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Lanthanide Nitrates as Effective Promoters of a Ru/Al_2O_3 Catalyst for Ammonia Synthesis

Shuzo MURATA, Ken-ichi AIKA,* and Takaharu ONISHI
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 227

Nitrates of La, Ce, and Sm were proved to be better promoters than $CsNO_3$ for an ammonia synthesis Ru/Al_2O_3 catalyst. A small amount of lanthanide nitrate (M/Ru = 1) was as effective as a large amount of $CsNO_3$ (Cs/Ru = 10) for 2wt% Ru/Al_2O_3 prepared from $Ru_3(CO)_{12}$.

Ruthenium is known to be quite sensitive to a support and a promoter when it is used for ammonia synthesis.[1,2] Roughly speaking, the effectiveness of promoter is inversely related with the electronegativity of "compound" (Cs < K < Na < CsOH < KOH < NaOH).[1 — 3] In this sense, none of La_2O_3, Ce_2O_3, and Sm_2O_3 has been expected to be an effective promoter. Here, such a lanthanide was also found to be a quite effective promoter on a Ru/Al_2O_3 catalyst.

γ-Al_2O_3 (Catal. Soc. Jap., JRC-ALO-4; 180 m^2g^{-1}) which was baked at 773 K was impregnated with $Ru_3(CO)_{12}$ (Aldrich) in tetrahydrofurane. After evaporated and dried, a sample was heated in vacuo to remove CO at 623 K for 2 h. The sample corresponding to one gram of 2 wt% Ru/Al_2O_3 was transferred to aqueous solution of a lanthanide nitrate. The dried sample was treated with H_2 at 623 K for 4 h. A rate of ammonia synthesis was measured using a flow system with a flow rate of 60 ml min^{-1}($N_2 + 3H_2$). H_2 chemisorption (273 K) and XPS spectra (ESCA-750) were also measured.

Rates of ammonia synthesis at 588 K over 2 wt% Ru/Al_2O_3 catalysts with various promoter nitrates are shown as a function of promoter(M)/Ru mole ratio in Fig. 1. The activity increased gradually with an addition of Cs^+ up to Cs/Ru = 10. On the other hand, a small amount of La^{3+}, Ce^{3+}, and Sm^{3+} increased the activity. They are most effective with 1 to 3 mole ratio of M/Ru. The catalyst with even 1 mole ratio of M/Ru is as active as that with 10 mole ratio of Cs/Ru. $CsNO_3$ has been discussed to be decomposed to Cs_2O and/or CsOH by the presence of Ru.[2] It is suggested that the lanthanide nitrates are also decomposed to the oxides over Ru

surface and migrate to the support Al_2O_3, while some of them may stay on the Ru surface or the Ru-support boundary. XPS spectra of the used catalysts disclosed that the $3d_{5/2}$ binding energies of the lanthanides were identical to those of the reference lanthanide oxides (3+). An activity of 2 wt% Ru-Sm^{3+}/Al_2O_3 (Sm/Ru = 3) was constant for 100 h at 603 K.

H_2 adsorption was measured for various Ru/Al_2O_3 catalysts and compared with the promoter content. The value H(a)/Ru is drastically decreased from 0.59 to 0.57 and 0.18 when Sm/Ru ratio is increased from 0 to 3.0 and 10.0. On the other hand, the values are 0.59, 0.59, and 0.45 when Cs/Ru ratios are 0, 3.0, and 10.1. This means that the hindrance of Ru surface by Sm^{3+} is more serious than that by Cs^+. It is suggested that Cs_2O and/or CsOH which is produced through a hydrogenolysis of $CsNO_3$ at the Ru surface moves easily to the Al_2O_3 surface and the Cs_2O and/or CsOH reacts with acidic centers on the Al_2O_3 surface. Thus, the Cs^+ ions stay less on the Ru surface. However, lanthanides are not movable and stay much on the Ru surface or the Ru-support boundary. Melting points of La_2O_3 (2588 K), Ce_2O_3 (1965 K), and Sm_2O_3 (2573 ± 50 K) are higher than that of CsOH (545 K), which could be another reason.

The earlier studies concluded that an electron donation to Ru surface from a support or a promoter was generally most important for an activation of N_2 over Ru surface. Since a lanthanide oxide is not a stronger base than an alkali metal oxide, the effectiveness of a lanthanide oxide as a promoter has not been expected. We need further studies to clarify the state of lanthanide promoters during the reaction.

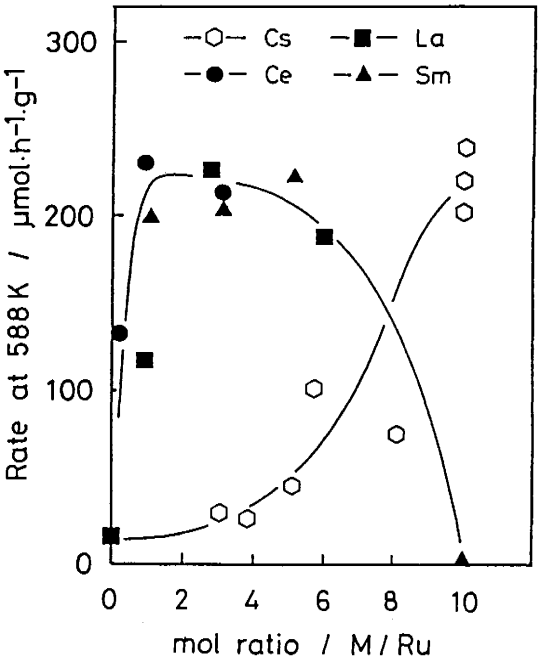

Fig. 1. Rates of ammonia synthesis at 588 K over a promoted 2 wt% Ru/Al_2O_3 catalyst as a function of promoter(M)/Ru mole ratio.

References

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