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.[1] 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, $BaTiO_{2.5}H_{0.5}$.[2] 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 $BaTiO_{2.5}N_{0.2}$.[3] 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_4Cl/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. N_2 adsorption energy calculations were performed using the CASTEP program[15] as provided within the Materials Studio package using the PBE-GGA exchange correlation functional. Dissociative heats of adsorption were defined as $(E_{slab}+E_{N2})-E_{slab+2N}$, and molecular heats of adsorption were defined as $(E_{slab}+E_{N2})-E_{slab+N2}$. 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 NH_3 synthesis at 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 TiH_2 and $BaTiO_{2.5}H_{0.5}$ 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 CaH_2, TiO_2, and $BaTiO_3$ show a marked contrast with not catalytic activity observed. Long-term tests（Fig. 1c, d) show that the activity is stable, with total NH_3 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.

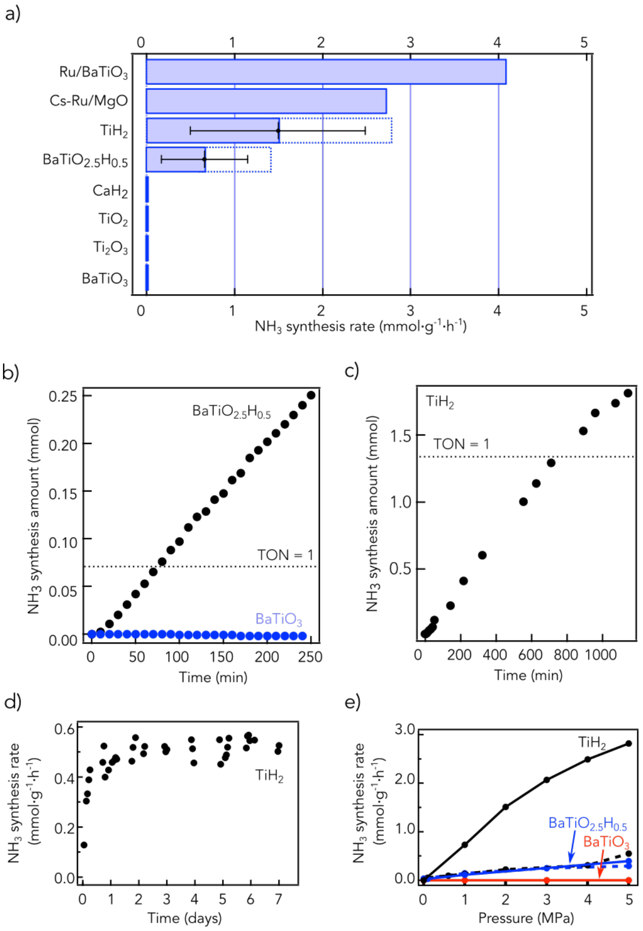

Figure 1. a) Comparison of NH_3 synthesis activities at 5 MPa, 400˚C. The error bars for TiH_2 and $BaTiO_{2.5}H_{0.5}$ indicate standard deviations from four trials (each from batches with different thermal and pressure histories); the dotted bar line indicates the highest observed activity. Ru was nominally loaded at 1 wt% for $Ru/BaTiO_3$ and Cs-Ru/MgO. b) Comparison of $BaTiO_{2.5}H_{0.5}$ and $BaTiO_3$. c,d) Time dependence of activity for TiH_2, e) Pressure dependence of various Ru, Fe, Co-free catalysts.

4. Conclusions

. Conventional scaling rules in heterogeneous catalysis dictate that Ti, with its strong Ti-N bond, should be inactive to NH_3 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 NH_3. 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 N_2 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

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