

X-Ray Photoelectron Spectroscopic Studies of Ruthenium-Oxygen Surfaces

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The technique of X-ray photoelectron spectroscopy (XPS) has been used to study the complex surface chemistry of the ruthenium-oxygen system as a function of temperature and under the influence of Ar^+ and O_2^+ ion-bombardment. Interaction of molecular oxygen and O_2^+ ions with metallic ruthenium produced two forms of oxygen which are not attributable to RuO_2 , RuO_3 and RuO_4 . A variety of species has been identified on RuO_2 . On anhydrous RuO_2 we found a surface layer of RuO_3 present as a gross defect structure of RuO_2 . On commercially available hydrated samples, both the XPS signal for the oxide and for the water could be observed. In addition, a carbon contamination indicated from a mass spectral analysis and microanalysis was characterized as RuOCO_3 . In general the XPS approach was found to be valuable in monitoring the surface concentrations of these species and thus in characterizing the chemical composition of this catalyst surface.

1. INTRODUCTION

The technique of X-ray photoelectron spectroscopy (XPS or ESCA) has been singularly useful in studying the surface of many catalytically and electrochemically important materials. The chemical specificity of the photo-ejected electrons and their semisurface nature are desirable properties which can be used to characterize the various surface species. Details relating to surface structure have now been described for several systems. For example, a specific chemical shift of the O 1s and Ni $2p_{3/2}$ levels has been found for the defect structure (Ni_2O_3) of NiO on the NiO surface (1, 2). In certain cases, polymorphism and hydrates of surface and bulk species can be monitored (3-5). The spacial distribution of various oxidation states of an element throughout the surface region has also been probed by combining XPS measurements with Ar^+ ion-bombardment (1, 6). The O_2^+ ion-bombardment has been useful in XPS identification of surface oxides with gross defect structures of bulk oxides (1, 6) which may have high catalytic activity (7). Other

investigations have been successful in measuring the binding energies of electrons ejected from chemisorbed gases (4, 7-10) including O_2 , H_2O and CO. Hopefully, these studies can lead to a clearer picture of charge distribution for this type of bonding. Information can also lead to identifying the active sites involving heterogeneous catalysis.

Ruthenium dioxide has been used as a redox catalyst for organic and inorganic reactions, an electrode for the electrolytic production of chlorine, and a material in thick film resistors. Very few studies, however, have attempted to determine the nature of any active species responsible for its excellent catalytic properties. In this work, we have sought to characterize various preparations of RuO_2 using XPS and have examined a number of the different oxides. For example, we find that RuO_3 exists as a stable surface species on RuO_2 . In addition, the commercially available hydrated RuO_2 shows a distinct carbon contamination probably due to the carbonate. We have used Ar^+ and O_2^+ ion-bombard-

ment to characterize these oxides and their distribution.

2. EXPERIMENTAL METHODS

XPS spectra were obtained on a Hewlett-Packard 5950A spectrometer using monochromatic Al $K_{\alpha_{1,2}}$ X-rays. The configuration of the spectrometer sample-handling system has been described elsewhere (1). Base pressure in the spectrometer was typically 2×10^{-8} Torr except during heating of hydrated samples where the pressure rose to 5×10^{-5} Torr. An ion beam was focused to about 0.5 cm^2 at normal incidence to the sample surface at gas pressures of about 5×10^{-5} Torr. Binding energies were referenced to the Au $4f_{7/2}$ level of Au at 84.0 eV evaporated *in situ* onto the sample. Charge compensation of nonconducting materials was accomplished by flooding the sample with nearly zero kinetic energy electrons. Measured binding energies were repeatable to ± 0.1 eV. Spectral deconvolutions were performed with gaussian peak shapes using a Dupont Model 610 curve resolver. Peak positions and full-width at half maxima (FWHM) were obtained on well-characterized samples before attempting any deconvolutions of mixed materials.

The RuO_2 was prepared by heating Ru powder or $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ in air at 900°C for 20 hr. RuO_2 was also obtained from Engelhard and MBI. All of these RuO_2 samples were heated in air at 900°C before spectral analysis. A single crystal of RuO_2 was prepared by the chemical transport method (11). The "hydrated RuO_2 " samples were obtained from Engelhard and MBI. Since their composition is seriously in doubt, a number of analyses were performed to check for the types of impurities present. The results are summarized as follows:

Mass spectral analysis: The mass spectrum of gases desorbed from the sample was carried out *in situ* by increasing the temperature from -100 to 300°C and collecting the gases at 50°C intervals in a reservoir attached to the mass spectrometer. Below 100°C the desorbed gas was almost entirely water but above 100°C the $\text{CO}_2/\text{H}_2\text{O}$ ratio increased steadily. No other

impurity gases were detected over this temperature range.

TGA analysis: By heating the sample to 500°C at $9^\circ\text{C}/\text{min}$ a weight loss of 25% was recorded. The weight loss-temperature curve was almost linear from 100 to 430°C but became constant at 500°C .

DTA analysis: Exotherms were observed at 230 and 414°C from the Engelhard samples and at 186 and 286°C from the MBI samples. These results are considerably different than those reported in the literature (12, 13) for hydrated RuO_2 . The contamination in our samples is clearly influencing the dehydration process.

Microanalysis: For hydrated RuO_2 directly from the bottle, C, $2.2 \pm 0.2\%$; H, $2.4 \pm 0.2\%$, and for the sample kept at 10^{-7} Torr for 2 hr, C, $2.2 \pm 0.2\%$; H, $2.0 \pm 0.1\%$ (in the mole ratio of $\text{CO}_2:\text{H}_2\text{O}:\text{RuO}_2$, 0.35:2.3:1 and 0.33:1.8:1, respectively).

The RuO_4 was obtained from Engelhard. Since RuO_4 (mp, 27°C) decomposes to RuO_2 at room temperature in the atmosphere, samples were prepared for spectral analysis by evaporating onto a Au foil held at -80°C at 10^{-6} Torr. This procedure was carried out directly in the instrument to avoid any contamination.

3. RESULTS AND DISCUSSION

The surface chemistry for ruthenium-oxygen surfaces is highly complex, consisting of various stoichiometric oxides, hydrates, as well as carbon impurities. To begin to unravel this large variety of species, we have first attempted to characterize ruthenium powder. As shown in Fig. 1a, by covering a gold surface with a thick layer of Ru powder and bombarding the surface with Ar^+ ions, a surface which is carbon free and showing a minimal oxygen signal can be obtained. The Ru $3d_{5/2}$ and $3d_{3/2}$ peaks exhibit an area ratio close to the theoretical value of 1.50. The significance of the two small oxygen peaks at 531.5 and 529.9 eV (see Table 1) is not completely clear since the background pressure in the instrument is near 10^{-8} Torr and interaction with a variety of background gases is likely. Exposure of this surface to 100 Torr of

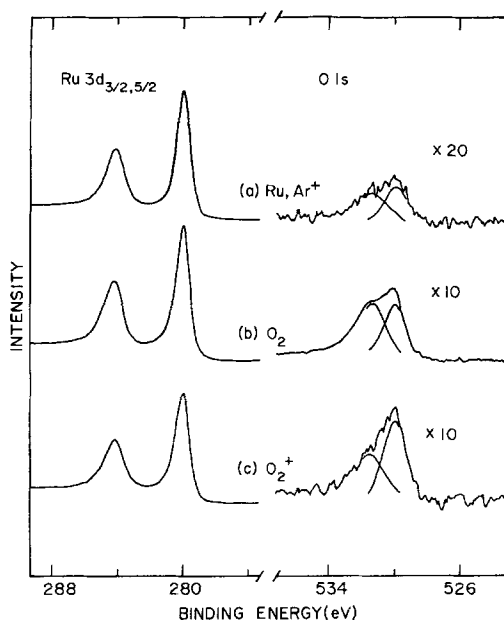


FIG. 1. X-Ray photoelectron spectra of Ru $3d_{5/2}$ and O $1s$ levels of (a) Ru powder exposed to 400 eV Ar^+ ions (6 μA , 10 min), (b) Ar^+ ion-cleaned Ru powder in (a) exposed to O_2 (100 Torr) for 3 hr, and (c) Ar^+ ion-cleaned Ru powder prepared as in (a) exposed 400 eV O_2^+ ions (3 μA , 5 min).

oxygen for 3 hr *in situ*, however, increases the intensity of these peaks by a factor of four while leaving the Ru peaks almost unaffected (Fig. 1b). This observation strongly suggests the oxygen signal results from the reaction of ruthenium metal with molecular oxygen rather than with trace H_2O , CO or CO_2 impurities. Note, also, that oxidation using 400 eV O_2^+ ions, a more vigorous oxidative procedure, emphasized the 529.9 eV peak. Since further exposure to O_2 or O_2^+ ion does not increase the O $1s$ intensity any further, we suspect both species are present only within the first couple layers of the surface. The O $1s$ /Ru $3d_{5/2}$ intensity (area) ratios are about 0.9 and 0.1 for RuO_2 and O_2 or O_2^+ -exposed Ru shown in Fig. 1, respectively. Since the ratios for a compound with a composition of RuO will be about 0.9/2, the composition of the O_2 or O_2^+ -exposed Ru is roughly equivalent to $\text{RuO}_{0.2}$ if oxygen is distributed homogeneously in the surface region of the XPS effective depth which is about 30 Å (14). However,

TABLE 1
BINDING ENERGIES (eV)^a OF Ru-OXYGEN SYSTEM

	Ru $3d_{5/2}$	O $1s$
Ru	280.0	
$\text{RuO}_{\text{ads}}^b$		531.5
RuO^b		529.9
RuO_2	280.7	529.4
RuO_3	282.5	530.7
RuO_4	283.3 ^c	^d —
$\text{RuO}_2 \cdot \text{XH}_2\text{O}^e$	281.4	529.3 (oxide)
		530.5 (H_2O)
RuOCO_3^e		530.5 (CO_3^{2-})

^a Referenced to Au $4f$ level (84.0 eV) of a discontinuous gold film evaporated onto the sample.

^b See discussion in text.

^c Referenced to partially decomposed RuO_4 .

^d Could not be determined because of strong H_2O peak. Note that RuO_4 was evaporated onto the probe at -80°C .

^e See discussion in text. The binding energies for the Ru $3d_{5/2}$ and the O $1s$ electrons in RuOCO_3 not related to CO_3^{2-} are difficult to determine due to the low relative concentration of this species.

since oxygen is present primarily within the first couple layers of the surface, the amount of oxygen in the O_2 or O_2^+ ion-exposed Ru shown in Fig. 1 will be more than that in 2 layers of RuO or more than one layer of oxygen atoms. Since the lower O $1s$ binding energy indicates the greater interaction between Ru and O, it is likely that the 529.9 eV oxygen exists beneath the surface, perhaps as RuO , while the 531.5 eV peak arises from chemisorbed atomic oxygen. Clearly two oxygen forms are observable but from the XPS data alone, it is not possible at present to more explicitly describe the structural differences between them. Although the splitting (1.1 eV) of the O $1s$ level into two components with intensity ratio of 2:1 is observed in free molecular oxygen due to spin splitting (15), the two O $1s$ peaks observed in Fig. 1 cannot be attributed to adsorbed molecular oxygen. It is to be noted that adsorption will decrease the spin splitting whereas the observed splitting is 1.6 eV and the intensity ratio of two O $1s$ peaks from the Ru surface varies.

Commercially obtained or freshly prepared " RuO_2 " powder invariably contains

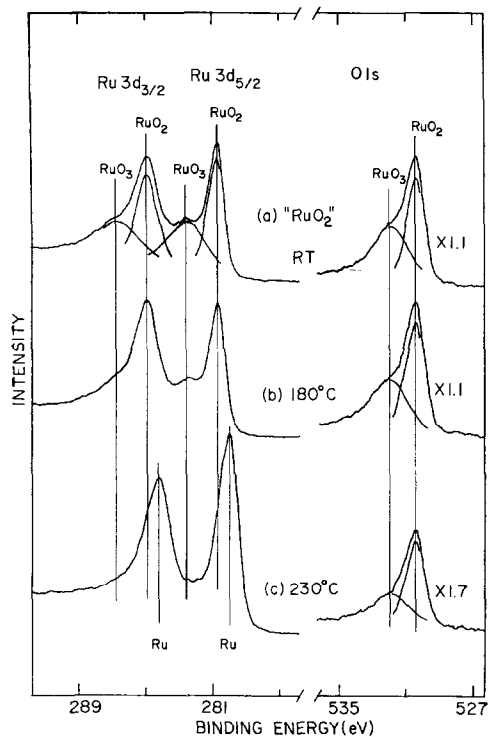
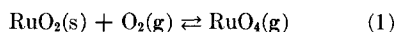
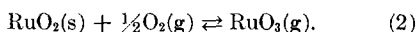


Fig. 2. X-Ray photoelectron spectra of Ru $3d_{3/2,5/2}$ and O $1s$ levels of RuO_2 powder kept at various temperatures *in situ*. The temperature was raised at the rate of about $1^\circ\text{C}/\text{min}$.

an additional Ru compound as indicated by the high binding energy structures at 282.5 eV in the Ru $3d_{5/2}$ region and at 529.4 eV in the O $1s$ region, as shown in Fig. 2a. A single crystal of RuO_2 also showed similar spectra. Note that the Ru $3d_{5/2}$ binding energy value for RuO_2 is clearly distinguishable from that of Ru metal. The following reversible reactions have been reported to occur when RuO_2 is heated in oxygen (16, 17):



and



The predominant species in the gas phase at temperatures greater than 1000°C is RuO_3 and at lower temperatures ($\sim 800^\circ\text{C}$) is RuO_4 . These results suggest that RuO_3 and/or RuO_4 may be present on the surface of RuO_2 as intermediates. Since most of the high binding energy species may be

formed when the sample is being cooled, we first believed that the set of high binding energy Ru peaks was due to a surface layer of RuO_4 . As discussed below the high binding energy species is *not* attributable to hydrate or carbonate. To check the hypothesis concerning RuO_4 , we obtained the spectra of an authentic RuO_4 sample on a cold tip held at -80°C . The sample exhibited a large charging effect and reproducible binding energies were difficult to obtain even with the electron flood gun turned on. In addition, the O $1s$ region was badly contaminated with adsorbed water which is common at this temperature. However, as shown in Fig. 3a and b, the sample decomposes after several hours to a mixture of RuO_4 and RuO_2 , allowing the Ru $3d_{5/2}$ binding energy for RuO_4 to be evaluated as 283.3 eV. From this observation, it is clear that the sample in Fig. 2a does not contain RuO_4 since the Ru $3d_{5/2}$ binding energy for the additional species is 282.5 eV. Therefore, we suspect this additional species is RuO_3 . Note the O $1s$ peak associated with this species is also clearly observable. Since

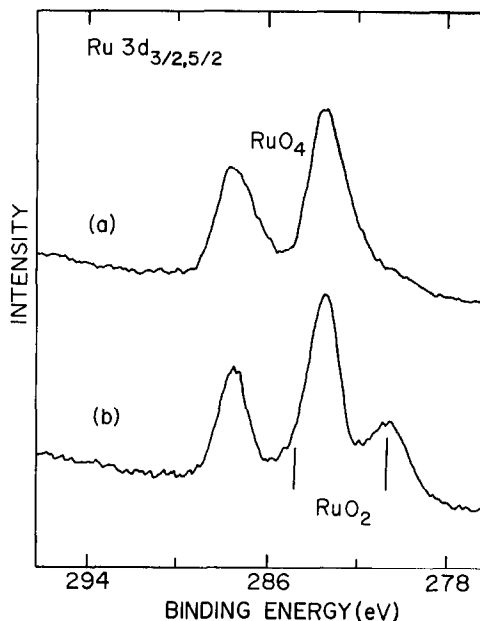
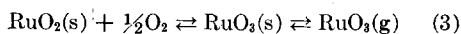
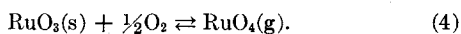


Fig. 3. X-Ray photoelectron spectra of Ru $3d_{3/2,5/2}$ and O $1s$ levels of (a) RuO_4 freshly evaporated onto a Au blank held at -80°C at 10^{-6} Torr *in situ*, and (b) sample in (a) kept at $-50\sim -80^\circ\text{C}$ for 3 hr *in situ*.

the RuO₃/RuO₂ O 1s intensity (area) ratio is about one for "RuO₂" samples, the thickness of RuO₃ is roughly equivalent to 4 molecular layers. This strongly suggests that RuO₃ observed is not simply an oxygen-chemisorbed RuO₂, but a gross defect structure on the surface of RuO₂. These XPS results for RuO₂ samples agree with others. According to Pizzini *et al.* (18), RuO₂ prepared by thermal decomposition of RuCl₃·3H₂O in air at 800°C shows a Ru deficit and an oxygen excess. Sommerfeld and Parravano (19) have reported that interaction of oxygen with RuO₂ is dissociative. The XPS results suggest that the reactions (1) and (2) may at least partially occur as follows:



and



The stability of the RuO₃ species can be tested by varying the substrate temperature *in situ*. At 180°C, for example, the relative amounts of RuO₃ to RuO₂ remain essentially constant (Fig. 2b). At 230°C, this ratio still does not change noticeably even though the system is losing oxygen, forming a mixture of Ru metal, RuO₂ and RuO₃. Apparently as oxygen is lost, the equilibrium between RuO₂ and RuO₃ is maintained at least on the surface of RuO₂. Since O₂⁺ ion-bombardment on the RuO₂ samples enhanced the O 1s peak (RuO₃) at 530.7 eV, this peak cannot be correlated with adsorbed gases such as H₂O and CO₂ or hydrate and carbonate (see below). It is interesting that the amount of RuO₃ on RuO₂ does not decrease with increased heating in air, whereas Ni₂O₃ (a gross surface defect structure of NiO) on NiO disappeared after prolonged heating (1, 2). This difference is probably due to a continuous evaporation of the surface of RuO₂ as RuO₃ and RuO₄. Annealing of the surface is therefore inhibited by this chemical reaction.

XPS analysis of both hydrated RuO₂ samples obtained from Engelhard and MBI show a complex structure in the O 1s region. This observation certainly agrees with the mass spectral results described earlier

which showed that both CO₂ and H₂O are desorbed from heated RuO₂ samples. Since no other measurable XPS signals are seen for any possible cations other than Ru⁴⁺ (i.e., Na⁺, K⁺, etc.), the CO₂ is most probably associated with this cation. We have sought further information concerning the structure of the bound CO₂: whether it is best described as a surface chemisorbed CO₂, a surface CO₃²⁻ or a bulk CO₃²⁻. Although the XPS data cannot answer this question directly, following spectral changes with changing environmental conditions often can produce added information. For this system, XPS spectra were recorded for samples heated *in situ* and for samples bombarded with Ar⁺ or O₂⁺ ions. These techniques have already been shown to be valuable in elucidation of structure and distribution of oxides at metal surfaces (1, 6) and we hoped to be able to desorb or sputter H₂O and CO₂ selectively from the surface region to obtain similar information.

For the hydrated RuO₂ samples at temperatures below 100°C a 3d_{5/2} peak at 280.7 eV (RuO₂) is not seen (Fig. 4a and b) suggesting that each RuO₂ unit in the surface region is associated with H₂O and/or CO₂. In the O 1s region at least two peaks are observed which must be assigned to the oxygen from RuO₂, CO₂ and H₂O. Based on mass spectral and microanalysis data, any XPS changes due to heating at ~100°C are primarily attributable to the loss of H₂O. Heating of the sample to 130°C shifts the Ru 3d_{5/2} peak maximum from 281.4 eV to 280.7 eV [due to the appearance of a peak at 280.7 eV (RuO₂)], decreases the intensity of the 530.5 eV O 1s peak, and makes the 529.5 eV peak distinctive (Fig. 4c). We therefore attribute the Ru 3d_{5/2} 280.7 eV peak and the reduced portion of the 530.5 eV peak to the dehydration of the sample, and the left portion of the 530.5 eV peak to CO₂. Further heating did not change the 529.3/530.5 eV peak intensity ratio although their total intensity decreased because of decomposition as indicated by the appearance of metallic Ru peaks. Thus, CO₂ is not lost without a corresponding reduction of Ru⁴⁺ to Ru metal strongly suggesting that CO₂ is not in the

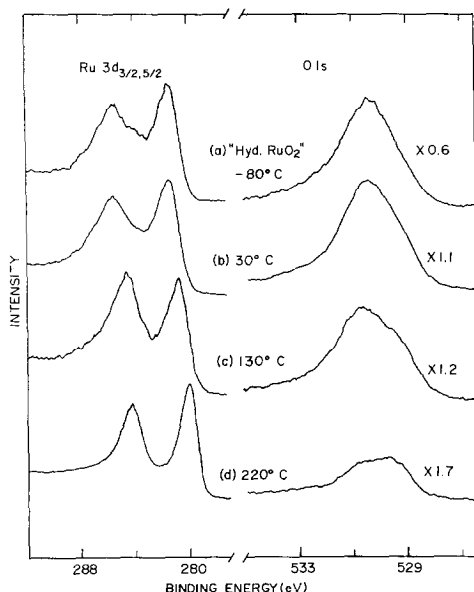


FIG. 4. X-Ray photoelectron spectra of Ru $3d_{3/2,5/2}$ and O $1s$ levels of "hydrated RuO_2 " (Engelhard) kept at various temperatures *in situ*. The temperature was increased at the rate of about $1^\circ\text{C}/\text{min}$. The spectra of "hydrated RuO_2 " at 60°C are shown in Fig. 5a. Intensity factors are given in terms of peak height.

chemisorbed state but rather in the CO_3^{2-} state.

When the hydrated RuO_2 was bombarded with Ar^+ ions, the reduction of Ru^{4+} to metal was observed in the Ru $3d$ region but the O $1s$ band shape was not changed. This indicates that Ar^+ ion-bombardment cannot desorb or sputter CO_2 and H_2O preferentially without reduction of the oxide and that CO_2 is firmly bound to the oxide oxygen. To desorb CO_2 and H_2O avoiding reduction, the sample was bombarded with 400 and 900 eV O_2^+ ions. As shown in Fig. 5, O_2^+ ion-bombardment produced anhydrous RuO_2 . Since the $530.5/529.3$ eV intensity ratio decreased with increasing kinetic energy of O_2^+ ions and since 400 and 900 eV O_2^+ ions should penetrate a mean distance of about 13 and 25 Å, respectively (20, 21), CO_3^{2-} is present not only on the surface layers but also below this region. We can best conclude that the hydrated RuO_2 obtained from Engelhard and MBI is composed of hydrated RuO_2 and a CO_3^{2-} -

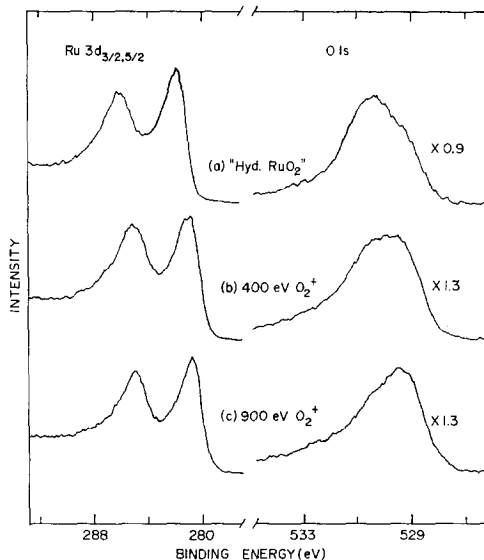


FIG. 5. X-Ray photoelectron spectra of Ru $3d_{3/2,5/2}$ and O $1s$ levels of (a) "hydrated RuO_2 " (Engelhard), (b) sample in (a) exposed to 400 eV O_2^+ ions ($3 \mu\text{A}$, 5 min), and (c) sample in (b) exposed to 900 eV O_2^+ ions ($3 \mu\text{A}$, 10 min). Further exposure of sample in (b) to 400 eV O_2^+ ions caused only a small change in the spectra. The temperature of samples was 60°C . Intensity factors are given in terms of peak height.

like Ru species, possibly RuOCO_3 , which is in all likelihood also hydrated.

4. CONCLUSIONS

The XPS technique has unique sensitivity and inherent chemical specificity for characterizing the complex nature of oxide surfaces and for aiding in understanding heterogeneous catalytic reactions. For example, in the ruthenium-oxygen system, seven different species could be separately noted including the defect structure of RuO_3 on RuO_2 . The XPS observation that surface defect structures can indeed be directly monitored as a function of environmental conditions is not unique to the Ru-oxygen system. We have previously reported that Ni_2O_3 exists on the NiO surface as a defect structure (1, 2). Evidence also suggests that Cu_3O_2 on Cu_2O (unpublished data) and MoO_x ($2 < x < 3$) (6) can be monitored with equal ease. We

suspect, in general, that this approach will be quite valuable in direct spectroscopic characterization of active sites in many catalytically important systems.

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