

## CO-Breathing Ruthenium Carbido Clusters on MgO in CO/H<sub>2</sub> Reaction Conditions

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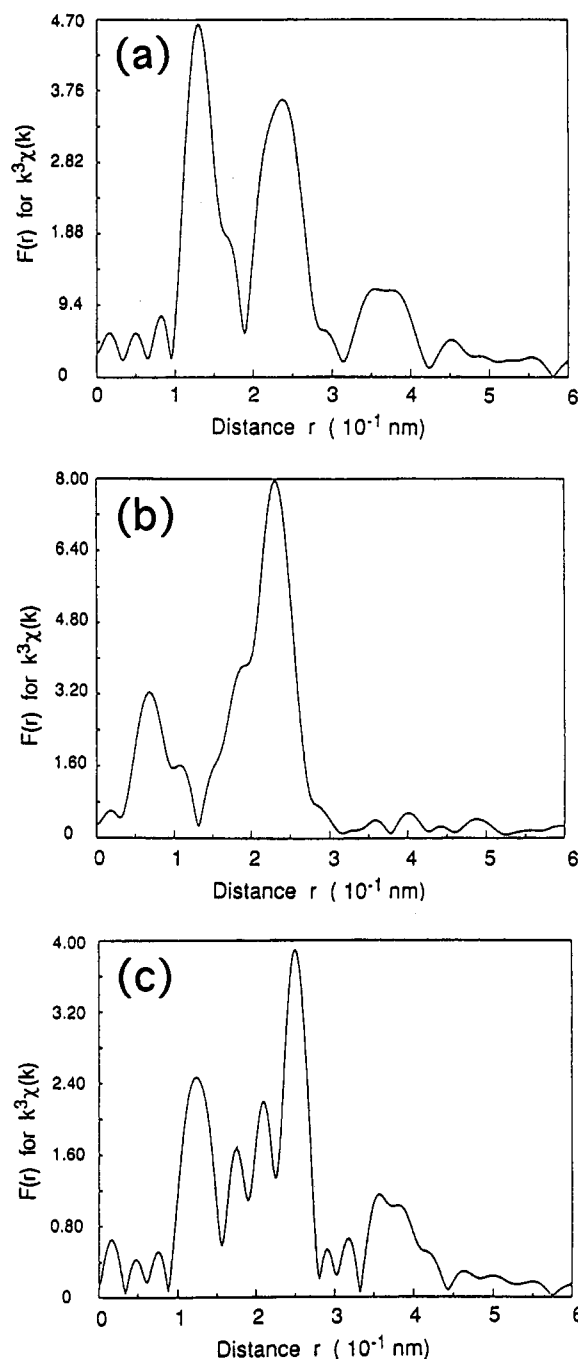
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Supported metal clusters are often transformed to ill-defined microparticles or to degraded species under catalytic reaction conditions,<sup>1-3</sup> though limited examples for reversible decarbonylation of metal clusters have been reported.<sup>4-6</sup> The ruthenium carbido cluster [Ru<sub>6</sub>C(CO)<sub>16</sub>(CH<sub>3</sub>)]<sup>-</sup> supported on Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, MgO, and La<sub>2</sub>O<sub>3</sub>, keeping the hexamer framework [Ru<sub>6</sub>C], catalyzed both ethene hydroformylation to form propanal and CO hydrogenation to form oxygenates with good selectivities, in contrast to the poor catalysis of the usual supported ruthenium catalysts for these reactions.<sup>7</sup> In this study we have found reversible structural change in the cluster framework [Ru<sub>6</sub>C] with interstitial carbon by CO adsorption/desorption under CO/H<sub>2</sub> reaction conditions.

[N(CH<sub>3</sub>)<sub>3</sub>CH<sub>2</sub>Ph]<sup>+</sup>[Ru<sub>6</sub>C(CO)<sub>16</sub>(CH<sub>3</sub>)]<sup>-</sup> (1)<sup>8</sup> was reacted with MgO (200 m<sup>2</sup> g<sup>-1</sup>) as previously reported.<sup>7</sup> The loading of Ru was fixed at 1.8 wt %. The Ru K-edge EXAFS spectra (KEK proposal no. 91012) were analyzed by a curve-fitting method on the basis of the formula of plane-wave single scattering theory<sup>9</sup> using empirical phase shift and amplitude functions extracted from the cluster 1 for Ru-C, Ru-Ru (cluster), and Ru(-C-)Ru bonds, [RuCl<sub>2</sub>(CO)<sub>3</sub>]<sub>2</sub> for the Ru(-C-)O bond, RuO<sub>2</sub> powder for the Ru-O bond, and Ru powder for the Ru-Ru (metallic) bond.

Upon the reaction between the [Ru<sub>6</sub>C(CO)<sub>16</sub>(CH<sub>3</sub>)]<sup>-</sup> cluster and the MgO surface, the methyl ligand of the cluster reacted with the surface hydroxyl group of MgO to form methane at 290 K, accompanied by the release of about two CO ligands from the cluster. The observation of Ru-Ru (nearest neighbor) (0.291 nm, *N* = 4.1) and Ru(-C-)Ru (in diagonal line of octahedral [Ru<sub>6</sub>C] framework) (0.410 nm, 1.0) by EXAFS (Figure 1a and Table I) assures the retention of the [Ru<sub>6</sub>C] structure.

The [Ru<sub>6</sub>C] framework was shrunk by evacuation at 523-623 K, as characterized by *r*<sub>Ru-Ru</sub> = 0.263 nm (Table I, entry b). Besides the Ru-Ru bonds, a shoulder peak at the lower distance side of the Ru-Ru peak appeared in the Fourier transform (Figure 1b) which was assigned to the Ru-O bond at 0.212 nm by the



**Figure 1.** EXAFS Fourier transforms for [Ru<sub>6</sub>C(CO)<sub>16</sub>(CH<sub>3</sub>)]<sup>-</sup>/MgO. (a) Incipient supported species; (b) evacuated at 623 K; and (c) treated in CO (14.6 kPa) + H<sub>2</sub> (14.6 kPa) at 523 K for 1 h.

curve-fitting analysis (Table I). The Ru-O bonds are similar to those for other supported clusters recently reported.<sup>4,10-12</sup> The loss of one CH<sub>3</sub> and two CO ligands in the incipient supported cluster mentioned above implies the advantageous interaction between a cluster face composed of three Ru atoms and the support surface. In this geometric arrangement of the supported cluster, three of the six Ru atoms are able to attach to the MgO surface. The averaged coordination number of the Ru-O bond was observed to be nearly one (1.1; Table I). Thus we propose the [Ru<sub>6</sub>C(μ-OMg)<sub>3</sub>] cluster structure with three bridging oxygen

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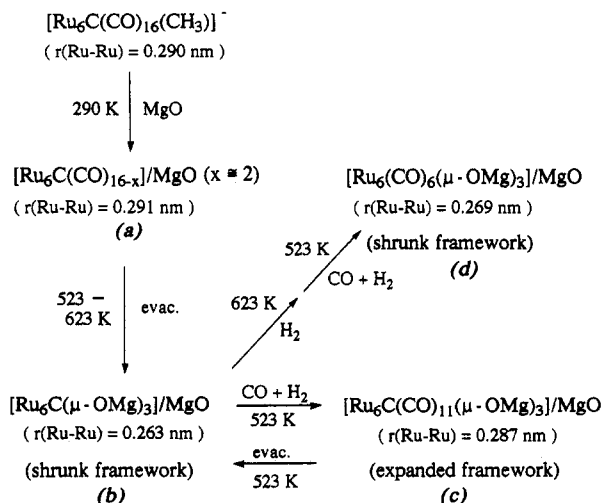
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**Table I.** Results of the Curve-Fitting Analysis of Ru K-Edge EXAFS for  $[\text{Ru}_6\text{C}(\text{CO})_{16}(\text{CH}_3)]^-$  on MgO under Various Conditions<sup>a</sup>

entry <sup>b</sup>	Ru-C			Ru-Ru			Ru(-C-)O			Ru(-C-)Ru <sup>c</sup>			Ru-O			Ru-Ru			Rf <sup>d</sup> /%
	N	r/nm	$\Delta E/\text{eV}$	N	r/nm	$\Delta E/\text{eV}$	N	r/nm	$\Delta E/\text{eV}$	N	r/nm	$\Delta E/\text{eV}$	N	r/nm	$\Delta E/\text{eV}$	N	r/nm	$\Delta E/\text{eV}$	
a	2.1	0.190	-4.5	4.1	0.291	-0.3	2.2	0.301	-1.9	1.0	0.410	0.8							1.7
b				4.2	0.263	-3.4							1.1	0.212	3.1				3.2
c	1.6	0.188	-5.8	3.9	0.287	-3.6	1.7	0.299	-4.3	0.8	0.410	0.8	0.8	0.204	4.5				2.6
d	1.0	0.187	-7.8	4.2	0.269	-5.5	1.2	0.300	-6.0				0.7	0.211	4.7	1.0	0.381	-6.0	1.7
XRD	2.8	0.190		4.0	0.290		2.5	0.302		1.0	0.410								

<sup>a</sup> Each Debye-Waller factor was taken to be equal to that obtained in the analyses for the model compounds. <sup>b</sup> a, incipient supported species; b, a was evacuated at 523–623 K; c, b was treated in CO (14.6 kPa) + H<sub>2</sub> (14.6 kPa) at 523 K; d, b was reduced in H<sub>2</sub> (14.6 kPa) at 623 K and treated in CO (14.6 kPa) + H<sub>2</sub> (14.6 kPa) at 523 K. <sup>c</sup> A multiple-scattering shell corresponding to a diagonal line of octahedral [Ru<sub>6</sub>C] framework. <sup>d</sup> Residual factor =  $\int |k^3\chi^{\text{obs}}(k) - k^3\chi^{\text{calc}}(k)|^2 dk / \int |k^3\chi^{\text{obs}}(k)|^2 dk$ . <sup>e</sup> XRD analysis for  $[\text{N}(\text{CH}_3)_3\text{CH}_2\text{Ph}]^+[\text{Ru}_6\text{C}(\text{CO})_{16}(\text{CH}_3)]^-$ .

### Scheme I. Structure Transformation of the CO-Breathing Ruthenium Carbido Clusters on MgO



atoms incorporated from the MgO surface (Scheme Ib). The shrunk  $[\text{Ru}_6(\mu\text{-OMg})_3]$  cluster on MgO is suggested to be distorted from an octahedral symmetry because of no observation of the multiple-scattering Ru(-C-)Ru peak by EXAFS.<sup>13</sup>

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The Ru(-C-)Ru peak around 0.37 nm (phase shift uncorrected) in the Fourier transform was observed again under CO/H<sub>2</sub> for 1 h at 523 K (Figure 1c). The Ru(-C-)Ru distance (0.410 nm) and its coordination number (0.8) in Table I are almost the same as those for the incipient species. The distance of the nearest-neighbor Ru-Ru bond also increased from 0.263 to 0.287 nm, similar to 0.290 nm for the original cluster (XRD). The coordination number of 1.6–1.7 for Ru-CO implies ~11 carbonyl ligands per [Ru<sub>6</sub>C]. The CO uptake value was consistent with those determined by adsorption measurement and IR peak intensity. The amount of CO adsorption on the [Ru<sub>6</sub>C] clusters on MgO was much larger at 523 K (10.7) than at 290 K (2.9), indicating that the expansion of the cluster framework is an activated process induced by CO uptake. The expanded cluster was shrunk again by CO release by evacuation or at lower pressure of CO at 523 K. The expansion-shrink cycle of the [Ru<sub>6</sub>C] framework reversibly takes place in conjunction with CO breathing.

The octahedral [Ru<sub>6</sub>] structure without interstitial carbon characterized by the next-nearest Ru-Ru bond at 0.381 nm by EXAFS revealed no significant expansion of the [Ru<sub>6</sub>] framework (Table I and Scheme Id). These results demonstrate that the interstitial carbon has a key role, like a central spring to make the cluster structure flexible. Only the expanded [Ru<sub>6</sub>C] clusters on MgO selectively produced oxygenated compounds from CO/H<sub>2</sub>.