in titania as well as in Rh on titania up to 573 K, but beyond this temperature, a large rise in uptake was observed only in the case of Rh on titania (curve C) as compared to reduced titania (curve B). The sharp rise in nitrogen adsorption and the increase in the signal intensity of Ti^{3+} both originate at 573 K.

Reduction of Ti^{4+} to Ti^{3+} has been reported to be a primary step in the origin of SMSI in a Rh/TiO_2 system.⁶ The increase in the amounts of nitrogen with increase in the signal intensity of Ti^{3+} suggests the possibility of a direct interaction between

Ti^{3+} and the nitrogen molecule. The enhancement observed in nitrogen adsorption in Rh/TiO_2 as compared to reduced TiO_2 is due to the further addition of surface Ti^{3+} sites arising from the well known migration of ' TiO_x ' suboxide on to the metal surface of the catalyst. The fact that adsorption does not occur on unreduced titania indicates that nitrogen is most probably bound to Ti^{3+} sites adjacent to oxygen vacancies in the surface as shown in Scheme 1. The i.r. study on the pre-reduced sample has suggested that the orientation of nitrogen on the surface is mainly 'end-on,' with very little 'side-on' orientation.⁷

In conclusion, the electrophilicity of Ti^{3+} species present on the reduced surface is responsible for the fixation of molecular nitrogen on titania-supported Rh system. If the relatively high coverage of nitrogen and the known property of hydrogen activation at high temperature are unified on an easily reducible oxide-supported catalyst, then an SMSI catalyst may be a potential catalyst for the synthesis of ammonia.

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