Catalysis on Ruthenium Clusters Supported on CeO$_2$ or Ni-Doped CeO$_2$: Adsorption Behavior of H$_2$ and Ammonia Synthesis

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Catalysis on Ru clusters supported on CeO$_2$ or Ni-doped CeO$_2$ was investigated. Ru$_3$(CO)$_{12}$ was reacted with CeO$_2$, followed by heating in vacuum at 673 (i) or 813 K (ii) and then in H$_2$ at 588–1073 K ($T_{\text{Hi}}$). Activities of both catalysts had the $T_{\text{Hi}}$ dependence, which has a maximum at $T_{\text{Hi}} = 873$ K for ammonia synthesis. The rates on i were faster than those on ii by a factor of 2.0–1.1 in the range of $T_{\text{Hi}} = 588–973$ K. On a sample in which Ru$_3$(CO)$_{12}$ was supported on previously reduced Ni/CeO$_2$ (in H$_2$ at 773 K) iii, the highest synthesis rate was 1.5 × 10$^{-3}$ mol h$^{-1}$ g$_{\text{cat}}^{-1}$ at $T_{\text{Hi}} = 588$ K on iii. The activity order iii > i > ii can be understood in terms of two factors: (A) reduction extent of support and (B) number of active Ru sites. The two factors conflicted with each other when the treatment temperature in H$_2$ increased. By heating the samples in H$_2$ up to 873 K to satisfy factor A, the aggregation of Ru clusters for i or physical blocking of surface Ru sites by CeO$_{2-x}$ for ii occurred: factor B was not satisfied. The two factors should be optimized in catalyst iii, where the support cerium oxide was thoroughly reduced through the doped Ni. On reduced Ni/CeO$_2$, the Ru cluster implantation can be done at low temperature (588 K). Obtained values of $r_{\text{Ru-Ru}}$ at 2.62 Å ($N = 7.1$) and $r_{\text{Ru-O(s)}}$ (O(s) is the oxygen atom at surface) at 2.12 Å ($N = 1.2$) by EXAFS for Ru$_3$–Ni/CeO$_2$ suggested a flat Ru cluster model comprised of several Ru atoms on reduced Ni/CeO$_{2-x}$ surface. The H/(a)/Ru$_{\text{total}}$ ratio exceeded unity for catalysts i and iii, suggesting new H adsorption sites. The temperature-programmed desorption for hydrogen (simultaneous desorption of HD and D$_2$ for iii at 330–430 K suggested that the H at the new site and H on Ru surface were exchangeable above 330 K. The “reservoir” effect of the new site for H on catalysts is discussed in relation to new kinetic design of hydrogenation catalyst.

Introduction

Recently, we studied hydrogen adsorption and ammonia synthesis on Ru cluster catalysts by means of EXAFS (extended X-ray absorption fine structure) and FTIR (Fourier transform infrared spectroscopy). Several adsorption sites of H were detected by FTIR. The in situ structure change of Ru clusters was observed by the interaction with H$_2$ by EXAFS. The promotion of ammonia synthesis was suggested by elongating the Ru–Ru bonding distance to facilitate the dissociative adsorption of N$_2$. The H adsorption was examined for Rh/TiO$_2$ and Ru/SiO$_2$ by solid-state $^{1}$H-NMR. Two peaks were observed for Rh/TiO$_2$ when heated in H$_2$ above 573 K. The α peak around δ = −130 ppm was assigned as H atom on Rh particles on the basis of $P_{\text{Hi}}$, spin–lattice relaxation time $T_1$, and peak intensity decreased when the sample was heated in H$_2$ above 723 K in relation to the SMSI (strong metal–support interaction) effect. A part of β peak around 0 ppm was implied as “weakly bound H” on Rh particles present at relatively higher $P_{\text{Hi}}$ (≥2 kPa) compared to α peak H. Two peaks were observed for Ru/SiO$_2$ around −60 (α) and −30 ppm (β) in H$_2$. The α and β peaks were assigned as H on Ru particles and “weakly bound H” on Ru particles, respectively, on the basis of heat of adsorption, $T_1$, and H/Ru(s) ratio. The β peak was only observed at $P_{\text{Hi}} > 13$ kPa. The weakly bound H was implied to have an interaction with lower coordination Ru sites because the β peak population increased as the Ru particle size decreased.

CeO$_2$ is an effective promoter or support of Ru catalysts, and the importance of metal–support interaction is often implied when reduced at high temperatures. In this paper, we report promoted catalysis over Ru clusters supported on CeO$_2$ or on Ni-doped CeO$_2$ as a first objective. The support was reduced at high temperatures (~873 K) in H$_2$ (CeO$_2$) or at moderate temperatures (623–773 K) by spillover H atoms from doped Ni (Ni/CeO$_2$). The major control factors of ammonia synthesis should be the number of active sites, the nature of the Ru/support interface, and the electronic effect of support. The catalyst preparation procedure, reacting the Ru$_3$(CO)$_{12}$ with previously reduced Ni-doped CeO$_2$, optimized these control factors.

The second objective is the clarification of the promoted reaction mechanism. The hydrogen uptake exceeded unity for Ru clusters on CeO$_2$ or Ni-doped CeO$_2$. We propose the condensation of H atoms at the interface between Ru clusters and the reduced CeO$_{2-x}$ surface. The “reservoir” effect of the interface site on catalysis is discussed.

Experimental Section

Cerium oxide was prepared from a 0.2 mol L$^{-1}$ Ce(NO$_3$)$_3$·6H$_2$O (Wako, 99.9%) solution. The 5% ammonia was added until the pH of solution was 10. The obtained Ce(OH)$_4$ was filtered and repeatedly washed. Yellow powder of CeO$_2$ (BET surface area 57 m$^2$ g$^{-1}$) was obtained by heating Ce(OH)$_4$ in air (4 h), evacuating (1 h) at 773 K, and then treating in O$_2$ at 290 K. Ru$_3$(CO)$_{12}$ (I) was interacted with CeO$_2$ in distilled THF (tetrahydrofuran) (Wako, Special Grade) at 290 K for 2 h, with the subsequent removal of THF in vacuum (Ru$_3$/CeO$_2$). The obtained CeO$_2$ was impregnated with Ni(NO$_3$)$_2$·6H$_2$O (Wako, 99.9%) to give 0.25 wt% Ni and treated in H$_2$ (12 h) at 773 K, followed by a procedure similar to the case of Ru$_3$/CeO$_2$ (Ru$_3$–Ni/CeO$_2$). The loading of Ru was 1.7 wt%. All procedures of sample preparation and transfer were performed...
in argon (99.99%) or in vacuum. Incipient supported clusters were heated (elevating rate of temperature 4 K min\(^{-1}\)) in vacuum up to 673 or 813 K, followed by the treatment in \(\text{H}_2\) for 1 h (588–1073 K). The catalysts were denoted as \(\text{Ru}_x\text{-Ni}/\text{CeO}_2\)-673ev, for example, where the evacuation temperature was noted. Subsequent treatment temperature in \(\text{H}_2\) (\(T_{\text{H}_2}\)) is noted in each description.

The conventional Ru/\text{CeO}_2 catalyst was prepared from \(1\text{ in air}\). \(1\) was interacted with \text{CeO}_2 and decomposed (the color of the solution turned from orange to dark yellow) in THF for 12 h (1.0 wt % Ru). After evaporation of the THF, the powder was heated in \(\text{O}_2\) (1 h) and then in \(\text{H}_2\) (1 h) at 773 K before being used as catalyst. The weight of the catalyst was 0.015–0.030 g for \(\text{Ru}_x\text{-Ni}/\text{CeO}_2\), \(\text{Ru}_x\text{-Ni}/\text{CeO}_2\), and conventional Ru/\text{CeO}_2.

The ammonia synthesis reactions were carried out under 101 kPa of reaction gas (\(P_{\text{H}_2}/P_{\text{N}_2} = 3.0\)) at 588 K in a flow system (flow rate 60 cm\(^3\) min\(^{-1}\)). The produced ammonia was analyzed by the decrease of electron conductivity (1.7–0.8 mS cm\(^{-1}\)) in the \(\text{H}_2\text{SO}_4\) solution (<0.004 N). The linearity of the correlation between the produced amount of \(\text{NH}_3\) and the decrease of electron conductivity was checked. The chosen reaction temperature was relatively low (588 K) to realize differential working conditions. The catalytic rates were stable in 36 h, and the rates at 2 h were listed for all the catalysts in this paper. The rates on \(\text{Ru}_y\text{CeO}_2\)-673ev and \(\text{Ru}_x\text{-Ni}/\text{CeO}_2\)-673ev catalysts were relatively unstable only when treated in \(\text{H}_2\) at lower temperatures (588–673 K) before catalysis. They increased in 2 h (within 30%), and a smaller increase was observed during 2–10 h (within 10%).

Hydrogen uptake (\(v\)) measurements were carried out in a closed circulating system connected to the manometer. The equilibrium gas pressure (\(P\)) was varied in the range 1.3–20 kPa, and the \(b\) of adsorption isotherm

\[
v^{-1} = (ab)^{-1}P^{-1/2} + b^{-1}
\]

was obtained by the extrapolation of obtained data (five to seven points; \(a\) is a constant). The samples were kept in ice (273 K) during measurements. As fast uptake (adsorption on Ru + hydrogen spillover from Ru to support surface) terminated in 1 h followed by linear increase of uptake during 1–10 h (hydrogen spillover), uptake on \(v\) was estimated by subtracting the H spillover amount during initial 1 h from total (observed) uptake amount at 1 h. The temperature-programmed desorption (TPD) was monitored in the closed circulating system connected to the mass. The samples were treated (i) in 76 kPa of \(\text{H}_2\) (1 h) at 293 K, evacuated (0.5 h) at 293 K, and then treated in 76 kPa of \(\text{D}_2\) (1 h) at 293 K (adsorption A), or (ii) treated in \(\text{D}_2\) at 293 K (1 h) (adsorption B). The elevation rate of temperature was 4 K min\(^{-1}\).

The EXAFS spectra of Ru K edge were measured at the beamline 10B and 6B (2.5 GeV, current 360–260 mA) of the Photon Factory in the National Laboratory for High Energy Physics (Proposal No. 93G150). The X-ray radiation was monochromized through double crystals of Si(311), and the spectra were obtained in transmission mode with ionization chambers at 100–293 K. The sample was transferred to an EXAFS Pyrex cell (0.073 < \(\Delta\mu\) < 0.25) with Kapton films. The analysis was performed by the program EXAFASH written by Yokoyama, Hamamatsu, and Ohta (the University of Tokyo, 1994).\(^2\) The background subtraction was performed by calculating the cubic spline with three blocks, and the obtained function \(\mu(k) = \mu_{\text{bg}}(k)\) was normalized by using Victoreen parameter \(\mu_{\text{bg}}(\lambda) = C\lambda^3 - D\lambda^4\). The Fourier transform (FT) of the \(k^3\)-weighted EXAFS oscillation was carried out over the range of

\[
\int \left( k^3 \chi_{\text{obs}}(k) - k^3 \chi_{\text{calc}}(k) \right)^2 dk / \int \left( k^3 \chi_{\text{obs}}(k) \right)^2 dk
\]

The impurities (as molecular content) for the \(\text{H}_2\) (99.999%, Toyo Sanso Co., Ltd.) and \(\text{D}_2\) (99.99%, Syoko Co., Ltd.) gas were \(\text{H}_2\text{O} < 10\), \(\text{N}_2 < 50\), \(\text{O}_2 < 10\), \(\text{CO} < 10\), \(\text{CO}_2 < 10\) ppm, and total hydrocarbons < 10 ppm (as carbon content). The deuterium content in total hydrogen was >99.8% for the \(\text{D}_2\) gas. The gas was introduced to the EXAFS or IR cell after purification by passage through a liquid nitrogen trap.

The supported Ru clusters were suspended in ethanol (exposed in air during few minutes), and mounted on a TEM (transmission electron microscope) apparatus (JSM-T220, JEOL). The dispersion (\(D\)) of a Ru particle was estimated from the average diameter of Ru particles (2\(d\)) by TEM by using the following equation assuming the closest packed structure of Ru surface (Avogadro number \(N_A\), molecular weight MW, interatomic distance \(r_{\text{Ru-Ru}}\), and the density \(\rho\) of Ru).

\[
D = \frac{4\pi d^2/3}{(4/3)\pi d^2 /N_A /MW} = \frac{4\pi d^2}{(4/3)\pi d^2 /N_A /MW} = \frac{4\pi d^2}{(4/3)\pi d^2 /N_A /MW} = \frac{4\pi d^2}{(4/3)\pi d^2 /N_A /MW} = \frac{4\pi d^2}{(4/3)\pi d^2 /N_A /MW} \approx 6.7
\]

\(d\) is the average diameter of Ru particles (2\(d\)) by TEM by using the following equation assuming the closest packed structure of Ru surface (Avogadro number \(N_A\), molecular weight MW, interatomic distance \(r_{\text{Ru-Ru}}\), and the density \(\rho\) of Ru).

**Results**

**Catalysis.** When incipient Ru/\text{CeO}_2 cluster was heated in vacuum, the carbonyl ligands were totally desorbed as CO (and a few \(\text{CO}_2\)) until 673 K. Figure 1 shows ammonia synthesis rates at 588 K on Ru/\text{CeO}_2 heated in vacuum at 673 or 813 K. At \(T_{\text{H}_2} = 588\) K, the rate for Ru/\text{CeO}_2-673ev was faster by 1.2 times than that for Ru/\text{CeO}_2-813ev (Table 1a,c).

The two cluster catalysts were treated in hydrogen (76 kPa) between 673 and 1073 K (Figure 1 and Table 1). The rates on Ru/\text{CeO}_2-673ev had a maximum at \(T_{\text{H}_2} = 873\) K. Similarly, the rate over Ru/\text{CeO}_2-813ev reached a maximum at \(T_{\text{H}_2} = 873\) K. The maximum synthesis rate for Ru/\text{CeO}_2-813ev was 63% of the maximum for Ru/\text{CeO}_2-673ev (Figure 1), suggest-
TABLE 1: Rates of Ammonia Synthesis on Ru Catalysts Supported on CeO$_2$

<table>
<thead>
<tr>
<th>entry</th>
<th>catalysts</th>
<th>$T_H$/K</th>
<th>rate/10$^{-3}$ mol h$^{-1}$ g$_{Ru}$-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>Ru/CeO$_2$-673ev</td>
<td>588</td>
<td>0.24</td>
</tr>
<tr>
<td>b</td>
<td></td>
<td>873</td>
<td>1.2</td>
</tr>
<tr>
<td>c</td>
<td>Ru/CeO$_2$-813ev</td>
<td>588</td>
<td>0.20</td>
</tr>
<tr>
<td>d</td>
<td></td>
<td>873</td>
<td>0.75</td>
</tr>
<tr>
<td>e</td>
<td>Ru$_3$-Ni/CeO$_2$-673ev</td>
<td>588</td>
<td>1.5</td>
</tr>
<tr>
<td>f</td>
<td>conventional Ru/CeO$_2$</td>
<td>773</td>
<td>0.69</td>
</tr>
</tbody>
</table>

* Temperature = 588 K. Total pressure = 101 kPa, $P_{H_2}/P_{H_2}$ = 1/3.

TABLE 2: Amounts of Hydrogen Uptake for Ru Catalysts Supported on CeO$_2$

<table>
<thead>
<tr>
<th>catalysts</th>
<th>$T_H$/K</th>
<th>H/Ru$_{total}^a$ (molar ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru/CeO$_2$-673ev</td>
<td>588</td>
<td>1.5</td>
</tr>
<tr>
<td>Ru$_3$-Ni/CeO$_2$-673ev</td>
<td>588</td>
<td>4.3</td>
</tr>
<tr>
<td>conventional Ru/CeO$_2$</td>
<td>773</td>
<td>0.5</td>
</tr>
</tbody>
</table>

* By manometer, at 1 h in H$_2$ (1.3–20 kPa) at 273 K. The amount of H spillover for 1 h was subtracted from the observed total uptake at 1 h.

Ammonia Synthesis on Ru$_3$–Ni/CeO$_2$

The isotope effects of hydrogen were examined for ammonia synthesis in N$_2$ at 588 K, respectively. This difference implied that the adsorption of H on Ru was weak for Ru/CeO$_2$-673ev because adsorbed H in the first adsorption step in H$_2$ should be easily replaced by D in the second adsorption step in D$_2$. The origin of H atoms of desorbed HD and lesser amounts of H$_2$ can be ascribed to inversely spillover H from cerium oxide surface to Ru clusters because the H(a) on cerium oxide (as hydroxyl, etc.) was desorbed only as H$_2$O in the absence of Ru clusters.

The order of beginning temperature of desorption (D$_2$ < HD < H$_2$) was the same for conventional Ru/CeO$_2$ (Figure 2b) after adsorption A. Compared to Figure 2a, the adsorption of D should be weaker on Ru particles of conventional Ru/CeO$_2$ to make the first maximum of D$_2$ desorption as low as around 390 K. The higher temperature peak of D$_2$ (around 690 K) may originate from inversely spillover D by the recombination on Ru. After adsorption A, TPD was measured for Ru$_3$-Ni/CeO$_2$-673ev. D$_2$ and HD began to be desorbed at the same temperature (around 330 K) (Figure 2c). The temperature where H$_2$ began to be desorbed (around 430 K) was similar to those for HD in Figure 2a,b (around 450 K).

TPD was observed also for Ru$_3$-Ni/CeO$_2$-673ev after adsorption B. Around 310–450 K, only D$_2$ was desorbed (Figure 2d). HD and H$_2$ began to be desorbed around 450 K similar to HD in Figure 2a,b or H$_2$ in Figure 2c. The inverse hydrogen spillover (from support to Ru) should occur above 450 K also for Figure 2c,d compared to the HD desorption in Figure 2a,b. The ratio of total desorbed hydrogen amount in Figure 2 (1.2:0.70:4.0:3.8) corresponded to the uptake ratio in Table 2 (Ru$_3$-CeO$_2$-673ev:conventional Ru/CeO$_2$:Ru$_3$-Ni/CeO$_2$-673ev = 1.2:0.5:4.1) except for the relatively higher value for Figure 2b probably because the amount of spillover hydrogen onto support was also included for TPD observation.

**Ru Cluster Structures.**

1. **EXAFS. a. Incipient Cluster.** When I was reacted with CeO$_2$ in THF, the yellow solution turned transparent in 3 min, suggesting fast reaction between I and CeO$_2$. In fact, the EXAFS drastically changed on supporting on CeO$_2$ from EXAFS for I. The data for incipient Ru/CeO$_2$ were well fitted with three waves (Ru–C, Ru(=C–)O, Ru–O) with $R_f = 1.2\%$ (Table 3a). Alternative fitting with four waves (three waves and Ru–Ru) did not improve the fitting ($R_f = 2.0\%$), indicating the cleavage of Ru–Ru bonds of I upon the reaction with CeO$_2$.

2. **Ru$_3$/CeO$_2$.** Incipient Ru$_3$/CeO$_2$ was heated at 673 or 813 K in vacuum. The FT of the Ru K-edge EXAFS is shown in
Figure 3c for the sample heated at 673 K. The main peak around 2.4 Å (phase shift uncorrected) can be ascribed to Ru–Ru bonding. The shoulder on the lower-distance side in Figure 3c can be Ru–O(s) bonding. In fact, the EXAFS was well fitted with two waves Ru–Ru and Ru–O(s) (Figure 3d). The obtained $r_{\text{Ru–Ru}}$ ($2.62$ Å in Table 3b) meant the metallic bonding compared to clusterlike distance $2.85$ Å (average) for $1.9$. The $N_{\text{Ru–Ru}}$ ($4.4$ in Table 3b) suggested the Ru cluster size of less than 10 Å.

The $k^3$ oscillation in the EXAFS for Ru$_3$/CeO$_2$-813ev was slower than that in Figure 3b. The peak around 1.6 Å (phase shift uncorrected) was strongest in its FT. The curve-fitting analysis was performed with two waves Ru–O and Ru–Ru (second coordination in RuO$_2$ bulk). The best fit result was $r_{\text{Ru–O}} = 2.02$ Å ($N = 4.7$) and $r_{\text{Ru–Ru}} = 3.37$ Å ($N = 6.2$) (Table 3d) ($r_{\text{Ru–O}} = 1.98$ Å ($N = 6$) and $r_{\text{Ru–Ru}} = 3.55$ Å ($N = 8$) for bulk RuO$_2$). The smaller value for $r_{\text{Ru–Ru}}$ may be because the formed [RuO$_x$] particles on cerium oxide were too small to constitute regular crystals. Alternative fitting with two waves Ru–O and Ru–Ru (Ru metal) did not fit in the entire wavenumber region, excluding the possibility that the second shell around 2.5 Å was Ru–Ru bonding.

The Ru$_3$/CeO$_2$-673ev was put in H$_2$ at 588 K. The Ru K-edge EXAFS was fitted with Ru–Ru ($r = 2.62$ Å) and Ru–O(s) ($r = 2.14$ Å) (Table 3c). The value of $N_{\text{Ru–Ru}}$ increased by 0.6 and $r_{\text{Ru–O(s)}}$ decreased by 0.9 by heating in H$_2$ at 588 K.

Similarly, the EXAFS was observed for Ru$_3$/CeO$_2$-813ev heated in H$_2$ at 588–773 K (Table 3e). These data were well fitted with two waves Ru–Ru and Ru–O(s), demonstrating the transformation of [RuO$_x$] into Ru metal clusters at lower than 588 K in H$_2$. With the increase of $T_{\text{H}_2}$ from 588 to 773 K, the structural data did not change very much ($r_{\text{Ru–Ru}} = 2.62 \pm 0.01$ Å, $N_{\text{Ru–Ru}} = 7.0 \pm 0.6$, $r_{\text{Ru–O(s)}} = 2.08 \pm 0.01$ Å) except for the gradual increase of $N_{\text{Ru–O(s)}}$ (1.1 – 2.1).

### Table 3: Results of Curve-Fitting Analysis of Ru K-Edge EXAFS Spectra for Ru$_3$/CeO$_2$-673ev, Ru$_3$/CeO$_2$-813ev, and Ru$_3$–Ni/CeO$_2$-673ev before/after Hydrogen Treatment at 588 K

<table>
<thead>
<tr>
<th>Entry</th>
<th>Sample</th>
<th>Hydrogen Treatment at 588 K</th>
<th>Ru–C</th>
<th>Ru–Ru</th>
<th>Ru(–C)–O</th>
<th>Ru–O</th>
<th>Ru––Ru</th>
<th>$R_f$/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>incip Ru$_3$/CeO$_2$</td>
<td>before</td>
<td>3.1</td>
<td>1.95</td>
<td>3.0</td>
<td>3.0</td>
<td>2.10</td>
<td>1.2</td>
</tr>
<tr>
<td>b</td>
<td>Ru$_3$/CeO$_2$-673ev</td>
<td>before</td>
<td>4.4</td>
<td>2.62</td>
<td>1.5</td>
<td>2.04</td>
<td>4.7</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>Ru$_3$/CeO$_2$-673ev</td>
<td>after</td>
<td>5.4</td>
<td>2.62</td>
<td>0.6</td>
<td>2.14</td>
<td>2.4</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>Ru$_3$/CeO$_2$-813ev</td>
<td>before</td>
<td>7.0</td>
<td>2.61</td>
<td>1.1</td>
<td>2.08</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>Ru$_3$/CeO$_2$-673ev</td>
<td>after</td>
<td>7.1</td>
<td>2.62</td>
<td>1.2</td>
<td>2.12</td>
<td>1.7</td>
<td></td>
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</table>
c. Ru$_3$–Ni/CeO$_2$. For Ru$_3$–Ni/CeO$_2$–673ev heated in H$_2$ at 588 K, the curve-fitting result (Table 3f) was similar to those for Ru$_3$/CeO$_2$–673ev and Ru$_3$/CeO$_2$–813ev heated in H$_2$ at 588 K (Table 3c,e). $N_{Ru-Ru}$ ($=7.1$) was a little larger than those for corresponding samples heated in H$_2$ at 588 K (5.4–7.0).

d. The Interaction of Ru$_3$/CeO$_2$–673ev with H$_2$. In the Ru K-edge EXAFS in H$_2$ (53 kPa), the shoulder of Ru–O(s) bonding became weaker compared to the main peak of Ru–Ru (Figure 4c) than in the case in vacuum (Figure 3c). The curve-fitting result indicated the decrease of $N_{Ru-O(s)}$ from 1.5 to 0.6 by hydrogen adsorption. The distances $r_{Ru-Ru}$ and $r_{Ru-O(s)}$ increased by 0.03–0.09 Å in H$_2$ (Table 4a,b).

2. TEM. No Ru particles were observed for Ru$_3$/CeO$_2$–673ev in H$_2$ at 588 K by TEM. Considering the lower limit of detection (about 12 Å), this does not contradict results with the $N_{Ru-Ru}=5.4$ by EXAFS (Table 3c). By heating the sample in H$_2$ at 773 K, the average Ru particle size was 16 Å. Real average size may be smaller because the smaller ($<\sim$12 Å) particles must not be detected. The $N_{Ru-Ru}$ of 6.9 by EXAFS for the sample ($T_{H_2}=773$ K) corresponds to Ru particle size of ca. 14 Å with the assumption of complete sphere shape.

In the TEM image for Ru$_3$–Ni/CeO$_2$–673ev heated in H$_2$ at 588 K, black particles with an average particle size of 70 Å were observed. The hydrogen uptake measurement for Ni/CeO$_2$ heated in H$_2$ at 773 K resulted in H/Ru$_{total}=0.10$. The $N_{Ru-Ru}$ ($=7.1$, Table 3f) by EXAFS corresponds to particles of 10–15 Å. Hence, it is reasonable to think that the detected particles by TEM consisted of Ni. The dispersion of Ru was calculated to be 0.55 from an average particle size of 24 Å for conventional Ru/CeO$_2$ by TEM (eq 1), consistent with hydrogen uptake data (H/Ru$_{total}=0.50$) in Table 2.

Discussion

In THF at 290 K, cluster I was rapidly reacted with CeO$_2$. The EXAFS analysis ($N_{Ru-C}=3.1$, $N_{Ru-C-x}=3.0$, and $N_{Ru-O}=2.0$ in Table 3a) and the TPD for incipient Ru$_3$/CeO$_2$ (9.3 CO desorbed per 1 Ru$_3$) suggested the formation of monomeric [Ru(CO)$_3$(µ-O(s))$_2$] species (Figure 5a). I should be reacted with Ni/CeO$_2$ similarly. Besides the cleavage of Ru–Ru bonds by the coordination of O(s) to [Ru$_3$] cluster in the case of cerium oxide, the higher oxidation ability of cerium oxide surface was also evidenced as the formation of [RuO$_x$] ($x$ $\sim$ 2) particles (Figure 5d) by heating [Ru(CO)$_3$(µ-O(s))$_2$] on cerium oxide at 813 K in vacuum (Table 3d). By heating at 673 K in vacuum, the incipient [Ru(CO)$_3$(µ-O(s))$_2$] transferred to Ru clusters of less than 10 Å (Figure 5b) on the basis of the $N_{Ru-Ru}$ of 4.4 (Table 3b).

Reduction of Ru/CeO$_2$ and Catalysis. According to the increase of $T_{H_2}$, ammonia synthesis rates increased up to at $T_{H_2}=773–873$ K and decreased at higher $T_{H_2}$ than 873 K on Ru$_3$/CeO$_2$–673ev, Ru$_3$/CeO$_2$–813ev, and conventional Ru/CeO$_2$ (Figure 1). The corresponding curve-fitting results for EXAFS are listed in Table 3. With the increase of $T_{H_2}$ from 588 to 873 K, $N_{Ru-Ru}$ increased from 5.4 (Table 3c) to 9.3 for Ru$_3$/CeO$_2$–673ev, while it remained almost unchanged around 7.0 ± 0.6 for Ru$_3$/CeO$_2$–813ev (Table 3e).
The surface part of CeO$_2$ is reduced to transfer to Ce$_2$O$_3$ by the CeO$_{1.91}$. The stoichiometry CeO$_{1.90}$ was reported by the factor B is the number of surface Ru active sites. The number of Ru(s) decreased by the aggregation of Ru cluster as indicated by the increase of $N_{Ru-Ru}$ according to the increase of $T_{H_2}$ from 588 to 873 K for Ru$_3$/CeO$_2$-673ev (Figure 5b,c). In the case of Ru$_3$/CeO$_2$-673ev, $N_{Ru-O(s)}$ gradually increased from 1.1 to 2.1 at $T_{H_2} = 773$ K, keeping $N_{Ru-Ru}$ almost unchanged (Table 3e). Hence, the number of Ru(s) decreased by the growth of CeO$_{2.4}$ at the interface by the increase of $T_{H_2}$ (Figure 5d-f). The reduction of support was facilitated by the spillover H from Ru clusters, and formed CeO$_{2.4}$ at the interface may further react with interface Ru atoms to physically cover the Ru particle surface (SMS1).

On the basis of the difference of $N_{Ru-O(s)}$ (>2.1 and 0.3, respectively), the extent of Ru site blocking by CeO$_{2.4}$ was the major reason for lower maximum rate for Ru$_3$/CeO$_2$-673ev (Table 1). The optimum $T_{H_2}$ was lower by about 100 K for conventional Ru/CeO$_2$ than the other two. This difference may be because both Ru particle growth and the blocking of Ru site by CeO$_{2.4}$ inhibited catalysis in conventional Ru/CeO$_2$.

Reduction of Ru$_3$-Ni/CeO$_2$ and Catalysis. In the catalyst preparation, the amount of hydrogen consumption was 5.04 × 10$^{-4}$ mol of H$_2$ g$^{-1}$ for Ni/CeO$_2$ in H$_2$ at 773 K for 12 h: 17.4% of incipient CeO$_2$ was converted to CeO$_3$ (CeO$_2$ → CeO$_{1.91}$). The stoichiometry CeO$_{1.90}$ was reported by the thermogravimetry after heating CeO$_2$ powder in H$_2$ at 773 K. The particles around 70 Å were detected by TEM, and H$_2$ uptake measurement (0.10) also supported the data. On the other hand, the Ru cluster size of Ru$_3$-Ni/CeO$_2$-673ev in H$_2$ at 588 K was estimated to be 10–15 Å on the basis of $N_{Ru-Ru} = 7.1$ (Table 3f). As the Ru-O(s) bonds were observed by EXAFS (Table 3f), the Ni and Ru clusters should be attached on the cerium oxide surface separately. Geometrically, it is not likely that the Ru clusters bonded to the larger Ni particles also coordinate to O(s) of cerium oxide with average $N_{Ru-O(s)}$ of 1.2. The EXAFS curve-fitting analysis in Table 3f without Ru-Ni bonds should be valid.

As expected from higher reduction extent of support Ni/CeO$_2$, the ammonia synthesis rates were best on Ru$_3$-Ni/CeO$_2$-673ev (Figure 1). The number of surface Ru sites should have decreased by the growth of Ru particles at higher $T_{H_2}$ (factor B), resulting in the rate decrease, while factor A was kept unchanged because the reduction temperature in catalyst preparation for Ni/CeO$_2$ was higher (=773 K).

Hydrogen Adsorption on Ru$_3$/CeO$_2$ and Ru$_3$-Ni/CeO$_2$. The hydrogen uptake measurements (Table 2) and TPD observations for hydrogen (Figure 2) indicated that the H/Ru$_{total}$ exceeded 1 for Ru$_3$/CeO$_2$-673ev and Ru$_3$-Ni/CeO$_2$-673ev. Excessive amounts of hydrogen adsorption are reported for Ru/SiO$_2$ (H/Ru(s) = 3.3−5.6),$^3$ Rh/Al$_2$O$_3$ (H/Rh(s) = 0.70−1.39),$^{11}$ Rh/CeO$_2$ (H/Rh$_{total}$ = 0.75−3.97),$^{12}$ or Pt/zeolite (H/Ru$_{total}$ = 1.4−1.7).$^{13}$

The TPD were observed for samples after adsorption A (Figure 2a−c) and adsorption B (Figure 2d). In the range of 300−450 K (region I), D$_2$ was exclusively desorbed in Figure 2a,b,d. In these three spectra, the incorporation of H (as HD for Figure 2a,b,d and as H$_2$ for Figure 2d) began at ~450 K, in good coincidence. It should be noted that only Figure 2c had HD desorption in region I and that the total desorption amount (H$_2$ + HD + D$_2$) was larger in Figure 2c,d than in Figure 2a,b by the factor of 3.2−5.7 (the y-axes in Figure 2 are common on the basis of per gram of catalyst). Hence, we believe that the Ru$_3$-Ni/CeO$_2$ had a different kind of adsorption site for H, compared to the Ru$_3$/CeO$_2$ or conventional Ru/CeO$_2$.

The H incorporation in region II (450−750 K) seems due to inverse hydrogen spillover, similar to H spillover initiated at ~413 K on Rh/TiO$_2$.$^2$ The inversely spillover H should have reacted with D on Ru sites to form HD (Figure 2a,b). However, Ru$_3$-Ni/CeO$_2$ had again different desorption character. Namely, a significant amount of H$_2$ was also desorbed in region II of Figure 2c besides HD. The total desorption curve of HD + D$_2$ in Figure 2c was similar to that of D$_2$ in Figure 2d.

Taking these facts into account, we propose an interface adsorption site for H in the case of Ru$_3$-Ni/CeO$_2$. The H on this new site was not replaced by D even in D$_2$ (second adsorption step before TPD for Figure 2c), different from replaceable H on ordinary Ru sites where only D$_2$ was desorbed as in region I of Figure 2a or Figure 2b. This new site for H on Ru$_3$-Ni/CeO$_2$ should be different from ordinary Ru sites (D$_2$ in region I) or cerium oxide surface sites (H as HD or H$_2$ in region II). The H of HD in region I in Figure 2c can be
understood to be derived from this new site, in equilibrium with D(a) on ordinary Ru sites at >~330 K on the basis of the coincidence of the beginning temperatures of HD and D₂ desorption in Figure 2c (~330 K). The reason why H₂ failed to form in region I of Figure 2c besides HD and D₂ is unclear. The very fast recombination of H from the proposed new site with D(a) on Ru sites near the interface may be the reason.

Figures 4 and 5 show the structure change for Ru clusters of Ru₃/CeO₂-673ev by interaction with H₂. The bonding distances r(Ru₂-Ru) (2.62 Å) and r(Ru-Ru₃) (2.04 Å) in vacuum were enlarged by 0.03 and 0.09 Å, respectively, in H₂ (Table 4a,b). The relaxation induced by H adsorption was also observed for Ru₃/CeO₂-673ev heated in H₂ at 588 K. r(Ru-Ru₃) was already enlarged to 2.14 Å by heating in H₂ at 588 K (Table 4c), and it did not show further change by hydrogen adsorption (Table 4d). The r(Ru₂-Ru) changed from 2.62 to 2.65 Å by H adsorption, same as the change by the H adsorption on Ru₃/CeO₂-673ev (Table 4a,b). The relaxation of metal cluster by hydrogen adsorption was reported for supported Ru catalysts (Δ(r(Ru₂-Ru)) = 0.03−0.08 Å and Δ(r(Ru-Ru₃)) = 0.03−0.04 Å)² and supported Pt catalysts (Δ(r(Pt-Pt)) = 0.12−0.19 Å).¹⁴

**Adsorption Sites of Excessive Hydrogen. 1. Weakly Bound Hydrogen.** Weakly bound H was proposed on metal catalysts by using NMR: part of a peak around 0 ppm on Rh/TiO₂ and peak β around −30 ppm on Ru/SiO₂. In comparison between two Ru/SiO₂ samples (Ru₃/SiO₂total = 0.29 and 0.19), “weakly bound H” was implied to have an interaction with lower coordination Ru sites because the β peak population increased as the Ru particle size decreased. The dispersions of Ru in this study were nearly 100% except for conventional Ru/CeO₂. “Weakly bound H” on lower coordination Ru atoms or hydrogen overlayer was possible as a new site for H discussed above because the largest average Ru particles (24 Å by TEM) for conventional Ru/CeO₂ are still smaller than those for Ru/SiO₂ in NMR study.

2. Hydrogen Absorption in Ru. Another possibility is the subsurface hydrogen incorporation. On the basis of the N(Ru₂-Ru) = 4.4 by EXAFS for Ru₃/CeO₂-673ev (Table 3b), a monolayer-like flat Ru cluster (packed cluster of 4 atoms × 4 atoms has an average N(Ru₂-Ru) of 4.3) or octahedral 6-Ru (or a little larger) cluster (N(Ru₂-Ru) of 4) is postulated on supports. In these plausible small clusters, almost no space for hydrogen incorporation remains. The larger N(Ru-Ru₃) (=1.5) for Ru₃/CeO₂-673ev (Table 3b) suggests a flat structure of Ru clusters (Figure 5b) rather than a spherical structure. N(Ru-Ru₃) was 1.2 for Ru₃/Ni/CeO₂-673ev (Table 3f), also suggesting flat Ru morphology. H incorporated in Ru bulk sounds very unlikely as a new site for H.

3. Interface Site for Hydrogen. The H uptake on Ru₃-Ni/CeO₂-673ev was 4.3 H per total Ru atoms (Table 2), and subsequent TPD had concomitant HD and H₂ desorption below 450 K (Figure 2). These facts suggest the new site for H is closely related to the reduction of cerium oxide support. Adsorbed hydrogen was monitored by FTIR; however, we could not discriminate between “weakly bound H” and “interface site H” (see the Appendix).

**Relevance to Catalysis.** The reaction mechanism of ammonia synthesis on Ru catalysts was investigated. No N₂ adsorption was reported on Ru/MgO (183 K) or Ru−Cs⁺/MgO (293 K) in N₂ + H₂. The adsorbed amount of N₂ per Ru(s) decreased drastically when the adsorbed H increased for Ru−Cs⁺/MgO at 293 K. These results demonstrated preferable adsorption of H on surface Ru sites rather than N₂. In fact, P(H₂) pressure dependence of ammonia synthesis rate was ~0.5 to +0.5 for Ru catalysts compared to ~1.5 for Fe catalysts, demonstrating that adsorbed H retarded catalysis by the strong blocking of Ru active sites not to afford enough ensemble sites for N₂ dissociative adsorption for Ru catalysts.

In the TPD for Ru₃−Ni/CeO₂-673ev (Figure 2c), the ratio of HD and D₂ desorption was about 2:1 (D/H ~2) in region I, in fast equilibrium of hydrogen between the “new site” (interface H site or weakly bound H site) and normal Ru surface sites. In region II of Figure 2c, the peak ratio of HD/H₂ was about 1:1. The stronger intensity of H₂ peak than HD peak in Figure 2c compared to in Figure 2a or Figure 2b suggests that the H₂ was not only native to H(a) on cerium oxide but was also native to the new site H. The new site H was still exchangeable with D(a) on the Ru cluster surface in region II. As the ammonia synthesis temperature (588 K) was within region II, about half or an equivalent amount of new site hydrogen may be in equilibrium with hydrogen on surface Ru active sites on the basis of the D/H ratios. The contribution of the new H site can be one important factor for catalysis as a “reservoir” of reactant.

**Conclusions.** The Ru cluster supported on reduced Ni/CeO₂ was a good catalyst for ammonia synthesis. The Ru cluster size was less than 10 Å and within 10−15 Å for Ru₃/CeO₂ and Ru₃−Ni/CeO₂, respectively. The Ru−O(s) bondings were observed at 2.02−2.14 Å for these catalysts. The flat Ru clusters were suggested as active sites. The amounts of hydrogen uptake exceeded unity for Ru₃/CeO₂ and Ru₃−Ni/CeO₂, and H on the new site was proposed in relation to an excess amount of H uptake and subsequent TPD for H(a). The interface between Ru clusters and the reduced CeO₂, surface is one possible new site.

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**Appendix**

**FTIR.** FTIR spectra of Ru₃−Ni/CeO₂ and Ni/CeO₂ were recorded on a FTIR spectrometer (JASCO, Valor III, resolution 1 cm⁻¹). CeO₂ with higher surface area (165 m² g⁻¹, Anan Kasei Co.) was used. Five peaks were observed at 3687m, 2206w, 2087w, 1947vw, and 1895w cm⁻¹ for Ru₃−Ni/CeO₂-673ev in H₂ at 203 K for 30 min (Figure A1 in the supporting information). Compared to the spectrum in H₂ for 5 min, three peaks at 3687, 1947, and 1895 cm⁻¹ grew stronger as the time passed in H₂. Three peaks around 3687, 2206, and 2087 cm⁻¹ were also seen for Ni/CeO₂. Ru₃−Ni/CeO₂-673ev was evacu-

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**TABLE 4: Results of Curve-Fitting Analysis of Ru K-Edge EXAFS Spectra for Ru₃/CeO₂-673ev in Vacuum or in H₂ (53 kPa)**

<table>
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<th>ambient gas</th>
<th>N</th>
<th>r(Å)</th>
<th>Δ(σ²)/10⁻³ Å²</th>
<th>N</th>
<th>r(Å)</th>
<th>Δ(σ²)/10⁻³ Å²</th>
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</tr>
</thead>
<tbody>
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<td>2.62 (±0.02)</td>
<td>2.8</td>
<td>1.5 (±0.4)</td>
<td>2.04 (±0.03)</td>
<td>5.6</td>
<td>4.7 (±2.4)</td>
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</tr>
<tr>
<td>b</td>
<td>H₂</td>
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<td>2.65 (±0.02)</td>
<td>0.45</td>
<td>0.6 (±0.3)</td>
<td>2.13 (±0.02)</td>
<td>−0.6</td>
<td>3.8 (±1.9)</td>
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<tr>
<td>c</td>
<td>vacuum</td>
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<td>2.62</td>
<td>2.9</td>
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<tr>
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</tbody>
</table>

a Observed at 290 K. b Observed at 100 K.
ated and in D$_2$ for 30 min. A new peak appeared at 2675 cm$^{-1}$, and two peaks at 1947 and 1895 cm$^{-1}$ disappeared.

The peak at 3687 cm$^{-1}$ can be assigned to hydroxyl on the cerium oxide surface because it shifted to 2675 cm$^{-1}$ in D$_2$. The two peaks at 2206 and 2087 cm$^{-1}$ may arise from electronic transitions for Ce$^{3+}$. The remaining two peaks at 1947 and 1895 cm$^{-1}$ may be assigned to H on (or near) Ru clusters based on Table 3 of ref 3 or Table 1(a) of ref 1. The proposed new site (see Discussion) for H may be at the interface between Ru clusters and cerium oxide surface as detected around 3687 cm$^{-1}$ in FT-IR, probably overlapping ordinary surface hydroxyl groups.

X-ray Photoelectron Spectroscopy (XPS). XPS was measured by ESCALAB 202I (VG). The catalyst sample (powder) was sealed off from the glass vacuum system in a glass ampule and transferred inside the ESCALAB without contact with air. The peak of C 1s was taken as the standard of binding energy (=284.5 eV). In Table A1 (see the supporting information) compared to the Ru 3P$_{3/2}$ peak for neutral Ru powder at 462.0 eV, the Ru 3P$_{3/2}$ peak was at lower binding energy by 0.7 eV for Ru$_3$/CeO$_2$-673ev in H$_2$ at 588 K and by 1.3 eV for Ru$_3$-Ni/CeO$_2$-673ev in H$_2$ at 588 K. It should be noted that conventional Ru/CeO$_2$ had a main neutral peak at 462.0 eV and a weaker shoulder peak at 461.1 eV.

Supporting Information Available: Table A1 lists XPS binding energies for Ru catalysts, and Figure A1 shows the FTIR spectra of Ru$_3$-Ni/CeO$_2$-673ev and Ni/CeO$_2$ in H$_2$ (2 pages). Ordering information is given on any current masthead page.

**References and Notes**