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X-RAY ABSORPTION SPECTROSCOPY OF SILICA-SUPPORTED Ir-Ru BIMETALLIC CLUSTERS

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X-Ray absorption spectroscopy (XAS) studies at the L_{III} absorption edge of Ir and the K absorption edge of Ru were conducted on silica-supported Ir-Ru samples. The samples were prepared by co-impregnation of silica with an aqueous solution of $IrCl_4$ and $RuCl_3$. The XAS data indicate segregation of an Ir-Ru alloy on the surface of the Ir particles. The L_{III} absorption threshold resonance associated with the Ir atom suggests that Ir in Ir/SiO_2 and $Ir-Ru/SiO_2$ is more electron deficient than bulk metallic Ir powder.

Structural characterization of catalysts by XAS has been reviewed.$^{1)}$ Numerous bimetallic clusters such as Ru-Cu,$^{2)}$ Os-Cu,$^{3)}$ Pt-Ir,$^{4)}$ and Ir-Rh$^{5)}$ have been successfully investigated with XAS. One of us has reported$^{6)}$ that silica-supported Ir-Ru bimetallic catalysts were effective for the selective preparation of C_2-oxygenated compounds from synthesis gas. In this system, a strong interaction between Ir and Ru atoms was observed. The structure of similar samples as revealed by XAS is reported here.

All the bimetallic samples used in this study were prepared by co-impregnation of silica (Davison No. 57) with an aqueous solution of $IrCl_4$ and $RuCl_3$ followed by reduction with flowing dihydrogen at 773 K for 3 h. X-Ray diffraction patterns of the $Ir-Ru/SiO_2$ showed very broad peaks, suggesting the presence of clusters of $\leqslant$2 nm. The samples were pressed into self-supporting wafers. The sample wafers were re-reduced at 673 K for 1 h in a controlled atmosphere cell$^{7)}$ equipped with beryllium windows. The XAS data were obtained with the sample in the cell at room temperature in a dihydrogen atmosphere. Reference materials were Ir and Ru powders. The XAS data were collected in transmission mode at the Stanford Synchrotron Radiation Laboratory (SSRL).

Figure 1a shows the XAS data for 4.8% Ir/SiO_2 and 2.5% Ru/SiO_2. Plots of $k^2 \cdot \chi(k)$ vs. k, where k is the photoelectron wave vector and $\chi(k)$ is the normalized extended X-Ray absorption fine structure function (EXAFS), are shown in Fig. 1b for these samples. The Fourier transform of $k^2 \cdot \chi(k)$ yields the radial structure function (RSF) shown in Fig. 1c. The plots of $k^2 \cdot \chi(k)$ vs. k for a 1.0% - 1.5% $Ir-Ru/SiO_2$ sample obtained at the Ir L_{III} edge and the Ru K edge are shown in Fig. 2a. The Fourier transform of these $k^2 \cdot \chi(k)$ functions yielded the RSFs shown in Fig. 2b. The inverse Fourier transform indicated by the solid curves in Fig. 2c was evaluated in order to isolate the contribution of the nearest neighbor atoms to the EXAFS. The dashed curves in Fig. 2c represent the fit of the EXAFS equation to the data. Figure 2c shows the quality of the fit. The curve-fitting procedure used to obtain structural information follows that described by Sinfelt *et al.*[2)]

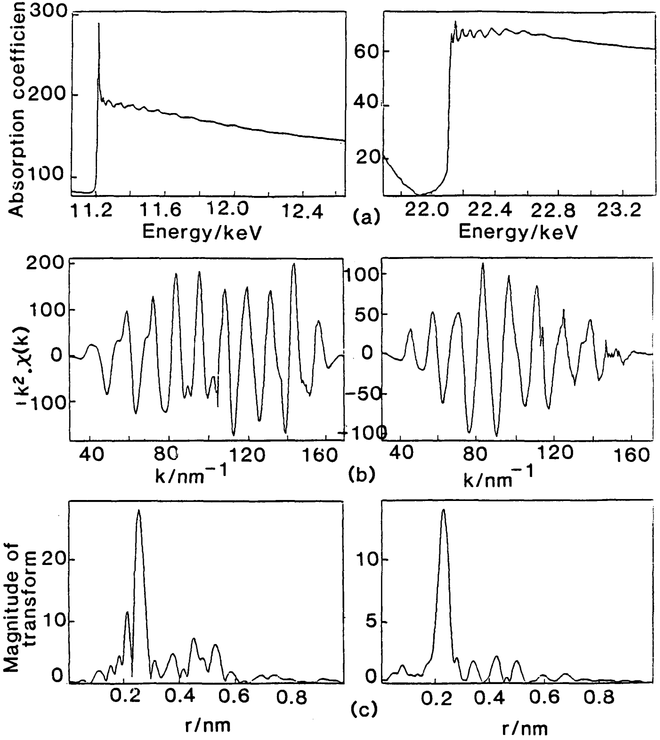

Fig. 1. X-Ray absorption spectra (a), normalized EXAFS functions (b), and associated Fourier transforms (c).
Left: 4.8% Ir/SiO_2 at the Ir L_{III} edge.
Right: 2.5% Ru/SiO_2 at the Ru K edge.

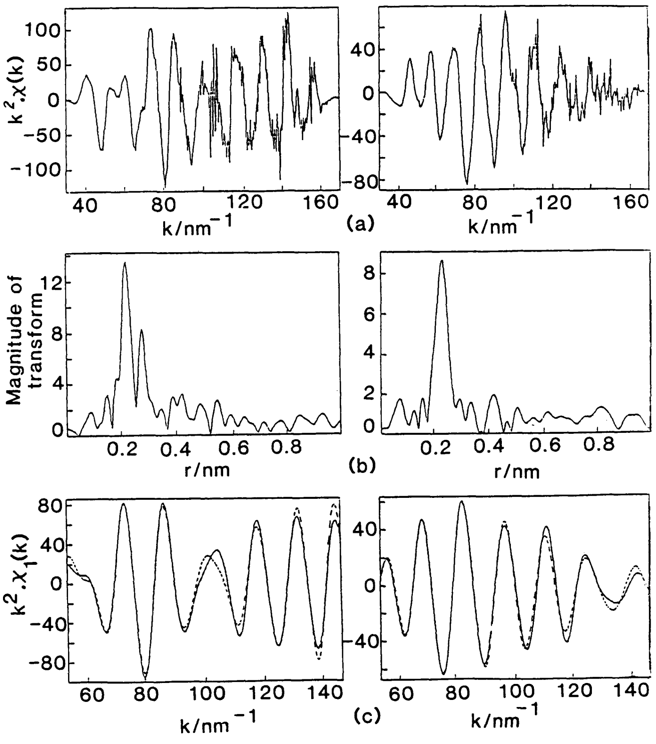

Fig. 2. Normalized EXAFS functions (a), associated Fourier transforms (b), and inverse Fourier transforms with fitting curves (c) for 1.0-1/5% $Ir-Ru/SiO_2$.
Left: Ir L_{III} EXAFS.
Right: Ru K EXAFS.

The final results are summarized in Table 1. The coordination number for Ru in the Ru/SiO_2 sample is smaller than the coordination number for Ir in the Ir/SiO_2 sample, suggesting that Ru forms smaller particles on SiO_2 than Ir.

Table 1. EXAFS Results on Ir-Ru Bimetallic Catalysts

Sample	Metal Loadings/%		Distance/pm			Number of atoms in first coordination shell			
	Ir	Ru	Ir-Ir	Ru-Ru	Ir-Ru	Ir(Ir)	Ru(Ir)a)	Ru(Ru)	Ir(Ru)
Ir powder			271.4			12			
Ru powder				267.8				12	
Ir/SiO_2	3.8	0	271.4			12.4			
Ir-Ru/SiO_2	1.9	1.0	270.2	266.1	267.4	10.6	3.5	4.4	0.2
Ir-Ru/SiO_2	1.0	1.5	270.0	265.1	266.8	10.9	6.5	8.5	1.9
Ru/SiO_2	0	2.0		266.8				10.0	
Ir/SiO_2	4.8	0	271.9			13.8			
Ir-Ru/SiO_2	4.7	2.4	269.6	266.4	267.2	10.7	4.9	7.2	3.5
Ru/SiO_2	0	2.5		267.1				10.6	

a) Ru(Ir) = Ru surrounding Ir.

In the case of bimetallic Ir-Ru/SiO_2 samples, the composition of the nearest coordination shell of atoms about Ir or Ru does not agree with a model in which Ir and Ru form a homogeneous alloy which requires the total number of atoms in the first coordination shell of Ir and Ru to be equal [i.e., Ir(Ir) + Ru(Ir) = Ru(Ru) + Ir(Ru)]. Moreover, the Ru-Ru and Ir-Ru distances are quite similar and they are different from the Ir-Ir distance. These results indicate the presence of two different metal phases, namely, the Ir metal phase and the bimetallic Ir-Ru alloy phase. The coordination numbers suggest that the size of the Ir-Ru alloy phase is smaller than the Ir metal phase. Furthermore, since Ru(Ir) is larger than Ir(Ru), it indicates that the alloy phase is richer in Ru than the bulk Ir-Ru composition. This effect can be expected due to the presence of a separate Ir metal phase. Thus it is likely that either there is formation of separate particles of Ir and Ir-Ru alloy, or there is segregation of Ir-Ru alloy on the surface of Ir particles. The latter case is more probable, because the previous catalytic study of CO hydrogenation showed an increase in CO conversion and selectivity to hydrocarbons heavier than CH_4 with the increase in Ru/Ir ratio.8) It was concluded that Ir and Ru are homogeneously mixed on the surface and no pure Ir or Ru surface exists.

From a study of the L_{III} absorption threshold resonances, information on the chemical environment of the absorbing atom can be obtained.9) The magnitude of the absorption threshold resonance is higher for Ir atoms present in Ir/SiO_2 and and Ir-Ru/SiO_2 than for Ir atoms in bulk Ir powder as indicated in Fig. 3. There was no difference in the magnitude of the absorption threshold resonance between Ir/SiO_2 and Ir-Ru/SiO_2. It can be concluded that Ir on silica appears to be more electron deficient than bulk metallic Ir, and at this point it is not clear why this electron deficiency of Ir is not affected by the presence of Ru.

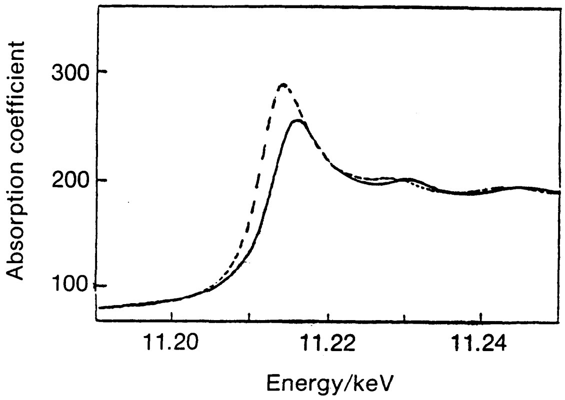

Fig. 3. Effect of silica on the Ir L_{III} X-Ray absorption threshold resonance.
Solid line: Ir powder.
Dotted line: Ir/SiO_2.

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