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Studies of Fluorine in Catalysts with Ultrasoft X-Ray Absorption Spectroscopy

S. M. DAVIS,* G. D. MEITZNER,†,[1] D. A. FISCHER,‡ AND J. GLAND§

**Exxon Research and Development Laboratories, Exxon Research and Engineering Company, Baton Rouge, Louisiana 70821-2226; †Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801; ‡Materials Science and Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, Maryland 20899; and §Chemistry Department, University of Michigan, Ann Arbor, Michigan 48109-1055*

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The structures of fluorine-doped alumina catalyst powders have been studied by fluorescence yield ultrasoft X-ray absorption spectroscopy. The results presented here demonstrate that important local structural information can be obtained by the technique. It is established that fluoride ions are substituted for oxygen in alumina at low concentration of adsorbed fluorine. For doping levels larger than those required for saturation of the monolayer, we observed AlF_3-like features in the radial structure function. These results are in agreement with previous observations of bulk AlF_3 in aluminas with high levels of fluorine doping. The fluorescence yield method is well suited for determining structures of a wide range of ceramic materials. © 1993 Academic Press, Inc.

The addition of halogen raises the acidity and modifies the catalytic activity of alumina. Promotion by fluoride of oxide solid acid catalysts (including aluminas) has been reviewed (*1*, *2*). The catalytic consequences of fluoride treatment (*3–6*) and the effect of fluoride on the physical structure of the alumina surface (*7–12*) have been the subjects of investigation. There is poor agreement among different groups as to the optimum loading of fluoride for promotion of either cracking or isomerization.

Structural studies at low fluoride loading, by use of probe reactions and adsorption of ammonia, have shown a reverse correlation of hydroxyl group density with fluoride loading, suggesting that adsorbed fluoride displaces surface hydroxyl groups (*5*). Structural studies at fluoride loadings over about 6 wt% have relied instead on X-ray diffraction to identify hydroxy fluoride phases or bulk aluminum fluoride (*7*, *11*). In one study where catalysts were prepared with AlF_3 supported on Al_2O_3, no diffraction lines of AlF_3 were detectable at 8 wt% fluoride (*11*), although in some cases an AlF_3 phase is detectable at lower fluoride loading. However, it is known that a fluoride monolayer can be formed by about 6 wt% fluorine on an alumina with around 200 m^2g^{-1} of surface area, at which point hydroxyl groups are depleted and the catalytic activity and surface properties are similar to pure AlF_3 (*5*). There has been no direct information on the physical environment of fluoride ions at low fluoride loading on alumina, where its promotional effect is strongest.

In this communication we report the development and application of soft X-ray fluorescence-yield extended X-ray absorption fine-structure spectroscopy (EXAFS) as a new experimental approach to structural study of fluoride-promoted aluminas. This technique builds on earlier work in fluorescence-yield near-edge X-ray absorption spectroscopy (FYNES) (*13–15*) and is illustrated by applications to oxygen and fluorine *K*-shell EXAFS in γ-Al_2O_3, AlF_3, and fluorided aluminas. These examples dem-

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[1] To whom correspondence should be addressed.

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onstrate that soft X-ray EXAFS is a practical new approach for characterizing the local atomic environment of light elements in high-surface-area ceramic powders representative of commercial-type catalysts. In contrast to partial-electron-yield EXAFS measurements, fluorescence-yield detection eliminates difficulties associated with predominant surface sensitivity and differential charging of insulating materials, rendering this technique especially well suited for studies of viable catalysts that are most commonly based on high-surface-area nonconducting refractory oxides. While much progress has been made in developing EXAFS for studies of local atomic structure (*16*, *17*), elements with atomic number below 16 have generally not been accessible due to vacuum requirements and the short absorption and scattering lengths of the soft X-rays. Consequently, the light elements which represent the building blocks of catalyst supports, and also some poisons, reactants, and promoters, have not been amenable to structural analysis by this approach.

METHODS

X-ray absorption spectra were measured at National Synchrotron Light Source, Brookhaven National Laboratory, on beamline U-1. The beamline is equipped with an extended range grasshopper monochromator and a fluorescence-yield end station described previously (*14*). This chamber consists of a window valve, ballast region, small volume sample chamber, and soft X-ray proportional counter. The chamber could be isolated from the synchrotron ring by a combination of the window valve and a ballast region. The window was made of aluminum, about 1000 Å thick, supported on a high transmission nickel grid that was in turn mounted on the center of a 2.75-inch gate valve. The transmission for the window was about 50% at 500 eV. The proportional counter incorporated cylindrical electrode geometry with a curved side window, providing the geometry for optimum energy resolution (*14*). The energy dispersive characteristics of the proportional counter were especially useful in studies of F/Al_2O_3 for filtering fluorine $K\alpha$ fluorescence from background oxygen $K\alpha$ fluorescence, using standard pulse height analysis techniques (*13*).

The sample chamber was equipped with a rotatable manipulator upon which thin pressed wafer samples (approximately 1 cm × 0.5 mm) could be mounted and heated or cooled over the temperature range from 125 to 775 K. The fluorided alumina samples contained 1 and 7 wt% fluorine, and were prepared by incipient wetness impregnation of Cyanamid γ-Al_2O_3 with NH_4F, followed by air calcination at 725 K. The AlF_3 was obtained from Aldrich. New samples were dehydrated *in situ* prior to data collection by heating to 625 K at 10^{-7} Torr for 15 min. The samples were then cooled to about 125 K. The resolution of the photon beam from the monochromator at the fluorine K edge, at 697 eV, was about 2 eV. The increment between data points was 1 eV, except it was 0.5 eV through a narrow range across the near-edge region. Several sequential spectra were averaged prior to analysis. Each data point corresponds to about 30,000 counts. The ultimate data collection time for each summed spectrum was about 4 h.

RESULTS AND DISCUSSION

A fluorescence-yield X-ray absorption spectrum for 7 wt% fluoride on γ-Al_2O_3 is shown in Fig. 1. Figure 1 also includes the spectrum from fluorine in AlF_3. The oxygen K edge at 543 eV contributes a high background at the position of the fluorine K edge in the case of the fluorided alumina sample. Figure 2 shows the background-subtracted fluorine EXAFS from the spectrum of 7 wt% fluorided alumina in Fig. 1, and also the EXAFS from fluorine in 1 wt% F/Al_2O_3.

The radial structure function (RSF) of oxygen EXAFS, from oxygen in γ-Al_2O_3, is shown in Fig. 3. The RSF, calculated by Fourier transforming K^1-weighted EXAFS

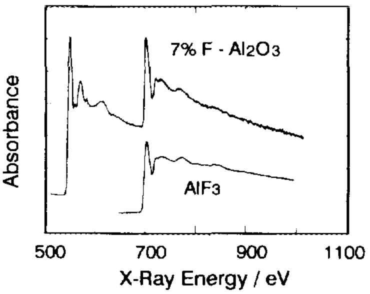

FIG. 1. X-ray absorption spectra from fluorine in AlF_3 (lower) and from oxygen and fluorine in a sample of 7 wt% F/Al_2O_3 (upper). In the upper spectrum the oxygen *K* edge is to the left, at 540 eV. The fluorine *K* edge appears in both spectra at 700 eV.

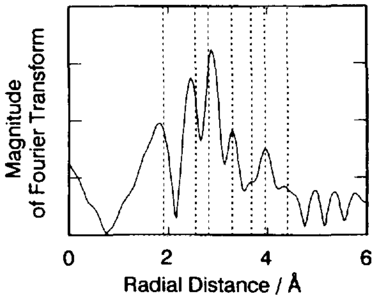

FIG. 3. The phase-corrected Fourier-transformed EXAFS (RSF) from oxygen in γ-Al_2O_3. The vertical lines are drawn at the positions of actual oxygen and aluminum coordination spheres about oxygen in the alumina (*19*, *20*).

in the range from 0.5 to 11.1 $Å^{-1}$, has been phase-corrected using the F–F phase-shift function. The F–F phase-shift function is a reasonable approximation to the O–O and O–Al phase-shift functions, since these functions change incrementally with atomic number (*18*), and fluorine lies between oxygen and aluminum in atomic number. Figure 3 has vertical lines drawn on it to show the positions of oxygen and aluminum coordination spheres determined for α-Al_2O_3 by X-ray diffraction (*19*, *20*). The structures of the γ- and the α-phases of Al_2O_3 are both based on cubic close-packed lattices.

Oxygen and fluorine EXAFS from pure γ-Al_2O_3 and pure AlF_3, respectively, were standards for interpreting our results. The Fourier-transformed EXAFS (RSFs) from the oxygen in γ-Al_2O_3 and from the fluorine in AlF_3 are shown by the solid lines in Fig. 4. These were calculated using the data between 0.5 and 8.8 $Å^{-1}$. Analyses of EXAFS traditionally discard the part of the spectrum at least below 2 $Å^{-1}$, to avoid spectral

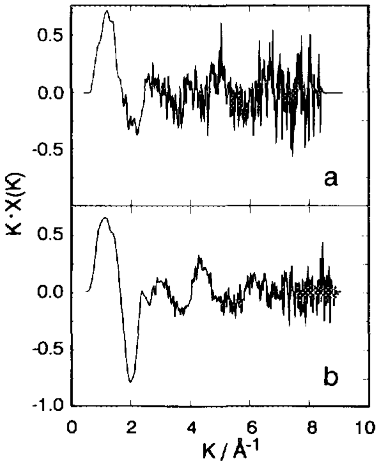

FIG. 2. The K^1-weighted EXAFS from the fluorine *K* edge (a) from fluorine in 1 wt% F/Al_2O_3, and (b) from fluorine in 7 wt% F/Al_2O_3 (from the spectrum in Fig. 1).

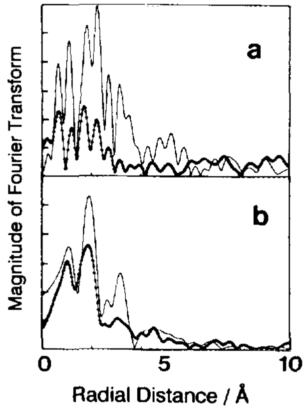

FIG. 4. Comparisons of RSFs from standards and from catalyst samples. (a) The RSF from oxygen in Al_2O_3 (———) is compared to the RSF from fluorine in 1% F/Al_2O_3 (◆◆◆◆). (b) The RSF from fluorine in AlF_3 (———) is compared to the RSF from fluorine in 7% F/Al_2O_3 (◆◆◆◆).

features that result from behaviors of low-energy electrons not compatible with the most common level of approximation. The very-low-K data were used because of the short range of the EXAFS in all spectra, and because we found that the new features introduced in the Fourier transforms by inclusion of low-K data corresponded to coordination spheres actually present in the standard compounds, as demonstrated by X-ray diffraction. It should also be noted, in this context, that the EXAFS signal from light elements such as fluorine and oxygen decays monotonically, and very sharply compared to EXAFS from heavier elements (*18*). The extreme low end of the spectrum therefore contains virtually all the signal in this case. The peaks in the RSFs in Fig. 4, corresponding to coordination spheres about the oxygen or fluorine absorber atoms, are not phase-corrected and therefore appear at positions shorter than their true radii.

The RSFs from fluorine in 1 and 7 wt% fluoride on γ-Al_2O_3 are superimposed on the RSFs from oxygen in γ-Al_2O_3 (upper field) and from fluoride in AlF_3 (lower field), respectively, in Fig. 4. The striking correspondence of features in the two cases indicates that fluoride is substituted for oxygen at low fluorine loading, but mainly contained in an AlF_3-like phase at high loading. Quantitative analysis to be presented in a future paper for catalysts with variable preparation and fluoride loadings shows that both phases are present in both materials, but their relative proportions are reversed. This is consistent with reports that the ratio of fluoride ions introduced to hydroxyl groups replaced slightly exceeds 1 below 2 wt% fluoride loading, although the excess of fluorides needed to replace a single hydroxyl group becomes quite large at high fluoride loading (*5*, *9*).

Fluoride treatment of aluminas has been reported to result in the formation of aluminum hydroxy-fluorides (*7*). Those compounds may be present in both the 1 and 7% fluorided aluminas represented by Fig. 4, since the bulk structures and Al–F distances are similar (*21*, *22*) in the compounds $Al(F_{3-x}(OH)_x)$ and AlF_3. The aluminum hydroxy-fluorides with x in the range of 1 to 2 lose waters of hydration but are otherwise stable up to 775 K; they disproportionate completely to Al_2O_3 and AlF_3 by 875 K (*21*). Information presented here does not reject the possibility that catalytically active acidic sites are associated with compounds of the type $Al(F_{3-x}(OH)_x)$. Complementary studies with ^{19}F-NMR spectroscopy or other structure-sensitive methods would be valuable to clarify this point.

The shape of the RSF discriminates, in principle, between surface and bulk substitution for the low-fluoride-loading phase. Actually, the volume-weighted radial structure functions reflect structure in a sphere centered on fluoride and penetrating into the bulk. The surface comprises a small volume fraction of the material described by the RSF, and the surface contribution is hard to discriminate. However, substitution of fluoride for hydroxyl groups would maintain charge balance, and would also help explain the limited capacity of aluminas for effective fluoride.

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