Lanthanum oxyhydrides as efficient promoters for ammonia synthesis

Kayato Ooya,[a] **Keiga Fukui,**[a] **Yuki Ono,**[a] **Masaaki Kitano,**[a] **Soshi Iimura,**[a] **Tomofumi Tada**[a] **and Hideo Hosono**[a,b,*]

[a]*Materials Research Center for Elemental Strategy, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

[b]*Laboratory for Materials and Structures, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*

**Corresponding author: 81-45-924-5009, E-mail address: hosono@msl.titech.ac.jp*

Abstract: Lanthanum oxyhydrides ($La_4H_xO_{(12-x)/2}$, x = 4~11) with high hydride ion conductivity have been synthesized by hydrogenation treatment of the mixture of LaH_3 and La_2O_3. All lanthanum oxyhydrides were demonstrated to function as efficient and stable promoters for ruthenium catalysts in low-temperature ammonia synthesis, and their catalytic activities are much higher than those of Ru/La_2O_3 and Ru/LaH_3. $Ru/La_4H_{10}O$ had the highest activity (818 μmol g^{-1} h^{-1} at 0.1 MPa and 260°C) and showed much lower activation energy than conventional Ru catalysts.

Keywords: Ammonia synthesis catalyst, Oxyhydride, High hydride ion conductivity.

1. Introduction

Catalytic ammonia synthesis is essential for the production of synthetic fertilizers and chemical products. However, high temperature (400-500°C) and high pressure (10-30 MPa) are required for industrial ammonia synthesis (Haber-Bosch process) because the bond energy of N≡N bonds is extremely large. Ruthenium catalysts are known as efficient catalysts that work under milder conditions than iron-based catalysts used in the industrial process because Ru has an optimum N_2 adsorption energy. In addition, it is well known that the activity of Ru catalyst is facilitated by electronic promoters such as alkali oxides, in which N_2 dissociation reaction is enhanced by electron injection from the promoter to Ru surface. We have recently reported that hydride materials such as Ca_2NH, CaH_2 and LaH_{2+x} promote the activity of Ru catalysts significantly at low reaction temperatures and with low activation energies when these materials are used as catalyst supports[1, 2]. These materials have very low work function because of the formation of anionic electrons at hydride vacancy sites. Recently, oxyhydrides have been extensively investigated because of their unique physicochemical properties such as electronic or ionic conductivity, and anion exchangeability[3]. These properties are expected to enhance the formation of anionic electrons in the lattice of oxyhidrides, which may promote the catalytic activity of Ru. In the present study, we focused on the lanthanum oxyhydrides as support materials of ruthenium catalyst in ammonia synthesis. In addition, the effect of H^- ion concentration on the catalytic activity was investigated.

2. Experimental

LaH_3, one of the precursors of lanthanum oxyhydride, was synthesized by hydrogenation of La metal at room temperature for more than 2 hours. The obtained LaH_3 was mixed with the desired amount of La_2O_3, which had been previously dried at 1200°C for 2 hours, and then the mixture was heated under hydrogen at 800°C for 20 hours, resulting in the formation of lanthanum oxyhydrides ($La_4H_xO_{(12-x)/2}$). Ru-loading was conducted by chemical vapor deposition of $Ru_3(CO)_{12}$ on each lanthanum oxyhydride. The amount of ruthenium was fixed at 2 wt% or 5 wt%. XRD, TEM, XPS, H_2-TPD and N_2 adsorption-desorption were used to characterize the catalysts.

Ammonia synthesis reactions were conducted in a fixed bed flow system with an ultrapure mixture of N_2/H_2 = 1/3. The concentration of ammonia in the stream that left the catalyst bed (0.1 g catalyst) was monitored under steady-state conditions of temperature (<260°C), gas flow rate (60 mL min^{-1}) and pressure (0.1 MPa). The produced ammonia was trapped in 5 mM sulfuric acid solution and the amount of NH_4^+ generated in the solution was determined using ion chromatography.

3. Results and discussion

$La_4H_xO_{(12-x)/2}$ with various hydrogen content were prepared by controlling the mixing ratio of LaH_3 and La_2O_3. XRD analysis revealed that $La_4H_xO_{(12-x)/2}$ except for $x = 4$ have tetragonal fluorite-type structure. In addition, the lattice constant of $La_4H_xO_{(12-x)/2}$ decreases with increasing the hydrogen content, indicating that O^{2-} ion sites in the lattice are replaced by H^- ions. Figure 1a shows the ammonia synthesis activities of $Ru/La_4H_xO_{(12-x)/2}$ and reference catalysts at atmospheric pressure. Although the catalytic activity is independent of the hydrogen content in $Ru/La_4H_xO_{(12-x)/2}$, these activities are higher than those of Ru/La_2O_3 and Ru/LaH_3. The maximum ammonia synthesis rate (818 $\mu mol\ g^{-1}\ h^{-1}$) was recorded for $Ru/La_4H_{10}O$. Furthermore, the $Ru/La_4H_{10}O$ exhibits ammonia synthesis activity down to 180°C, which is lower by 80°C than the case of Ru/La_2O_3 (Figure 1b). As a consequence, the apparent activation energy of $Ru/La_4H_{10}O$ for ammonia synthesis is determined to be 64 $kJ\ mol^{-1}$, which is close to those for Ru-loaded electrides and hydride materials (50-60 $kJ\ mol^{-1}$)[1, 4]. TEM measurements indicated that the mean Ru particle size (6.9 nm) of $Ru/La_4H_{10}O$ is almost identical to that of Ru/LaH_3 (6.0 nm) and smaller than that of Ru/La_2O_3 (13.9 nm). Therefore, the high catalytic activity of $Ru/La_4H_{10}O$ is not due to the structural effect of Ru nanoparticles but to the electronic promotion effect of the support material. As we reported previously, the formation of anionic electrons at hydride vacancy sites accounts for the strong electron donation ability that facilitates efficient N_2 cleavage on Ru. It is thus considered that the hydride vacancies are formed at Ru-$La_4H_{10}O$ interface during ammonia synthesis, which imparts high catalytic performance of Ru nanoparticles. In addition, reversible exchange between H^- ions and anionic electrons effectively takes place over $Ru/La_4H_{10}O$ as compared with Ru/LaH_3 because the $La_4H_xO_{(12-x)/2}$ has high hydride ion conductivity. Finally, the stability of the $Ru/La_4H_{10}O$ catalyst was investigated in a continuous flow of the reactant gas for 120 h. The catalytic activity slightly decreased in the initial stage of the reaction, but reached constant value after 50 h (Figure 1c), demonstrating the good stability of the catalyst.

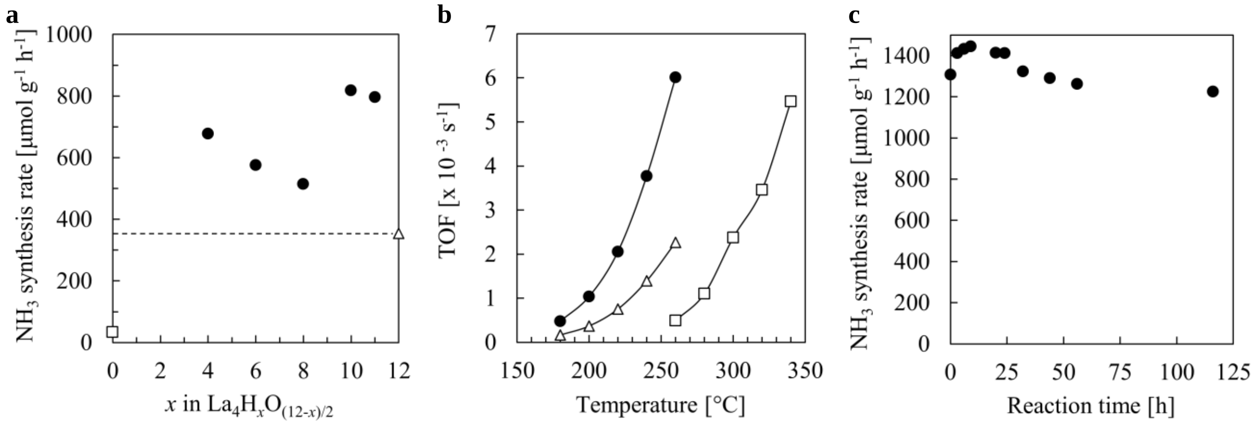

Figure 1. (a) Catalytic activities for ammonia synthesis over 2 wt% $Ru/La_4H_xO_{(12-x)/2}$ (x = 0 (La_2O_3), 4, 6, 8, 10, 11, 12 (LaH_3)) at 0.1 MPa and 260°C. (b) TOFs of ammonia synthesis over 2 wt% $Ru/La_4H_xO_{(12-x)/2}$ (x = 0 (□), 10 (●), 12 (△)) at 0.1 MPa as a function of reaction temperature. (C) Reaction time profile for ammonia synthesis over 5 wt% $Ru/La_4H_{10}O$ at 0.1 MPa and 260°C.

4. Conclusions

Lanthanum oxyhydride ($La_4H_xO_{(12-x)/2}$) was found to be efficient and stable electronic promoter of Ru catalyst for low-temperature ammonia synthesis. The $Ru/La_4H_xO_{(12-x)/2}$ exhibits much higher catalytic activity and lower activation energy than Ru/LaH_3 and Ru/La_2O_3. The present results demonstrate that oxyhydrides with high hydride ion conductivity effectively promote ammonia synthesis reaction over Ru catalyst.

References

1. M. Kitano, Y. Inoue, H. Ishikawa, K. Yamagata, T. Nakao, T. Tada, S. Matsuishi, T. Yokoyama, M. Hara and H. Hosono, Chem. Sci. 7 (2016) 4036.
2. H. Mizoguchi, M. Okunaka, M. Kitano, S. Matsuishi, T. Yokoyama and H. Hosono, Inorg. Chem. 55 (2016) 8833-8838.
3. K. Fukui, S. Iimura, T. Tada, S. Fujitsu, H. Hosono, T. Honda, K. Ikeda and T. Otomo, Annual Meeting of the Ceramic Society of Japan, 2018, 2F04.
4. M. Kitano, Y. Inoue, Y. Yamazaki, F. Hayashi, S. Kanbara, S. Matsuishi, T. Yokoyama, S. Kim, M. Hara and H. Hosono, Nat. Chem. 4 (2012) 934-940.