CHEMISTRY LETTERS, pp. 511 - 514, 1985.

SPECTROSCOPIC STUDIES ON THE SURFACE STRUCTURES OF RUTHENIUM CATALYSTS DERIVED FROM $Ru_3(CO)_{12}/\gamma\text{-}Al_2O_3$ OR SiO_2

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The surface structures of supported Ru catalysts derived from $Ru_3(CO)_{12}/\gamma\text{-}Al_2O_3$ and $Ru_3(CO)_{12}/SiO_2$ during the preparation procedures were studied mainly by EXAFS (Extended X-ray Absorption Fine Structure) analyses and also by IR and UV/VIS Diffuse Reflectance spectroscopies. A direct evidence was found for bonding feature in metal-support interaction, which explains the large difference in surface structures and catalysis of the Ru species supported on $\gamma\text{-}Al_2O_3$ and SiO_2.

Metal carbonyl clusters provide potential preparations of highly dispersed metal catalysts with well-defined structures. The surface structures and catalytic properties of supported metal catalysts are strongly affected by the nature of inorganic oxide supports. The catalytic activities and selectivities of the supported Ru catalysts prepared from $Ru_3(CO)_{12}$ for carbon monoxide hydrogenation reation markedly depend upon the nature of supports, e.g. SiO_2 or $\gamma\text{-}Al_2O_3$.1) The previous studies on $Ru_3(CO)_{12}$/inorganic oxide systems suggested that a unique interaction should exist between Ru clusters and inorganic oxides.2-8) In the present paper we report the direct information on the surface structures and the metal-support bonding of Ru catalysts derived from $Ru_3(CO)_{12}/\gamma\text{-}Al_2O_3$ and $Ru_3(CO)_{12}/SiO_2$ by means of EXAFS spectroscopy in combination with IR and UV/VIS spectroscopies in connection with the fundamental factors which control their catalytic properties.

$Ru_3(CO)_{12}$ was supported by immersing $\gamma\text{-}Al_2O_3$ (Nishio Industry Co.) or SiO_2 (Fuji-Davisson SiO_2-950) in the pentane solution of $Ru_3(CO)_{12}$ in a flow of high purity (99.9995 %) Ar, followed by evacuation at room temperature. The Ru contents were 2 wt% for $\gamma\text{-}Al_2O_3$ and 1.75 wt% for SiO_2. $\gamma\text{-}Al_2O_3$ and SiO_2 were treated at 573 K and 473 K for 2 h in dry air before use, respectively. The $\gamma\text{-}Al_2O_3$- and SiO_2-supported $Ru_3(CO)_{12}$ clusters were thermally decomposed at 473 K and at 400 K under vacuum, respectively. The reduction of the thermally treated samples were performed with H_2(26.6 kPa) at 673 K for 1 h. EXAFS measurements were carried out by use of Synchrotron radiation at BL 10B of the Photon Factory. The Ru K EXAFS data were analysed by means of curve fitting method employing empirical phase shift and amplitude parameters. The details of analysis will be described elsewhere.1)

Figure 1c shows the Fourier transform of the EXAFS of γ-Al_2O_3-supported $Ru_3(CO)_{12}$ ((1) of Fig. 2). From its curve fitting analysis in Table 1, no shrinkage of the Ru-Ru bond length was found, differing from the cases of the $Fe_3(CO)_{12}/\gamma$-Al_2O_3[9] and $Os_3(CO)_{12}/SiO_2$.[10] The liberation of 1 ~ 2 CO ligands per a cluster molecule during supporting of $Ru_3(CO)_{12}$ onto γ-Al_2O_3 was indicated by gas phase analysis, taking into account the amount of CO adsorbed on the γ-Al_2O_3 used for the present work. The IR spectrum of the species (1) was different from those of $Ru_3(CO)_{12}$ cluster and $[HRu_3(CO)_{11}]^-$, but much similar to those of the surface species $[Ru_3(CO)_{10}(H)(OSi\equiv)]$ on SiO_2 and the model compounds in table 2 though the peak position is shifted to higher frequency. It is most likely from our present results and the previously reported ones[6-8] that the surface cluster (1) was produced on the pretreated γ-Al_2O_3. Figure 1d shows the Fourier transform of the EXAFS data of the species (2) after the thermal decomposition of the species (1). The species (2) which holds two CO ligands per a Ru atom gave the twin ν_{CO} bands at 2080 cm^{-1} and 2030 cm^{-1} which may be assigned to $[Ru^{II}(CO)_2]_n$ species.[11] The two peaks in Fig. 1d can be attributed to Ru-C and Ru---O (carbonyl). No Ru-Ru interaction was found in the region of 2-4 Å. The EXAFS analysis indicated that Ru atoms are mono-atomically dispersed having the coordination of two support oxygen atoms with Ru-O distance of 2.17 Å, in addition to the two CO ligands as shown in Table 1.

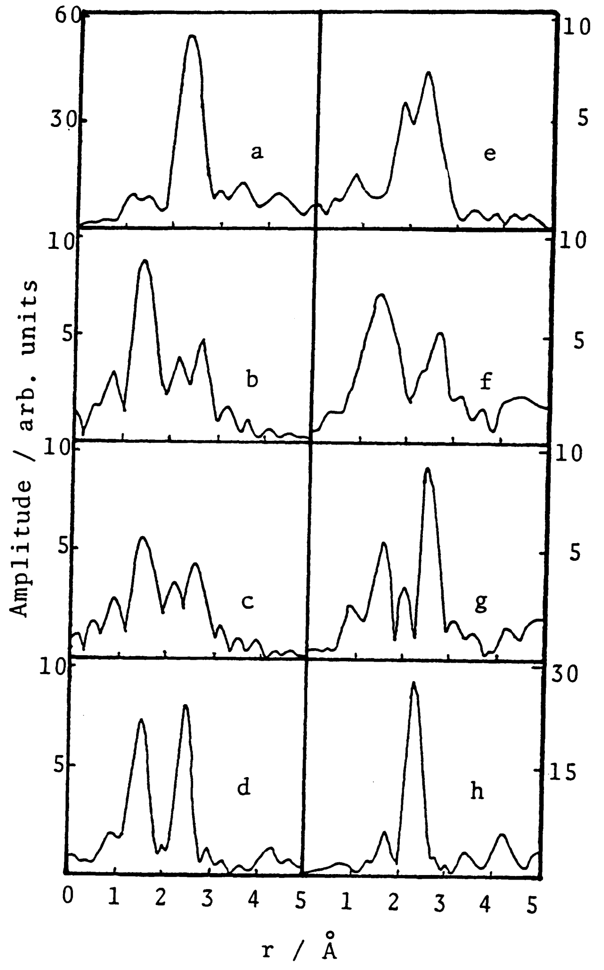

Fig.1. Fourier transforms of k^3-weighted EXAFS data. (a) Ru metal; (b) $Ru_3(CO)_{12}$; (c) (1); (d) (2); (e) (3); (f) (4); (g) (5); (h) (6).

Figure 1e shows the Fourier transform of species (3) after the H_2 reduction of the species (2). The EXAFS data show that Ru-Ru bond was formed again besides Ru-O support bonds to produce unique and small Ru clusters.

The behavior of $Ru_3(CO)_{12}$ clusters supported on SiO_2 was quite different from that of γ-Al_2O_3-supported clusters. Figure 1f shows the Fourier transform of SiO_2-supported $Ru_3(CO)_{12}$ (4). The EXAFS analysis showed that $Ru_3(CO)_{12}$ was supported on SiO_2 retaining the Ru_3 skelton. The IR and UV/VIS spectra were in good agreement with those of $Ru_3(CO)_{12}$ cluster. The Fourier transform of the EXAFS

Table 1. Curve fitting results of Ru K-edge EXAFS data[a,b)]

Sample	Ru-C		Ru--O		Ru-Ru		Ru-o	
	r/Å	N	r/Å	N	r/Å	N	r/Å	N
[$Ru_3(CO)_{12}$]	(1.93)	(4)	3.04	4.2	2.88	2.2		
(1)	1.90	2.5	3.04	3.0	2.89	1.1		
(2)	1.90	1.8	2.97	2.0			2.17	1.8
(3)					2.64	3.1	2.18	1.8
(4)	1.92	4.0	3.05	3.2	2.89	1.1		
(5)	1.84	2.0	2.99	1.7	2.76	1.2		
(6)					2.68	4.4		
Ru metal					(2.68)	(12)		

a) The phase shift and amplitude parameters of Ru-C, Ru-O and Ru-Ru were determined from the corresponding bonds of $Ru_3(CO)_{12}$, RuO_2 and Ru metal, respectively. Those of Ru--O were determined from those of the Fe---O in $Fe(CO)_5$ by assuming the validity of the partial phase transferability.

b) The values in parenthese were the crystallographical data and were used to determine the phase shift and amplitude parameters for the corresponding bonds.

Table 2. IR spectra of surface Ru subcarbonyls and Ru clusters

Compound	λ/cm^{-1}
[$Ru_3(CO)_{12}$]	2060vs, 2032s, 2018m[a)]
(1)	2130w, 2100m, 2075s, 2030vs, 2000sh
(2)	2080s, 2030s
(4)	2066s, 2036s
(5)	2072m, 2040m, 2020sh
[$Ru_3(CO)_{10}(H)(OSi\equiv)$]	2111w, 2077m, 2066s, 2033s br, 1995m[b)]
	2107w,2076s,2066s, 2026s,1991m[c)]
[$Ru_3(CO)_{10}(H)(SC_2H_5)$]	2105m,2064s,2056s, 2025vs, 2012m, 2008s 1994m[b)]
[Et_4N] [$HRu_3(CO)_{11}$]	2075vw, 2018s, 1985s, 1945m, 1702s[d)]

a) In hexane. b) Ref. 7. c) Ref. 8. d) Ref. 12.

data of species (5) after the thermal decomposition of (4) at 400 K (release of 6 CO ligands per a cluster) drastically changed as shown in Fig. 1g. The best-fit result was obtained when three-shell model (Ru-C, Ru---O(carbonyl) and Ru-Ru) was assumed. The fitting was not improved by adding the extra oxygen shell. The resultant Ru-Ru distance is shorter by 0.13 Å than the corresponding distance in $Ru_3(CO)_{12}$; the shortening of the Ru-Ru separation reflects a partial decarbonylation. It is interesting that the coordinatively unsaturated Ru clusters which can hardly be prepared in solution were formed on the solid surface. After the H_2 reduction (species (6)) the Fourier transform showed only one peak due to Ru-Ru, as shown in Fig. 1h. The Ru-Ru bond length and the coordination number were determined to be 2.68 Å and 4.4, respectively, indicating the formation of very small metallic Ru particles.

In summary, we concluded that the interaction of the Ru cluster with the γ-Al_2O_3 support is much stronger than that with SiO_2 support, the former involving definite chemical bonding between metal and support. The interaction through surface oxygen atoms is maintained even in the reducing atmosphere. This chemical bonding retains highly dispersed small Ru clusters and makes the clusters cationic. The C_2-C_5 selectivity (79%) in CO hydrogenation of the Ru/γ-Al_2O_3 catalysts (3) may be due to small cationic Ru clusters chemically attached on the γ-Al_2O_3 surface. On the contrary, the Ru/SiO_2 catalysts (6) with metallic small particles were very active for CH_4 formation.1)

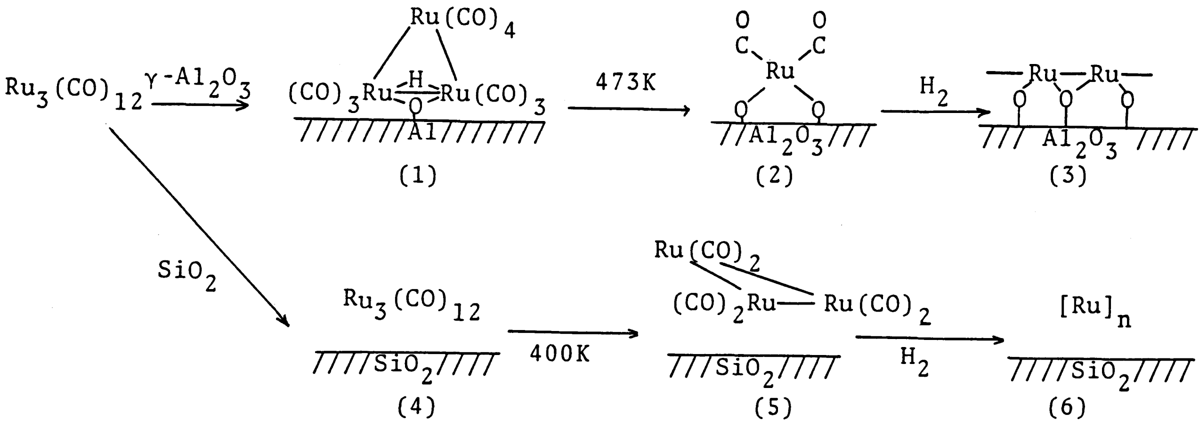

Fig. 2. Transformations of surface species.

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(Received January 21, 1985)