Preparation of [Ru₆N] Clusters on MgO, K⁺/MgO, Cs⁺/MgO, and Al₂O₃ and the Reactivities with H₂ and N₂

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The supported ruthenium clusters [Ru₆N] were prepared on MgO, K⁺/MgO, and Cs⁺/MgO from [Ru₆N(CO)₁₆]⁻ cluster as hydrogenation catalysts, stabilized, and chemically modified by nitrido nitrogen. The characterization and reactivities with H₂ and N₂ were investigated by EXAFS (extended X-ray absorption fine structure) in relation to their catalysis promoted by nitrido nitrogen. The [Ru₆N] cluster unit was found to remain on MgO after heating in vacuum at 813 K (decarbonylated) and in H₂ at 588 K (reaction condition of N₂ hydrogenation), whereas the [Ru₆N(CO)₁₆]⁻ cluster strongly interacted with the Al₂O₃ surface to degrade to [Ru₃] by heating in vacuum at 813 K. The decarbonylated [Ru₆N] framework also remained in H₂ at 588 K on K⁺/MgO and Cs⁺/MgO without aggregation or degradation. By changing the Ru loading from 0.48 to 3.9 wt % on MgO, the coordination number N₆-o, (O₆, oxygen atom at surface) decreased from 1.2 to 0.3, while the [Ru₆N] cluster unit remained unchanged for samples with Ru loading up to ~2.5 wt %. The preferable reaction of [Ru₆N] clusters with MgO(001) flat surfaces was suggested for the sample at 2.5 wt % Ru, but the cluster should have reacted mainly with lower coordination sites of MgO for the sample with lower Ru loading (~0.5 wt %). The r₆-o, was shorter for [Ru₆N] on K⁺/MgO and Cs⁺/MgO (2.00—2.03 Å) than on MgO (2.13 Å), implying that the [Ru₆N] was interacted with O₆ atoms bonded to K⁺ or Cs⁺ ions to have a direct support effect of basic oxide K⁺/MgO or Cs⁺/MgO on catalysis. H-induced structure changes were observed for [Ru₆N]MgO and [Ru₆N]−Cs⁺/MgO as the reversible changes on bonding distance r₆-o, of 0.03 and 0.08 Å, respectively, by the adsorption/desorption of H₂. The adsorption of N₂ was simple adsorption on [Ru₆N] without structural change of [Ru₆N] on MgO or Cs⁺/MgO.

Introduction

Metal clusters as homogeneous (in liquid) and heterogeneous (supported clusters) catalysts are expected to be effective catalysts associated with their multiple metal sites. The specific catalysis from C₂H₄ was suggested to have a chemical effect on catalysis. In relation to their catalysis promoted by nitrido nitrogen. The [Ru₆N] cluster unit was found to remain on MgO after heating in vacuum at 813 K (decarbonylated) and in H₂ at 588 K (reaction condition of N₂ hydrogenation), whereas the [Ru₆N(CO)₁₆]⁻ cluster strongly interacted with the Al₂O₃ surface to degrade to [Ru₃] by heating in vacuum at 813 K. The decarbonylated [Ru₆N] framework also remained in H₂ at 588 K on K⁺/MgO and Cs⁺/MgO without aggregation or degradation. By changing the Ru loading from 0.48 to 3.9 wt % on MgO, the coordination number N₆-o, (O₆, oxygen atom at surface) decreased from 1.2 to 0.3, while the [Ru₆N] cluster unit remained unchanged for samples with Ru loading up to ~2.5 wt %. The preferable reaction of [Ru₆N] clusters with MgO(001) flat surfaces was suggested for the sample at 2.5 wt % Ru, but the cluster should have reacted mainly with lower coordination sites of MgO for the sample with lower Ru loading (~0.5 wt %). The r₆-o, was shorter for [Ru₆N] on K⁺/MgO and Cs⁺/MgO (2.00—2.03 Å) than on MgO (2.13 Å), implying that the [Ru₆N] was interacted with O₆ atoms bonded to K⁺ or Cs⁺ ions to have a direct support effect of basic oxide K⁺/MgO or Cs⁺/MgO on catalysis. H-induced structure changes were observed for [Ru₆N]MgO and [Ru₆N]−Cs⁺/MgO as the reversible changes on bonding distance r₆-o, of 0.03 and 0.08 Å, respectively, by the adsorption/desorption of H₂. The adsorption of N₂ was simple adsorption on [Ru₆N] without structural change of [Ru₆N] on MgO or Cs⁺/MgO.

These chemical (electron donation from C) and structural (cluster framework expansion) effects found for supported [Ru₆C] and [Ru₆C] clusters implied the possibility of investigating new catalyst systems of transition metal + main group element, such as ruthenium carbide or nitride and rhodium carbide or nitride, although studies on these systems were very rare because they cannot exist as bulk in usual thermodynamic conditions. Recently, we reported the catalysis of nitrido-[Ru₆] clusters [Ru₆N(CO)₁₆]⁻ on MgO, K⁺/MgO, and Cs⁺/MgO, which retained the hexamer [Ru₆N] unit in the reaction conditions. The interstitial nitrido nitrogen was suggested to promote catalysis through the comparison of activities with other supported clusters and conventional Ru catalysts. Similar to the framework expansion/contraction of [Ru₆C] clusters by CO adsorption/desorption, expansion/contraction of the [Ru₆N] framework was observed by the adsorption/desorption of hydrogen. These data suggested that the catalyst systems of transition metal (Ru, Rh) + carbon or nitrogen were impossible as bulk, but possible as very small metal particles such as supported hexamer clusters + carbon or nitrogen.

The information about the interactions of supported clusters with H₂ is important in relation to catalysis (hydrogenation), but research on the interactions has been difficult because of the “invisibleness” of hydrogen to most spectroscopies and the instability of supported clusters in reaction conditions of hydrogenation. The hydrogenation effect on metal particle structure was investigated for Ir/Al₂O₃ after reduction (427 K) and subsequent heating in vacuum (650 K) by means of EXAFS. By heating at 650 K, the bonding distance r₆-o, and coordination number N₆-o, decreased from 2.71 to 2.64 Å (A = 10⁻¹ nm) and from 4.9 to 4.0, respectively. The interaction of Ir clusters with H₂ was not clear due to the change of cluster structure. It was suggested that the cluster structure was transformed from hemispherical to almost flat on the basis of the decrease of N₆-o,. The conventional Pd/C (average Pd particle size 35 Å) and Pd/ .
Supported [Ru$_n$N] Clusters and Reactivities

Al$_2$O$_3$ (34 Å) were treated in H$_2$ at 373 K, and subsequently the ambient gas was switched from H$_2$ to Ar at the same temperature. During the desorption of H(a), the $r_{Ru-Pd}$ was decreased from 2.82 to 2.76 Å (Pd/C) and from 2.82 to 2.75 Å (Pd/Al$_2$O$_3$) keeping the $r_{Pd-Pd}$ almost unchanged. The palladium hydride PdH$_x$ ($x \approx 0.44$) formation/decomposition on C or Al$_2$O$_3$ was suggested compared to $\alpha$-phase PdH$_x$ ($x \ll 0.6$) and $\beta$-phase PdH$_x$ ($x \approx 0.6$) as bulk Pd hydride.

The spectroscopic detection of H(a) was reported by IR (infrared absorption) and NMR (nuclear magnetic resonance). Different from the previous reports on supported metal catalysts, multifold (bridging and 3-fold) H(a) were detected in addition to the on-top H(a) on conventional RuO$_x$ and Ru–Cs$^+/MgO$ at 183 K. Two peaks were observed for conventional Ru$_2$SiO$_4$ near 60 ppm in H$_2$ (1.3–100 kPa) ($\alpha$) and around 30 ppm (13–100 kPa) ($\beta$) by solid $^1$H-NMR. The $\beta$ peak was implied to be weakly bound H species on Ru particles on the basis of the smaller heat of adsorption ($10 \text{kJ mol}^{-1}$) and larger H/Ru$_{surf}$ ratio (3.3–5.6 at $P_{H_2} = 33–100 \text{kPa}$).

In this paper, we report the preparation of [Ru$_n$N] clusters on MgO, K$^+$/MgO, and Cs$^+/$/MgO compared to that on Al$_2$O$_3$ as the first subject. The stability of [Ru$_n$C] clusters on MgO, La$_2$O$_3$, TiO$_2$, or Al$_2$O$_3$ was reported to be due to stabilization of the [Ru$_6$] framework by carbido carbon, and similar stabilization was expected for supported [Ru$_n$N].

Detailed characterization of supported [Ru$_n$N] clusters was performed to determine (1) the homogeneity of supported [Ru$_n$N], (2) the kind of MgO surface sites where [Ru$_n$N] was attached, the (3) nature of Ru–O–Mg bonds ($\theta_{O-Mg}$, oxygen atom at surface), through the EXAFS observations for samples at different Ru wt % and the TPR (temperature-programmed reduction) measurements. Secondly, the reactivities of thus-characterized supported nitrido clusters with H$_2$ or N$_2$ were investigated in $\text{in-situ}$ EXAFS measurements. These studies on the reactivity with H$_2$ and N$_2$ should be closely related with the catalysis (ammonia synthesis) on these nitrido clusters on a molecular level. The detailed discussions on the structures and their changes by the interaction with H$_2$ or N$_2$ are reported in this paper. The extension to catalysis is described in the accompanying paper.

**Experimental Section**

[PPN]$^+[$Ru$_n$N(CO)$_{12}$]$^-$(1) ($\text{PPN} = N(PPh$_3$)$_3$)$^{12}$ [PPN]$^+\text{Cl}^-$, Aldrich Chem Co., 97%; Na$_2$N$_3$, Wako Pure Chemical Ind., Ltd., >90%; Ru$_2$(CO)$_{12}$, Soekawa) was supported on MgO, K$^+$/MgO, Cs$^+/$/MgO, or Al$_2$O$_3$ by reaction at 290 K (1 h) in purified THF (tetrahydrofuran, Wako, Special Grade) and the subsequent removal of THF in vacuum. The MgO (surface area 200 m$^2$ g$^{-1}$) was prepared from Mg(OH)$_2$ (Wako, 99.99%) by heating at 773 K (2 h) in vacuum. A water solution of Cs$_2$CO$_3$ (Wako, >95%) or K$_2$CO$_3$ (Wako, >99.5%) was impregnated on MgO, followed by treatments in O$_2$ and then in H$_2$ at 773 K. The Al$_2$O$_3$ (aerosil C) (100 m$^2$ g$^{-1}$) was treated at 623 K (2 h) in vacuum. The loadings of Ru were 2.5 wt % for MgO, K$^+$/MgO, and Cs$^+/$/MgO and 1.6 wt % for Al$_2$O$_3$ except for the EXAFS experiments at different Ru wt % for MgO (0.48, 2.5, and 3.9 wt %). The experiments at 0.48 and 3.9 wt % Ru were specified in the text, and those without special notation for MgO-supported samples were at 2.5 wt % Ru. The molar ratios Cs$^+/$/[Ru$_n$N] and K$^+$/[Ru$_n$N] were fixed at 12 on the basis of the preliminary activity tests for ammonia synthesis. The supported nitrido–Ru clusters are denoted as [Ru$_n$N]/oxide.

[PPN]$^+[$Ru$_6$(CO)$_{18}$]$^2^-$ (2) and [NM$_6$CH$_2$PH$_3$$]^+[$Ru$_n$C(CO)$_{(15)}$Me$_2$$]$ (3) ([NM$_6$CH$_2$PH$_3$$]^+Cl$, Wako; CH$_3$I, Wako, Special Grade) were supported on MgO in THF solution in a similar manner to the case of 1 or ref 1. The supported Ru clusters are denoted as [Ru$_6$/MgO] and [Ru$_n$Cl/MgO] (2.5 wt % Ru). The process of cluster catalyst preparation and transfer was carried out in argon (99.99%) or helium (99.99%). As pretreatment, incipient supported clusters were heated (elevating rate of temperature 4 K min$^{-1}$) in vacuum at 813 K except for [Ru$_n$N]$^-$/Cs$^+/$/MgO and [Ru$_n$N]$^-$/K$^+$/MgO (heated at 673 K), followed by treatment in H$_2$ for 1 h (588–773 K).

The EXAFS spectra of the Ru K edge were measured for these supported clusters at the beamline 10B and 6B (2.5 GeV, current 360–260 A) of the Photon Factory in the National Laboratory for High Energy Physics (Proposal No. 93GO10) between June 1993 and November 1994. The X-ray was monochromated through a double-crystal monochromator of Si(311), and the spectra were obtained in the transmission mode with ionization chambers fitted with argon ($I_0$) and krypton ($I$). The energy resolution was ~1 eV at 9 keV, and the photon flux on the sample was >10$^7$ s$^{-1}$. The sample was transferred to an EXAFS Pyrex cell (0.13 < $\Delta \mu < 0.98$ dependent on the Ru wt %) with Kapton films on both sides by using the Schlenk technique from a closed circulating system for sample preparation. The data collection was performed at 30–293 K utilizing a closed cycle refrigerator (Cryo System, LTS-21). The analysis was performed by the program EXAFSH by Yokoyama et al. The background subtraction was performed by calculating the cubic spline with three blocks, and the obtained function $\mu_0(k) - \mu(k)$ was normalized by using the Victoren parameter $\mu_0(\lambda)$ = $C \lambda^3 - D \lambda^4$ to determine $\mu_0(k)$ and $t$. The Fourier transform (FT) of the $k^3$-weighted EXAFS oscillation was carried out over the range of $k_{min} = 3$ and $k_{max} = 13–16 \text{Å}^{-1}$ according to the signal/noise (S/N) of each spectrum. The window function (Hanning function) was multiplied with a width of $(k_{max} - k_{min})/20$ on both ends of the FT k range. The inverse FT was performed in the range of $k_{min} = 1.3–1.4$ and $k_{max} = 2.9–3.0 \text{Å}^{-1}$ multiplied by the window Hanning function with the width 0.1 Å on both ends. The curve-fitting analysis was performed by the method based on the formula of plane wave single-scattering theory, using empirical phase shift and amplitude functions extracted from ruthenium powder for the Ru–Ru bond (metallic), RuO$_2$ for the Ru–O bond, [RuCl$_2$(CO)$_{12}$] for the Ru–O bond, cluster 3 (Ru$_3$(C$_2$O$_4$)$_2$) for the Ru–O bond, and [Ru$_6$(CO)$_{12}$] (Ru–C bond) for the Ru–C and Ru–N bonds (in the case of N$_2$ adsorbed on supported [Ru$_n$N] clusters).

The parameters for the Ru–Ru bond (cluster) were obtained by subtracting the oscillation of the third shell of the complex [RuCl$_2$(CO)$_{12}$] (Ru–C–O) from the second shell of cluster 1 (Ru–Ru + Ru–(C–O)). Taking into account each coordination number, the EXAFS spectra for these reference compounds were taken at room temperature. The residual factor ($R_l$) was calculated by the following equation:

$$R_l = \int |k^2 \chi^{abs}(k) - k^2 \chi^{calc}(k)|^2 dk / \int |k^2 \chi^{obs}(k)|^2 dk$$

in the k region of 4–13 Å$^{-1}$ (4–12 for [Ru$_n$N]$^-$/Cs$^+/$/MgO in H$_2$ and 0.48 wt % [Ru$_n$N]/MgO because of their worse S/N) for the curve-fitting analysis. The H$_2$ (99.99%) and N$_2$ (99.99%) gas were purchased from Toyko Sanso Co., Ltd. The impurities (as molecular content) were less than the following values: H$_2$O < 10 ppm, N$_2$ < 50 ppm, O < 10 ppm, CO < 10 ppm, and total hydrocarbons < 10 ppm (as carbon content) in the H$_2$ gas, and H$_2$O < 10, O < 2 ppm, and total hydrocarbons < 1 ppm (as carbon content) in the N$_2$ gas. The H$_2$ or N$_2$ was introduced to the EXAFS sample cell after further purification by passage through a liquid nitrogen trap.
with NaCl windows on both sides combined with a closed circulating system. Support oxide disks were treated in the same conditions as powders in the IR cell and impregnated by a drop of a THF solution of cluster 1.

The temperature of the IR cell can be maintained at 295–823 K by a coil would around the cell.

Results

Characterization of Supported [Ru4N] Clusters on MgO, K+/MgO, Cs+/MgO, and Al2O3. 1. Incipient Supported Clusters. The EXAFS spectra were observed for incipient [Ru4N]/MgO, [Ru4N]−Cs+/MgO, and [Ru4N]/Al2O3. The obtained coordination numbers for Ru–Ru (first coordination) and Ru(N) for Ru-Ru (diagonal line of octahedral (Oh) cluster [Ru6N]) bondings, the Ru(N) peak around 3.7 Å (phase shift uncorrected) disappeared in the FT of k^3x for incipient [Ru4N]/Al2O3 compared to the FT for unsupported cluster 1 (crystal). This suggested the distortion of the [Ru4N] framework (the angle θRu−N−Ru was reduced from π) by strong interaction with the Al2O3 surface.

2. Heated and Reduced Clusters. The incipient [Ru4N]/MgO and [Ru4N]/Al2O3 were heated in vacuum at 813 K (up to the temperature where CO ligands had totally desorbed) and then in H2 at 588 K. The obtained EXAFS spectra were almost identical after heating and after subsequent H2 treatment for [Ru4N]/MgO (Figure 1a,b). Also, the corresponding two spectra were almost identical for [Ru4N]/Al2O3. Therefore, common ruthenium cluster species were suggested for samples with/without the H2 treatment at 588 K. The EXAFS spectrum for [Ru4N] after heating and in H2 is shown in Figure 1a. A strong peak ascribable to Ru−Ru bonding and a shoulder on the shorter distance side of the Ru−Ru peak were observed (Figure 1c). By the curve-fitting analysis with two waves (Ru−Ru, Ru−O), the coordination number of Ru−Ru bonding (NR−Ru−o) was calculated to be 4.1 with fRu−Ru = 2.62 Å (Table 1 and Figure 1d), similar to the value for cluster 1 (=4), indicating that the [Ru4N] unit remained on MgO in H2 at 588 K. An alternative curve-fitting analysis was performed with one wave (Ru−Ru) or three waves (Ru−Ru, two Ru−O), and the R^2 values were 6.8 and 2.8%, respectively. In the one-wave fitting (Ru−Ru), the calculated curve did not trace the inversely Fourier-transformed experimental curve in all wavenumber regions. In the three-wave fitting (Ru−Ru, two Ru−O), the fitting was not improved by the addition of one more Ru−O wave to two waves (Ru−Ru, two Ru−O). Thus, the analysis with two waves (Ru−Ru, two Ru−O) was reasonable with smaller R^2 values. The obtained NR−Ru−o (0.5) suggests that one triangle Ru3 face of the [Ru4N] framework was attached on the MgO surface through three Ru−O bonds. If the Oh−like structure was destroyed to a raftlike structure by the
interaction with the MgO surface, $N_{Ru-Ru}$ should be smaller than the observed 4.1. Hence, we suppose the formulation [Ru$_6$N-($\mu$-O$_{al2o3}$)] ($N_{Ru-O_{al2o3}} = 2.13$ Å). The cluster 1 was suggested to interact with the Al$_2$O$_3$ surface and be distorted to lose $O_6$ symmetry of the [Ru$_6$N] framework, as indicated by the disappearance of Ru($\neg N$)-Ru bonding for the incipient cluster (in the previous section). The EXAFS spectra for [Ru$_6$N]/Al$_2$O$_3$ after heating and in H$_2$ are shown in Figure 2, and curve-fitting result is listed in Table 1. The $N_{Ru-Ru}$ decreased to 2.0, and $N_{Ru-O_{al2o3}}$ was 1.9. The formation of the trimer [Ru$_3$($\mu_2$-O$_{al2o3}$)] cluster was suggested after the fragmentation from hexamer nitrido cluster [Ru$_6$N] by strong interaction with the Al$_2$O$_3$ surface. The coordination of $O_6$ should be $\mu_2$ (coordinate to two Ru atoms) in order to be consistent with $N_{Ru-O_{al2o3}}$ (1.9) taking into account the [Ru$_3$] cluster size and the population of $O_{al2o3}$ at the Al$_2$O$_3$ surface (see the Discussion section).

Also, [Ru$_6$N]−K$^+$/MgO and [Ru$_6$N]−Cs$^+$/MgO heated in vacuum at 673 K showed very little change of EXAFS spectra by subsequent H$_2$ treatment at 588 K. The EXAFS spectra shown in Figure 3 for [Ru$_6$N]−Cs$^+$/MgO heated in vacuum at 673 K and in H$_2$ at 588 K. Corresponding curve-fitting results are listed in Table 1. The result was similar to that for [Ru$_6$N]/MgO, and $N_{Ru-Ru}$ of 3.8 on K$^+$/MgO and 4.0 on Cs$^+$/MgO suggest retention of the [Ru$_6$N] unit on K$^+$/MgO and Cs$^+$/MgO. However, the $r_{Ru-O_{al2o3}}$ values were 2.00−2.03 Å for [Ru$_6$N]−K$^+$/MgO and [Ru$_6$N]−Cs$^+$/MgO, which were shorter by 0.10−0.13 Å than that for [Ru$_6$N]/MgO (2.13 Å) (Table 1).

3. The Change of [Ru$_6$N] Cluster Structure and MgO Sites at Different Ru wt %. The EXAFS spectra were also measured for [Ru$_6$N]/MgO at 0.48 and 3.9 wt % Ru. The EXAFS spectrum of a sample at 0.48 wt % Ru is shown in Figure 4. Compared to the Fourier transform for the 2.5 wt % Ru sample (Figure 1c), the peak around 1.7 Å (Ru−O) (phase shift uncorrected) became stronger, while the peak around 2.3 Å did not show significant change (Figure 4c). The best fit result is listed in Table 2 and shown in Figure 4d. The $N_{Ru-Ru}$ (4.0) suggested that the [Ru$_6$N] cluster unit was retained also at 0.48 wt % Ru on the MgO surface.
The \( N_{Ru-Ru} \) for [Ru\(_{2}\)N]/MgO at 3.9 wt % Ru was 5.0 with the same \( r_{Ru-Ru} \) (2.62 Å) as for the sample at 2.5 wt % Ru (Table 2). The [Ru\(_{2}\)N] clusters should have aggregated to larger Ru particles similar to [Ru\(_{2}\)N]/MgO at 2.5 wt % Ru in vacuum at 813 K and in \( \text{H}_2 \) at 588 K by EXAFS, indicating the aggregation of the [Ru\(_{2}\)N] cluster to larger particles in vacuum at 813 K and/or in \( \text{H}_2 \) at 588 K. The NR,,-R,, obtained by curve fitting (Figure 6d) was 2.71 Å for the sample in \( \text{H}_2 \) (Table 3), longer by 0.08 Å than for the sample in vacuum (2.63 Å, Table 1). Additional analyses were performed by changing the FT range, CF range, \( N \), or \( r \), independently, and also for another EXAFS spectrum of the same sample in the same conditions in order to estimate the errors. The errors for \( m_{1-Ru} \) were ±0.016 and ±0.015 Å for spectra corresponding to Figures 3 and 6 (Table 1 and 3). Therefore, it is valid to think that the \( m_{1-Ru} \) change (±0.08 Å) was induced by hydrogen expansion/contraction.

As a reference, incipient [Ru\(_{2}\)C]/MgO was heated in vacuum and in \( \text{H}_2 \) at 623 K. The non-nitrido Ru heptamer cluster [Ru\(_{7}\) (\( \mu_5\)-O\(_{2w}\))] was suggested to be formed from the equimolar desorption data for CH\(_4\) and the EXAFS data \( r_{Ru-Ru} \) (2.63 Å) and \( N_{Ru-Ru} \) (4.2) (Table 4). The number \( x \) should be 3–4.
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Figure 4. Ru K edge EXAFS spectra observed at 293 K for [Ru₆N(CO)₁₆]⁺/MgO (0.48 wt % Ru). The sample was heated in vacuum (813 K) and in H₂ (588 K). The captions for (a)-(d) are the same as in Figure 1.

TABLE 2: Results for the Curve-Fitting Analysis of Ru K Edge EXAFS (Observed at 293 K) for [Ru₆N(CO)₁₆]⁺/MgO at Different Ru wt % (0.48, 2.5, and 3.9 wt %)

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* The samples were treated in the same conditions as in Table 1. *In eV. *In 10⁻³ Å².

judging from N₉=O₉ (0.6). In H₂, the cluster showed no structural change of cluster framework (Table 4).

2. With N₂. The EXAFS spectrum was observed for [Ru₆N(μ-O₉₉₉)] on MgO in N₂ (25 kPa) at 193 K. In its FT, a shoulder peak on the lower distance side than Ru–Ru bonding became stronger than in Figure 1c. The data were best fitted with three waves, Ru–Ru, Ru–O₉₉₉, and Ru–N, with the distances 2.62, 2.13, and 1.95 Å (R₁, 1.7% in Table 3) rather than two waves (Ru–Ru, Ru–O₉₉₉) (R₂, 4.0%). The N₉=O₉ (0.4) by three-wave fitting suggested two or three on-top N₂(a) or one or two bridging N₂(a) on the Ru cluster because molecular N₂ should not be dissociated at 193 K. The N and r for Ru–Ru and Ru–O₉₉₉ bondings did not change by the adsorption of N₂ (N₁=O₁ = 4.1 ± 0.1, r₁=O₁ = 2.62 Å, N₁=O₉₉₉ = 0.5, r₁=O₉₉₉ = 2.13 Å (Tables 1 and 3).

The interaction with N₂ (25 kPa) was also examined for [Ru₆N]–Cs⁺/MgO. The curve-fitting analysis with three waves, Ru–Ru, Ru–O₉₉₉, and Ru–N, improved the fitting compared to two-wave (Ru–Ru, Ru–O₉₉₉) fitting, especially in the lower k region. The obtained r for Ru–Ru and Ru–O₉₉₉ bondings by three-wave fitting (Table 3) showed slight changes (ΔR₁=O₁ = 0.02 Å, ΔR₁=O₉₉₉ = 0.04 Å) compared to the sample in vacuum (Table 1). The r₁=O₉₉₉ was 2.02 Å, larger by 0.07 Å than for N₂(a) on [Ru₆N]MgO (Table 3).

Discussion

Cluster Structures. The [Ru₆N(CO)₁₆]⁺ cluster I interacted with MgO to form [Ru₆N(CO)₁₆]⁺/MgO at room temperature, and transformed to [Ru₆N(μ-O₉₉₉₃)] (Figure 7) by the decarbonylation in vacuum at 813 K (Figure 1 and Table 1). The attached cluster framework structure did not change by subsequent treatment in H₂ at 588 K or the treatment in N₂ and H₂ at 588 K (r₁=O₁ = 2.13 Å). On Cs⁺-doped MgO and K⁺-doped MgO, the cluster I interacted with Cs⁺/MgO or K⁺/MgO to form [Ru₆N(μ-O₉₉₉₃)] (x = 3-4), releasing three to four CO ligands from the cluster, and transformed to [Ru₆N(μ-O₉₉₉₃)] (Figure 7) by the evacuation at 673 K and hydrogen treatment at 588 K (r₁=O₁ = 2.00 Å on Cs⁺/MgO and r₁=O₁ = 2.63 Å, r₁=O₉₉₉ = 2.03 Å on Cs⁺/MgO and r₁=O₉₉₉ = 2.63 Å, r₁=O₉₉₉ = 2.00 Å on K⁺/MgO, in Table 1). In contrast, cluster I transformed to [Ru₆(μ₂-O₉₉₉₃)] on Al₂O₃ by the evacuation at 813 K (Figure 7), and the species were very stable in H₂ at 588-773 K (Table 1). This bangle cluster (r₁=O₁ = 2.61 Å, r₁=O₉₉₉ = 2.16 Å) should be similar to [Ru₆(μ₂-O₉₉₉₃)] on Al₂O₃ prepared from cluster 2 (r₁=O₉₉₉ = 2.06 Å). Considering the crystal structures of Al₂O₃ (corundum for α and spinel for γ) and MgO (NaCl-type), the smallest interatomic distances of two O₉₉₉ atoms at 2.8 Å for Al₂O₃ and 2.98 Å for MgO. Compared to the r₁=O₁ of attached Ru clusters (2.61 Å for Al₂O₃ and 2.62 Å for MgO, Table 1), the obtained N₁=O₉₉₉ (1.9) for [Ru₂] species on Al₂O₃ can be interpreted only as the μ₁ coordination.
MgO can be understood as three of three O\textsubscript{u} atoms. The $N_{\text{Ru}-\text{O}_\text{u}}$ (0.5) for [Ru\textsubscript{6}N] species on MgO can be understood as three O\textsubscript{u} atoms coordinated to one triangle face [Ru\textsubscript{3}] of the O\textsubscript{u}-like [Ru\textsubscript{6}N] species as the $\mu_1$ coordination. This coordination style of [Ru\textsubscript{6}N] species on MgO was ensured by the Ru wt % dependence of $N_{\text{Ru}-\text{O}_\text{u}}$ (see below). The other examples of metal−O\textsubscript{u} bond distances (2.00−2.83 Å) were summarized in ref 2 for the supported Ru, Rh, Pd, Re, Os, Ir, or Pt clusters, and the distances were classified as either in the range 2.00−2.24 Å or in the range 2.63−2.83 Å. Observed $r_{\text{Ru}−\text{O}_\text{u}}$ values for [Ru\textsubscript{6}N(μ−O\textsubscript{u})\textsubscript{3}] on MgO (2.13 Å), K\textsuperscript{+}/MgO (2.00 Å), Cs\textsuperscript{+}/MgO (2.03 Å), or Al\textsubscript{2}O\textsubscript{3} (2.16 Å) were within the range 2.00−2.24 Å, similar to other supported Ru, Rh, Re, or Os clusters. In the curve-fitting analyses in Tables 1−3 for N\textsubscript{2}-free samples, all the Fourier-filtered $k^3$$\chi$ were well fitted with two waves (Ru−Ru, Ru−O\textsubscript{u}). The addition of a Ru−N\textsubscript{alloy} (N\textsubscript{alloy} interstitial nitrogen) wave (2.06 Å) was needed to fit the EXAFS of cluster 1 (powder) as the bonding between Ru and N\textsubscript{alloy}. The reason that the additional wave was not needed to fit the experimental data in Tables 1−3 may be electron donation from N\textsubscript{alloy} to [Ru\textsubscript{6}N], as suggested by IR and the distorted framework structure of [Ru\textsubscript{6}N] from its $O_h$ symmetry when unsupported.\textsuperscript{15} Similarly, Ru K edge EXAFS for supported [Ru\textsubscript{3}C] was well fitted without a Ru−C\textsubscript{alloy} wave probably due to the chemical state of C\textsubscript{alloy} (with less electrons) as a backscattering atom in EXAFS and the distortion of the [Ru\textsubscript{3}C] framework.\textsuperscript{12}

The dependence of cluster structure on Ru wt % was examined for [Ru\textsubscript{6}N]/MgO at 0.48, 2.5, and 3.9 wt % Ru. On the basis of the surface area of MgO (200 m\textsuperscript{2} g\textsuperscript{−1}), $r_{\text{Mg}−\text{O}}$ (2.106 Å), and the number of surface OH groups of MgO heated at 773 K (≈5 nm\textsuperscript{−2}),\textsuperscript{16} the numbers of surface O atom (O\textsubscript{u}) and surface OH groups were estimated to be $2.3 \times 10^{21}$ and $1 \times 10^{21}$ per gram of MgO, respectively. On MgO, OH groups were observed as a sharp strong peak at 3757 cm\textsuperscript{−1} in addition to a weaker broad peak around 3614 cm\textsuperscript{−1} after pretreatment at 773 K, and the peak intensity of these peaks did not change by the interaction with cluster 1 in THF and/or heating in vacuum at 813 K. The number of attached [Ru\textsubscript{6}N] clusters was $4.8 \times 10^{18}$, $2.4 \times 10^{19}$, and $4.0 \times 10^{19}$ per gram of MgO in the case of 0.48, 2.5, and 3.9 wt % Ru samples, respectively. It was difficult to monitor the MgO surface sites which were reacted with [Ru\textsubscript{6}N] clusters because of the reaction of incipient [Ru\textsubscript{6}N(CO)\textsubscript{16−x}][\textsuperscript{1−}]\textsuperscript{−} (partially decarbonylated) with the MgO surface (to form Ru−O\textsubscript{u} bonds) occurred during heating in vacuum (813 K), accompanying the total decarbonylation. However, the number of surface OH groups was larger by about 30 times than that of [Ru\textsubscript{6}N] for the 3.9 wt % Ru sample, and the $N_{\text{Ru}−\text{O}_\text{u}}$ changed very critically with different Ru loadings (Table 2).

In this context, we believe the reaction of the cluster is with O\textsubscript{u} not with OH. As the (001) face is believed to be predominantly exposed for MgO even as a powder,\textsuperscript{15} two models of supported [Ru\textsubscript{6}N(μ−O\textsubscript{u})\textsubscript{3}] were proposed on major sites of MgO(001) (Figure 8a) and on fewer sites on MgO(001) with steps (Figure 8b). We think that the [Ru\textsubscript{6}N] with low Ru loading (Ru < 0.5 wt %) mainly interacted with the lower coordination MgO surface to form [Ru\textsubscript{6}N(μ−O\textsubscript{u})\textsubscript{3}] (x = 5−7), such as in Figure 8b ($N_{\text{Ru}−\text{O}_\text{u}} = 0.83$ as a model), on the basis of the obtained $N_{\text{Ru}−\text{O}_\text{u}}$ by EXAFS (1.2, Table 2). The [Ru\textsubscript{6}N] at moderate Ru loading (Ru < 2.5 wt %) mainly interacted with relatively flat MgO planes to form [Ru\textsubscript{6}N(μ−O\textsubscript{u})\textsubscript{3}], similar to Figure 8a ($N_{\text{Ru}−\text{O}_\text{u}} = 0.5$ as a model), on the basis of the obtained $N_{\text{Ru}−\text{O}_\text{u}}$ by EXAFS (0.5, Table 2). Heterolytic fragmentations of [Ru\textsubscript{6}N] by heating in vacuum at 813 K, such as from [Ru\textsubscript{6}N] to [Ru\textsubscript{6}N]+ Ru, seemed improbable on the basis of wavenumbers and the peak pattern of adsorbed CO (in IR) on [Ru\textsubscript{6}N]/MgO heated at 813 K and in H\textsubscript{2} at 588 K at 0.06 wt % Ru (1978w(sh), 1965w) similar to that at 2.5 wt % (2059w(sh), 2045w(sh), 1992s) without specific twin or triple peaks ascribable to surface Ru(CO)\textsubscript{x} species.\textsuperscript{18−20}

The nuclearity of [Ru\textsubscript{6}N] on MgO, Cs\textsuperscript{+}/MgO, or K\textsuperscript{+}/MgO did not change by heating in vacuum or in H\textsubscript{2} probably due to the strong binding of [Ru\textsubscript{6}N] by nitrido nitrogen on the basis of the experimental facts of the retention of nitrido N below ~600 K in H\textsubscript{2} in TPR (Figure 5a) and the $N_{\text{Ru}−\text{Ru}}$ (about 4) for EXAFS (Tables 1−3). The 100%-raft [Ru\textsubscript{6}N] on flat MgO(001) cannot mainly interact with relatively flat MgO(001) symmetry when [Ru\textsubscript{6}N] was heated at 813 K and H\textsubscript{2} at 588 K at 0.06 wt % Ru (1978w(sh), 1965s) similar to that at 2.5 wt % (2059w(sh), 2045w(sh), 1992s) without specific twin or triple peaks ascribable to surface Ru(CO)\textsubscript{x} species.\textsuperscript{18−20}

![Figure 5. Temperature-programmed reduction (TPR) in H\textsubscript{2} for incipient [Ru\textsubscript{6}N(CO)\textsubscript{16−x}]/MgO (●), [Ru\textsubscript{6}N(CO)\textsubscript{16−x}]/Cs\textsuperscript{+}/MgO (△), and [Ru\textsubscript{6}N(CO)\textsubscript{16−x}]/K\textsuperscript{+}/MgO (■) (a) NH\textsubscript{3} desorption monitored by mass; (b) the decrease rate of the IR peak at 1117 cm\textsuperscript{−1}. The heating rate is 4 K min\textsuperscript{−1}.](image-url)
TABLE 3: Results for the Curve-Fitting Analysis of Ru K Edge EXAFS (Observed at 193°, 100°, and 30 K°) for [Ru₆N(CO)₁₆]²⁻/MgO and [Ru₆N(CO)₁₆]²⁻/Cs⁺/MgO in H₂ or N₂

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*MgO catalyst in H₂ and N₂ and Cs⁺/MgO catalyst in N₂ observed at 193 K. *Cs⁺/MgO catalyst in H₂ observed at 100 K. *MgO catalyst in vacuum observed at 30 K. The samples were treated in the same conditions as Table 1. The error (within the 50% increase of Rf) is shown in parentheses. *In Å, /In eV, /In 10⁻³ Å².

Figure 6. Ru K edge EXAFS spectra observed at 100 K for [Ru₆N(CO)₁₆]²⁻/Cs⁺/MgO (2.5 wt % Ru, Cs⁺/[Ru₆N] = 12) in H₂ (76 kPa). The sample was heated in vacuum (673 K) and in H₂ (588 K). The captions for (a)–(d) are the same as in Figure 1.

TABLE 4: Results for the Curve-Fitting Analysis of Ru K Edge EXAFS (Observed at 293° and 100 K°) for [Ru₆(μ-O)₆]⁺ on MgO Prepared from [Ru₆(CO)₁₆]¹⁻ in Vacuum and in H₂ at 623 K

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*In vacuum at 293 K. *H₂ at 100 K. The samples were treated in the same conditions as in Table 1. /In Å. /In eV. /In 10⁻³ Å².

transformed to [Ru₆(μ-O)₆]⁺ ([Ru₆-Ru] = 2.63 Å, [Ru₆-O] = 2.10 Å) on MgO (Table 4). Corresponding TPR in H₂ for [Ru₆C]/MgO had a peak of CH₆ around 560 K (carbido C desorbed as CH₆, similar to the peak of NH₃ around 660 K for [Ru₆N]/MgO and [Ru₆N]–Cs⁺/MgO (Figure 5a). The cluster 2 without an interstitial atom readily aggregated to larger Ru particles on MgO during the evacuation at 813 K and/or subsequent H₂ treatment at 588 K (N[Ru₆-Ru] = 5.9—6.2). Thus, nitrido N (or carbido C) was suggested to maintain the [Ru₆] cluster framework by binding from the inside even at high temperatures or in H₂.

Cluster Structure Changes in H₂ or N₂. In the EXAFS measurements in H₂ or N₂, a drastic change of k²ₚ was observed for [Ru₆N]–Cs⁺/MgO in H₂ (Figure 6 and Table 3) compared to no change in vacuum at 30–293 K (Tables 1 and 3). Smaller changes of k²ₚ (and the fitted values) were observed for [Ru₆C]/MgO by the introduction of H₂ (Table 3). It should be noted that initial EXAFS spectra in vacuum were reproduced by the evacuation for these two cases in H₂, indicating these EXAFS changes by the adsorption/desorption of H₂ were reversible.

The causes of the spectral changes in H₂ or N₂ were classified as (1) simple adsorption of gas and (2) adsorption-induced structure changes of cluster framework (Δ[Ru₆-Ru]) and cluster/
support interface (ΔRu−Os). The adsorption of N2 should be simple nondissociative adsorption. Examples are reported for the distance r_{mean−N} for adsorbed N2 on metal catalysts or N2-coordinated organometallic complexes. The r_{Ru−N} were reported to be 1.91−1.94 Å for π-coordinated N2 in [(PhLi)2N2(N2)(Et2O)]3.21 The r_{N−N} were reported to be 1.832−1.83 Å for nearly straight V−N−N−V bonding in μ4-N(CH2)=N=CH2)2N=N(CH2)=N=CH2)2.22 The r_{Ru−N} were reported to be 1.857−2.18 Å for μ3-N2 in [μ3−N2(η^1:η^1:C6H6)(η^2:C6H6)(η^2:C6H6)]Ti(η^1:η^1:C6H6)(η^2:C6H6)(η^2:C6H6)]Ti(η^2:C6H6)2.23 The r_{Ru−N} were 1.95−2.02 Å for N(a) on [Ru6N/MgO and [Ru6N]/Cs+/MgO (Table 3). The adsorptions of molecular N2 were not accompanied by the expansion/contraction of cluster framework [Ru6N], keeping the r_{Ru−Ru} (almost) unchanged for [Ru6N/MgO (2.62 Å) and for [Ru6N]/Cs+/MgO (2.64 ± 0.01 Å) (Table 3).

The adsorption of H2 must be accompanied by adsorption-induced structure changes of cluster framework [Ru6N]. The r_{Ru−Ru} changes from 2.62 to 2.65 Å for [Ru6N/MgO and from 2.63 to 2.71 Å for [Ru6N]/Cs+/MgO (Table 3) by the adsorption of hydrogen. These H-induced structure changes also induced smaller changes of cluster/support interface; the r_{Ru−Os} changed from 2.13 to 2.17 Å for [Ru6N/MgO and from 2.03 to 2.06 Å for [Ru6N]/Cs+/MgO (Table 3). The changes of r_{Ru−Ru} (1.1% for [Ru6N/MgO and 3.0% for [Ru6N]/Cs+/MgO) are smaller than the [Ru6C] framework expansion/contraction induced by CO (9.1% for [Ru6C]/MgO and [Ru6C]/La2O3 (5.7%) and comparable to that induced by CO for [Ru6C]/Al2O3 (1.5%).1,2

The H-induced structure change of the Ru(0001) surface was monitored by VLEED (very low-energy LEED (low-energy electron diffraction)).24 It was found that the first layer Ru array expanded by 1.7% in the [1100] direction and by 0.9% in the [0001] direction by H adsorption (T_{ad} < 72 K). The other examples of H-induced structure change were reported for Co, Ni, Pd, Mo, and W single-crystal surfaces.25 The expansions of r_{Ru−Pd} on conventional Pd/C and Pd/Al2O3 by hydride or carbide formation were reported by means of EXAFS.7 The r_{Ru−Pd} increased by 2.0 and 2.4% with hydride formation and by 1.2 and 0.3% with carbide formation for Pd/C and Pd/Al2O3, respectively. The expansion of r_{Ru−Pd} of Pd/ZrO2 by carbide formation was measured during the CO disproportionation by XRD (X-ray diffraction).26 The carbon was incorporated up to 15 atom % in Pd, and the r_{Ru−Pd} was linearly increased by up to 2.6%. The change of r_{Ru−Ru} (Δ = 0.08 Å, 3.0%) for our [Ru6N]/Cs+/MgO (Table 3) was larger than the above H-induced reconstruction of Ru(0001) surface (0.9−1.7%) or “hydrogen-absorptive” or “carbon-absorptive” supported Pd catalysts (0.3−2.6%). This large expansion of the [Ru6N] framework may be due to the fact that all the Ru atoms of [Ru6N(N(μ-Os))3] were exposed and able to interact with H(a). The adsorbed amount of hydrogen atoms were three to four on [Ru6N/MgO at 185 K and five to six on [Ru6N]/Cs+/MgO at 77 K.11

The catalytic effect of [Ru6C] expansions of [Ru6C]/Al2O3, La2O3, or MgO induced by CO was discussed and summarized to afford enough space on [Ru6C] framework to dissociate H2 molecules, and CO-associative oxygenate compounds were selectively produced on the expanded [Ru6C].1,2 The catalytic effects of [Ru6N] expansion/contraction of [Ru6N/MgO and [Ru6N]+Cs+/MgO induced by hydrogen adsorption/desorption are described in the accompanying paper.

Conclusions

1. Supported [Ru6N(N(μ-Os))3] clusters were prepared on MgO, K+MgO, or Cs+/MgO from [Ru6N(CO)16] clusters (2.5 wt % Ru). The cluster [Ru6N(CO)16]− was cleaved to the trimer [Ru6N(μ-Os)3] on Al2O3 by heating at 813 K. These clusters were stable in H2 at 588 K.

2. The r_{Ru−Os} were in the range 2.09−2.17 Å for [Ru6N/MgO, and they were shorter (2.00−2.07 Å) for [Ru6N]/K+MgO and [Ru6N]/Cs+/MgO. The [Ru6N] was implied to be reacted with three Os(μ-atom bonded to K+ or Cs+ ions on K+MgO and Cs+/MgO.

3. The [Ru6N] was suggested to interact with lower coordination sites of the MgO surface, such as step sites, on the basis of the increase of N_{Ru−Os} when the Ru loadings were changed from 2.5 to 0.5 wt %.

4. The expansion and contraction of the [Ru6N] framework were observed by the hydrogen adsorption and desorption for [Ru6N/MgO (Δ_{Ru−Ru} = 0.03 Å) and [Ru6N]/Cs+/MgO (Δ_{Ru−Ru} = 0.08 Å). This expansion/contraction of the [Ru6N] framework was found to be reversible.

5. N2 was adsorbed on [Ru6N/MgO and [Ru6N]/Cs+/MgO at 193 K at r_{Ru−N} = 1.95−2.02 Å observed by EXAFS without structural modifications of the [Ru6N] framework.

References and Notes


Supported [Ru-N] Clusters and Reactivities

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