Titanium-based hydrides for ammonia synthesis

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Abstract: We hereby show that with the presence of hydride, titanium can serve as an active catalytic material. Previously, metals such as Ru, Fe, and Co were thought to be active, and activity for Ti was not demonstrated due to excessively strong Ti-N bonds. In the presence of hydride, titanium compounds such as TiH$_2$ and BaTiO$_{2.5}$H$_{0.5}$ show a sustainable catalytic activity for NH$_3$ synthesis under Haber-Bosch conditions, almost on par with supported Ru-based catalysts. We will also present results on TiH$_2$ and BaTiO$_{2.5}$H$_{0.5}$ as a catalytic support and discuss the possible roles for hydride in these Ti-based catalytic materials.

Keywords: Ammonia synthesis, hydride, Mars van Krevelen.

1. Introduction

N$_2$ activation and conversion to NH$_3$ has been studied intensively. With metal complexes, hydride complexes form a distinct class where strong reducing agents such as KC$_8$ or Na/Hg are not necessary to activate N$_2$; among these, numerous Ti complexes require only H$_2$ gas at ambient conditions to form hydrides. One common aspect of catalysis for NH$_3$ synthesis in both homogeneous and heterogeneous states is the importance of multiple metal centers; as for titanium, Shima et al. recently demonstrated a polynuclear Ti hydride complex with reactivity for a mixture of N$_2$/H$_2$, yielding an imido-hydride complex cluster. While this is an extraordinary example of imido group formation from N$_2$ and H$_2$ gas, no NH$_3$ is formed.

Turning to solids, titanium metal is one of the few elements relatively prone to oxidative addition of H$_2$ to yield TiH$_2$. As a related compound, we have recently reported the synthesis of a titanium-based perovskite oxyhydride, BaTiO$_{2.5}$H$_{0.5}$. Using H/D exchange experiments, we have shown that D$_2$ (H$_2$) bond dissociation is possible. We have also found that treatment with N$_2$ gas at the same temperature results in conversion to the oxynitride BaTiO$_{2.5}$N$_{0.2}$. Combined, these results suggest that the oxyhydride is a useful material for the activation of diatomic H$_2$ and N$_2$. However, despite these observations from complexes and the solid state, hydride-containing titanium compounds have not been investigated previously as heterogeneous catalysts. Here, we examine TiH$_2$ and BaTiO$_{2.5}$H$_{0.5}$ as ammonia synthesis catalysts under Haber-Bosch conditions, and find that they exhibit surprisingly robust catalytic activity.

2. Experimental/Theoretical Details

A commercial sample of BaTiO$_3$ (Sakai Chemical Industry, particle size ~100 nm) was used as a reference catalyst. The catalyst BaTiO$_{2.5}$H$_{0.5}$ was synthesized by mixing BaTiO$_3$ and CaH$_2$ in a N$_2$-filled glove box, pelletizing, and sealing in an evacuated pyrex tube for 1 week at 560˚C. After reaction, the blue-black BaTiO$_{2.5}$H$_{0.5}$ (about 1 g) was split in two batches, and each was washed with NH$_4$Cl/methanol (0.1M, 300 mL), and dried at 100˚C under vacuum. Ru was deposited using Ru$_3$(CO)$_{12}$ as a precursor.

A 0.1 g sample of catalyst was suspended in a stainless steel tube on a bed of quartz wool. Catalyst samples were initially treated with flowing H$_2$ at 400˚C; catalytic runs were then conducted at 5 MPa (gauge pressure). The synthesis gas composition was N$_2$ : H$_2$ : Ar = 22.5 : 67.5 : 10, unless otherwise noted. Apparent activation energies were measured at 5 MPa, over 325-400˚C while reaction orders were all examined at 5 MPa, 400˚C. At the experimental conditions, the typical ammonia concentration is far less than 1%, thus being far from the equilibrium value (approx. 15% at 5 MPa, 400˚C).
Computational studies. N₂ adsorption energy calculations were performed using the CASTEP program¹⁵ as provided within the Materials Studio package using the PBE-GGA exchange correlation functional. Dissociative heats of adsorption were defined as \((E_{\text{slab}}+E_{\text{N}2})-E_{\text{slab}+2N}\), and molecular heats of adsorption were defined as \((E_{\text{slab}}+E_{\text{N}2})-E_{\text{slab}+N2}\). Work functions were calculated by examining the electrostatic potential within the slab and at the vacuum separating the slabs.

3. Results and discussion

The catalytic activities of various catalysts for NH₃ synthesis at 400°C, 5 MPa are shown in Figure 1a. The loading amounts of the Ru-loaded catalysts are somewhat low (1 wt%), but it can be seen that TiH₂ and BaTiO₂.5H₀.5 are catalytically active in the absence of any known catalytic metals such as Ru, Fe, or Co. The catalytic activity seems to be sensitive on the thermal and pressure history, but the control experiments with CaH₂, TiO₂, and BaTiO₃ show a marked contrast with no catalytic activity observed. Long-term tests (Fig. 1c, d) show that the activity is stable, with total NH₃ yields surpassing that expected from lattice hydrogen in the catalyst. In a separate experiment, we find TiN to be largely inactive. Activation energies and reaction orders have also been obtained, and will be discussed in the presentation.

4. Conclusions

Conventional scaling rules in heterogeneous catalysis dictate that Ti, with its strong Ti-N bond, should be inactive to NH₃ synthesis, due to formation of a stable nitride resisting hydrogenation. However, our results show that in the presence of hydride, this restriction is eliminated, resulting in a continuous catalytic cycle producing NH₃. DFT studies show that electronic effects from sub-surface hydride alone are not sufficient to alter the surface Ti-N bond strength, so surface hydride probably takes an active role in the hydrogenation step. The N₂ reaction order is quite low; suggesting an unconventional reaction mechanism.

The activity dependent on the presence of hydride in the bulk also suggests a Mars van Krevelen type mechanism for hydrogen, which is previously unreported. In this presentation, we will also present results on Ru/Fe/Co supported systems and isotope-labeled studies to examine this point and further increase the activity.

References