Deciphering the structure of WO_3 on SBA-15 by XAFS and *Feff* simulation

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Introduction

Recently, the structure of Re_2O_7 on ZSM-5 was revealed based on analyses of the results of Raman spectroscopy and X-ray absorption fine structure (XAFS).[1] Generally, in XAFS measurements the first shell (such as Re-O or W-O) structure is straightforward to determine, and useful to construct an atomic structure model. However, second shell information from XAFS data, even the distance between specific atoms which can describe how the metal oxides are connected to the support, e.g. M-O-Si, is much more difficult to determine because of significant noise in the spectra at high wave vector, *k*, and spectral smearing due to multiple scattering.

Our group has reported a synthetic method for preparing supported transition metal oxide catalysts using a solution atomic layer deposition (ALD) approach[2] originally established for thin film deposition.[3] ALD processes offer the potential advantage to control catalyst structures at the atomic level. This ALD approach has been successfully applied to prepare well dispersed WO_3, V_2O_3 and Mo_3O_4 nanoparticles on mesoporous supports, which also results in improved catalytic performance.[2] However, the detailed structure of these ALD-prepared metal oxide on mesoporous silica catalysts have not been adequately determined. In the present work, we report the atomic structure of WO_3 supported on SBA-15 (~$1.33WO_3/nm^2$, prepared by ALD)[2], obtained from detailed XAFS data analyses

Materials and Methods

In order to get the long range structural information, the XAFS data was collected with good signal to noise ratio at Beamline 18B at the National Synchrotron Light Source and more than three data sets on the same sample were merged. The XAFS data were analyzed with IFEFFIT[4] using the *ab-initio Feff*6[5] program following a method described in the literature.[6]

Results and Discussion

Figure 1 illustrates the WO_3-like single unit structure found from the best fit (solid lines) to the experimental XAFS spectrum and its corresponding Fourier transform (open circles) of the ALD-prepared supported catalyst. The single scattering contribution at 0.360 nm and 0.367 nm was found to come from W-Si and W-W scattering for the ALD-prepared WO_3 sample. Estimated distances between two oxygens in the modeled O-W-O structure was 0.267 nm, consistent with the O-O distance in triclinic WO_3. Also, the Si-O bond distance was found to be 0.177 nm assuming almost collinear W-O-Si bonds, consistent with the Si-O bond distance in mesoporous silica, 0.162 ± 0.020 nm.

Figure 2 shows a scheme for the ALD process that includes possible WO_3 structures derived from the curve fitting analysis of W L_{III} XAFS. It is well known that the surface of SBA-15 is undulated, with large curvature pores as well as smaller openings that interconnect the large pores. Thus, WO_3 units will attach to these curved surfaces and may form dimeric species or higher order connected structures as illustrated in Figure 2. Depending on calcination temperature, it is possible that such a structure can be present in two forms, either hydroxylated or dehydroxylated. The schematic structures proposed here are consistent with the results of ^{1}H MAS NMR, TEM, XRD, Raman and optical spectroscopy.[2]

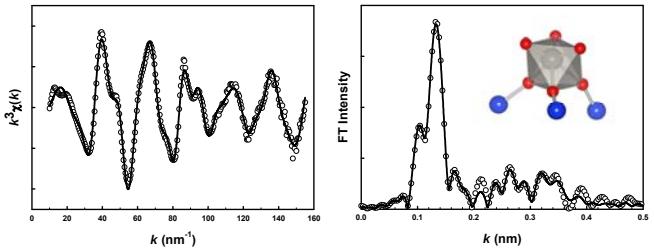

Figure 1. k^3-weighted X-ray absorption fine structure data (left panel) and the corresponding Fourier transformation (right panel) for the WO_3 supported on SBA-15 catalyst prepared with the atomic layer deposition method. The open circles and solid lines indicate the experimental and fitted data, respectively. The best fit structure is also shown as an inset in the FT data figure where the gray, red and blue spheres indicate tungsten, oxygen and silicon atoms, respectively.

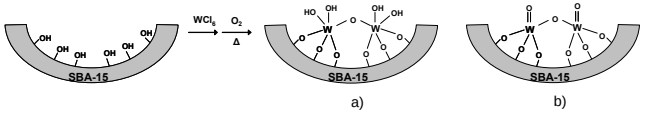

Figure 2. Scheme for the atomic layer deposition of WO_3 onto the SBA-15 surface, resulting in condensed WO_3-like structures that can be either a) hydroxylated, or b) dehydroxylated depending on calcination temperature.

References

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