Ruthenium Catalyst Supported on CeO_2 for Ammonia Synthesis

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Lanthanide oxides (Sm_2O_3, La_2O_3, especially CeO_2) were more effective for ammonia synthesis when used as the support of ruthenium catalysts rather than when used as the dopant. The activity of Ru/lanthana was superior to other metal oxide-supported ones such as Ru/MgO. The activity, Ru dispersion, BET surface area, and the amount of hydrogen consumption of Ru/CeO_2 were influenced remarkably by hydrogen treatment, suggesting the SMSI phenomena. Partially reduced CeO_2 donates electrons to Ru atoms, forming the active sites.

Ruthenium is known to be active for dissociation of dinitrogen. Basic support and promoter are desirable because of inducing electron-donating effect. Strong basic material such as alkali metal compounds, certainly, increase the activity of ammonia synthesis under atmospheric pressure remarkably, however, they are not so effective under high pressure because of a strong adsorption of hydrogen, which covers active site for nitrogen activation. Recently, lanthanide oxides were found to weaken the hydrogen inhibition when used as a "promoter" of Ru catalyst.[1,2] To clarify the effect of lanthanide oxides, we tried to use these oxides as "supports" free from any promoter.

Lanthanide oxides were prepared by the precipitation method from each nitrate. Deposited hydrates were filtered and then calcined in air at 873 K (1023 K in the case of Sm) for 4 h. These oxides were impregnated with $Ru_3(CO)_{12}$ (Tanaka Noble Metals Co.) in tetrahydrofuran. After evaporation and drying, a sample was heated in vacuo to remove CO at 773 K for 2 h and treated with $N_2 + 3H_2$ for 4 h at a given temperature before ammonia synthesis in a flow system. MgO was also prepared by the similar method as a reference metal oxide. 3% Ru/MgO was impregnated with $Ce(NO_3)_3$, dried and treated with H_2 at 623 K for 4 h giving 3% Ru-Ce_2O_3/MgO. The rate of ammonia synthesis was measured using the flow system with a flow rate of 60 ml min^{-1} ($N_2 + 3H_2$).

After evacuation treatment as stated above, the catalyst sample for the characterization was treated with pure hydrogen at a given temperature for 4 h with a liquid nitrogen trap in a closed circulation system. The extent of oxide reduction was determined by the hydrogen pressure decrease in a closed system. Nitrogen and hydrogen gas adsorption were also measured at 77 and 298 K in a closed circulation system, respectively.

Rates of ammonia synthesis on lanthanide oxide-supported Ru catalysts are shown as a function of hydrogen reduction temperature in Figure 1. The activity of each catalyst, especially Ru/lanthanide, was increased with the increase of the reduction temperature. The activity of 1% Ru/CeO_2 was increased from 355 to 700 µmol h^{-1} g-cat^{-1} with an increase of reduction temperature from 623 to 773 K. This reduction

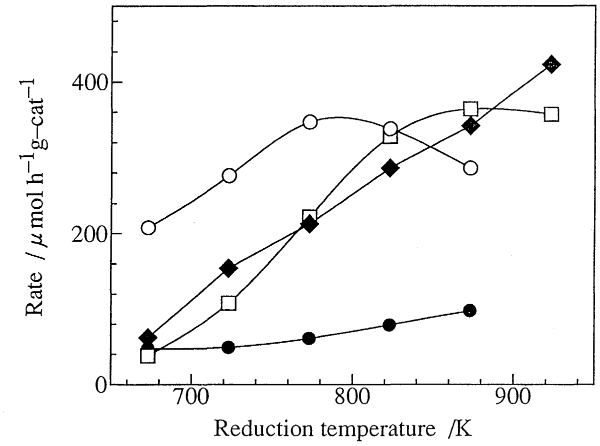

Figure 1. Ammonia synthesis rates at 588 K on supported Ru catalysts as a function of H_2 reduction temperature.
1 wt%Ru/MgO(●), 1 wt%Ru/CeO_2(○), 0.5 wt%Ru/La_2O_3(□), 0.4 wt%Ru/Sm_2O_3(◆).

Table 1. Characterization of Ru catalysts reduced at different temperatures

Support (M)	MgO		CeO_2			Sm_2O_3	
Ru wt%	1.0		1.0			0.4	
Reduction temperature (K)	673	873	673	773	873	673	873
H_2 consumption during (µmol H_2 g-cat^{-1})	-	-	223	640	1087	183	410
reduction (% reduction of oxide)	-	-	1.9	5.5	9.4	0.9	2.1
BET S.A. (m^{2}g^{-1})	93	90	54	43	38	29	24
Dispersion H(a)/Ru at 273 K	0.42	0.48	0.82	0.56	0.35	0.58	0.70
Activity at 588 K (µmol NH_3 h^{-1}g-cat^{-1})	47	98	208	350	286	62	342
TOF (NH_3 / s / H(a)) x 10^4 at 588 K	2.1	3.8	14	36	47	15	73

temperature dependency is similar to the result of hydrogenation of carbon dioxide.[3] The activities at 588 K of 3% Ru/MgO and 3% Ru-Ce_2O_3/MgO (Ce/Ru=1) were 218 and 424 μmol h^{-1} g-cat^{-1}, respectively. In the latter catalyst Ce_2O_3 was used as a promoter, the content of which was changed. The ratio Ce/Ru of 1 mol/1 mol gave the maximum activity. Moreover, the reduction temperature dependency with the maximum on the range of 623 to 673 K was obtained, and this dependency was similar to Ru-Cs^+/MgO or Ru-Sm_2O_3/Al_2O_3.[4] The comparison of three catalysts, Ru/CeO_2, Ru/MgO, and Ru-Ce_2O_3/MgO, shows that CeO_2 is much more effective when used as a "support" than as a "promoter". Incidentally, La_2O_3 and Sm_2O_3 as promoter on Ru/MgO had less effect compared with Ce_2O_3.

Ru/La_2O_3 and Ru/Sm_2O_3 catalysts were more active in spite of the low Ru-loading (0.4-0.5%). However, these catalysts were deactivated rapidly as is shown in Figure 2. On the other hand, Ru/CeO_2 was stable beyond 22 h. It should be noted that the activity is not deactivated in "ammonia synthesis," while hydrogenation on metal/CeO_2 is reported to be deactivated for a short time. Even Ru/La_2O_3 and Ru/Sm_2O_3 can restore the activity when treated with hydrogen at high temperature such as 923 K as shown in Figure 2.

Changes of catalysts during hydrogen treatment were studied and are shown in Table 1. In the case of CeO_2, Ru dispersion and BET surface area were decreased, whereas hydrogen consumption was increased with an increase of reduction temperature. As for Sm_2O_3, similar dependence was observed, however, the extent was smaller than for CeO_2. Ru/MgO was not changed.

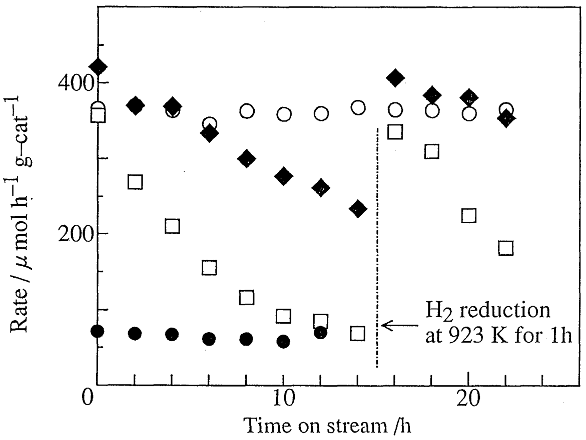

Figure 2. Time course of ammonia synthesis rate at 588 K on Ru catalysts which have been reduced at 923 K except for 1 wt%Ru/MgO (●,reduced at 773 K and measured at 603 K), 1 wt%Ru/CeO_2(○), 0.5 wt%Ru/La_2O_3(□), 0.4 wt%Ru/Sm_2O_3(◆).

The amount of hydrogen consumption (1087 μmol H_2 g-cat^{-1}) for Ru/CeO_2 at 873 K corresponds to 9.4% reduction of the oxide (Table 1). It is thought that reduced CeO_2 can donate electrons to Ru through the oxygen anion owing to the tendency to return to the stable high oxidation state.

Ce_2O_3 "promoter" might induce the similar electron donating effect to Ru on MgO (and Al_2O_3), however, the effect was not remarkable. What is the difference between Ce_2O_3 as a dopant promoter and that as a part of the support? Probably Ce^{3+} state formed around Ru particle in the CeO_2 support might have different structure (SMSI state). Partially reduced ceria is considered to create the active site of Ru atom for N_2 activation. SMSI phenomena have been pointed out to relate with the activity directly by several reports.[5-7]

MgO were not so influenced much by the hydrogen treatment compared with lanthanide oxides. Ru/Sm_2O_3 did not consume much hydrogen, but, the amount 410 μmol g-cat^{-1} is even greater than the total Ru atom number (40 μmol g-cat^{-1}). The activity is increased drastically, too.

We found that lanthanide oxides which were treated with H_2 at 773 to 873 K in the presence of Ru were the most effective support of promoter-free-ruthenium-catalysts for ammonia synthesis. Especially Ru/CeO_2 system is a stable catalyst. Promotion of catalysis is considered to be caused by the increase of electron donating effect, thus the morphologic change of lanthana around Ru particle should be studied further.

References and Notes

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