Size and Shape of Rhenium Nanoparticles

N. Yang[1], G.E. Mickelson[2], N. Greenlay[2], S.D. Kelly[3], F.D. Vila[4], J. Kas[4], J.J. Rehr[4], and Simon R Bare[2]

[1]Argonne National Laboratory, Argonne, IL 60439; [2]UOP LLC, Des Plaines, IL, 60016 , [3]EXAFS Analysis, Bolingbrook, IL 60440, [4]Department of Physics, University of Washington, Seattle, WA 98195

Abstract. In this paper the results from a detailed XAFS characterization of supported rhenium nanoparticles are presented. The Re nanoparticles are formed by the reduction of dispersed supported rhenium oxide in the presence of moist hydrogen. The shape of the wet–reduced Re clusters is determined by comparing the EXAFS spectra of Re-metal to the Re-wet-reduced clusters to 6 Å. A decrease in the signal from the 4th and 7th Re shells is an indication of sheet-like rather than spherical-like particles.

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INTRODUCTION

The chemistry of rhenium supported on alumina is a system of technological importance in heterogeneous catalysis. For example, rhenium oxide dispersed on alumina has been shown to have high activity and selectivity in olefin metathesis, and when Re is alloyed with Pt, the subsequent Pt-Re supported clusters are used in petroleum reforming catalysts. However, the chemistry of the reduced Re alone on γ-alumina is studied much less.

Here we present an XAFS study of supported rhenium after it has been reduced in a flow of moist hydrogen. The moisture results in the formation of nano-agglomerates of Re metal. The shape of the wet–reduced clusters is determined by comparing the EXAFS modeling of Re-metal to the Re wet-reduced clusters to 6 Å. Reduction of the amplitude in the signal from the 4th and 7th shells indicates the formation of sheet-like Re nanoparticles rather than spherical particles. This work is part of a larger, more detailed study detailing different reduction conditions of this catalyst system [1].

MATERIALS AND METHODS

Data reduction and analysis were performed using Athena and Artemis [2], which are interfaces to IFEFFIT [3]. The data were modeled in R-space with theoretical models constructed from Feff [4]. The Re L_3-edge EXAFS data were collected at beamline 33-BM-B at the Advanced Photon Source, Argonne National Laboratory. The APS was operated at 7 GeV with a constant ring current of 105 mA. Details of the beamline and sample preparation are given elsewhere, but briefly the sample contained 0.7wt% Re on a commercial (75% mordenite/25%γ-Al_2O_3) support [1].

A sample of appropriate thickness was placed in a custom-designed in situ reactor [5] and dried in situ. The sample was reduced in wet hydrogen (H_2 passed through a distilled water saturator held at 25ºC) with moisture content of 3.1 mol %. The sample was heated at 4ºC/min to 500ºC. The sample will be referred to as "wet reduced" or WR.

The EXAFS spectra from bulk Re-metal powder and WR are shown in Figure 1. The EXAFS models for both spectra are based on the hcp crystal structure of Re metal (see Figure 2). This cluster includes eight shells of Re atoms and several multiple scattering paths. The scattering paths are listed in Table 1. The Re-metal model is described by eight parameters, five Debye temperatures used to determine the values for σ^2, an energy shift parameter, an expansion/contraction parameter, and an S_0^2-parameter. The five different Debye temperatures were grouped with distance to describe (1) Re1 to Re4, (2) Re5 to Re6, (3) multiple scattering (MS) Re5, (4) all Re7, and (5) all Re8 paths. The model for the WR spectrum is similar to that of the Re-metal, but was generalized to allow for the unknown coordination numbers (CNs).

The CNs determined from modeling the EXAFS spectrum can be used to determine the average particle size. In addition, the CNs from several shells of Re atoms (five independent shells in our model) can be used to determine the average particle shape. Table 2

lists the dependence of the average CN on the cluster size and shape for five different sheet models, and three different spherical models. The CNs for bulk Re-metal are also listed for comparison. The sheet models are made of x-y plane clusters 30 Å in diameter that are stacked one to five layers in the z-direction. The spherical models are made of complete hexagonal structures. The CNs shown in Table 2 become larger as the number of atoms in the cluster grows, becoming more bulk-like. The largest differences between the spherical models and the sheet models are the ratio of the coordination numbers for the Re atoms located along the z-direction as compared to those located within the x-y plane.

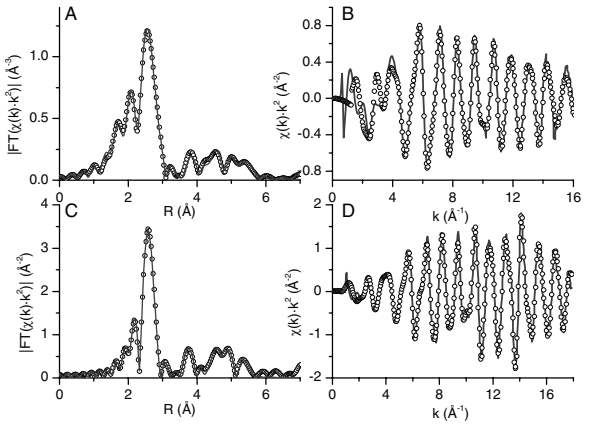

FIGURE 1. Re L_3-edge EXAFS data from WR catalyst (A and B) and Re-metal (C and D). (A and C) Magnitude of FT of EXAFS data (symbols) and model-fit (line). (B and D) EXAFS data (symbols) and model-fit (line). The data FT range is from 3.5-17.0 Å^{-1} for Re-metal and 4.0-14.0 Å^{-1} for WR. The fit range is from 1.5-5.7 Å for Re metal and 1.0-5.7 Å for WR. There are 38 and 32 independent points in the Re-metal and WR spectra, respectively. The model was fit to the data using a *k*-weighting in the FT of 1, 2, and 3. The Fourier transform using only *k*-weight of 2 is shown.

The Re-metal model applied to the WR EXAFS spectra, but with variable CNs, resulted in non-physical values for many parameters due to the high correlation between σ^2-values and the unknown CNs.

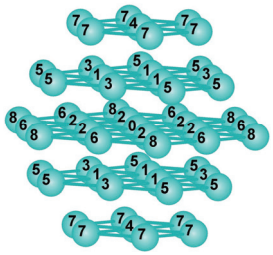

FIGURE 2. Schematic of Re metal cluster used to model the Re-metal powder EXAFS data. This cluster represents the spherical model with 57 atoms. The numbers on the blue spheres represent consecutive shells of atoms about the central Re atom labeled with a 0.

Our results from the Re-metal EXAFS spectra show that the five different Debye-values used to describe the σ^2 -values are indeed similar, particularly when the uncertainties in these values are considered. For the model of the WR data, the uncertainty in these T_{Debye} will increase because the CNs are unknown; therefore a single Debye-value is used to model the WR data. This model, which was highly successful at reproducing the gross features of the WR spectrum, was further refined by relaxing the bond lengths. Five independent expansion/contraction (α) terms were introduced. These parameters were grouped with increasing radial distance (1) for Re1 and Re2, (2) for Re3, (3) for Re4, all Re5 and Re6, (4) for all Re7, and (5) for all Re8 paths. Introducing several independent α-terms to represent the nonisotropic distortion of the crystal structure due to the small cluster size has been previously demonstrated for other systems [6].

Table 1. EXAFS Modeling Results.

Path	N_{degen}	R (Å) (Metal)	σ^2 ($\cdot 10^{-3}$ Å^2)	N_{degen}	α ($\cdot 10^{-3}$)	R (Å) (WR)	σ^2 ($\cdot 10^{-3}$ Å^2)
Re0-O1	-	-	-	1.7(4)	-	2.02(12)	9(4)
Re0-Re1	6	2.740(1)	3.9(1)	4.8(2)	-2(1)	2.734(3)	6.6(2)
Re0-Re2	6	2.761(1)	3.9(1)	4.8(2)	-2(1)	2.755(3)	6.6(2)
Re0-Re3	6	3.890(2)	4.8(1)	3.3(5)	-5(2)	3.87(1)	8.2(3)
Re0-Re4	2	4.458(2)	4.9(1)	1.3(9)	1(1)	4.47(1)	8.4(3)
Re0-Re5	12	4.770(2)	5.2(3)	5.9(7)	1(1)	4.78(1)	8.5(3)
Re0-Re6	6	4.782(2)	5.2(3)	5.9(7)	1(1)	4.79 (1)	8.5(3)
Re0-Re5-Re1	24	5.136(2)	3.1(13)	12(1)	1(1)	5.16(2)	8.5(3)
Re0-Re5-Re2	24	5.136(2)	3.1(13)	12(1)	1(1)	5.16(2)	8.5(3)
Re0-Re7	12	5.244(3)	6.4(11)	4(3)	5(4)	5.27(2)	8.5(3)
Re0-Re7-Re1	24	5.362(3)	6.4(11)	8(4)	5(4)	5.39(3)	8.5(3)
Re0-Re1-Re7-Re1	12	5.481(3)	6.9(12)	4(3)	5(4)	5.51(1)	9.3(3)
Re0-Re8	6	5.522(3)	5.0(4)	5.0(5)	5(2)	5.55(1)	8.6(3)
Re0-Re8-Re2	12	5.522(3)	5.0(4)	10(1)	5(2)	5.55(1)	8.6(3)
Re0-Re2-Re-Re2	6	5.522(3)	5.0(4)	5.0(2)	5(2)	5.55(1)	8.6(3)
Re0-Re2-Re8-Re2	6	5.522(3)	5.0(4)	5.0(2)	5(2)	5.55(1)	8.6(3)

Table 2. Average Coordination and Comparison of Reduced-χ^2 (RCS) Values for Re Metal Clusters.								
Model	Re at 2.75 (Re1+Re2)	Re at 3.89 (Re3)	Re at 4.45 (Re4)	Re at 4.77 (Re5+Re6)	Re at 5.24 (Re7)	Re at 5.52 (Re8)	RCS R=1to5.7	RCS R=4.8to5.7
Sheet models: # of rows in Z direction of a 30 Å sphere								
1	5.3	-	-	4.6	-	4.6		
2	8.0	2.6	-	9.5	-	4.5	60	
3	8.9	3.4	0.6	11.1	3.5	4.5	39	
4	9.4	3.9	0.9	11.9	5.2	4.4	36	13
5	9.7	4.1	1.2	12.5	6.3	4.5	39	
Spherical models: Number of atoms in cluster								
57	8.0	3.2	0.9	7.6	4.6	2	104	
421	9.9	4.5	1.4	12.3	7.9	4.0	43	38
587	10.1	4.6	1.4	12.8	8.4	4.1	45	
Bulk structure								
	12	6	2	18	12	6		
EXAFS results for Wet-Reduced sample								
	9.6 ± 0.4	3.3 ± 0.5	1.3 ± 0.9	11.7 ± 1.4	4.4 ± 2.6	5.2 ± 0.6		

RESULTS

The Re-metal spectra and model are shown in Figure 1. The model was simultaneously refined to the EXAFS spectrum processed with a *k*-weight of 1, 2, and 3 in the Fourier transform (FT). The best-fit values for the eight parameters used to describe the Re-metal model are: T_{debye1} = 279 ± 4 K, T_{debye2}=272 ± 4 K, T_{debye3} = 356 ± 80 K, T_{debye4} = 247 ± 22 K, T_{debye5} = 281 ± 11 K, ΔE_0 = 1.4 ± 0.4 eV, α = 0.0000 ± 0.0006, S_0^2 = 0.80 ± 0.03 (all within the expected ranges). Table 1 lists the corresponding shell distances and σ^2-values for each path included in the model. The excellent agreement between: (a) the model fit and the EXAFS data, and (b) the fit results and the crystal structure of Re metal gives confidence in the determined S_0^2-value.

The EXAFS data and model for the WR sample are also shown in Figure 1. The modified Re-metal model includes five α-terms, one T_{debye}, one energy shift, and five CNs, for a total of 12 variables. This model accurately describes the measured WR EXAFS spectra with reasonable values (Table 1). The best-fit values for the CNs were then compared to the calculated values for the spherical and sheet models (Table 2). Values for σ^2 are based on T_{debye}= 212 ± 3 K and ΔE_0= 6.0 ± 0.5 eV. The first shell CN was used to determine the range of cluster sizes to explore. Spherical clusters of 30 to 16 Å in diameter have an average first shell CN of 10.2 to 9.0. Both sheet and spherical models of this average size were modeled. The calculated CNs for the different clusters were used in the model, and the reduced-χ^2 (RCS) values for these models are compared and are listed in Table 2. In this comparison the CNs were held at the calculated values (Table 2), and a T_{debye}, an energy shift, and five α-terms were determined by the model fit. The sheet model of 4+/- 1 layer and the spherical models including 421 and 587 atoms are equivalent models with the RCS values ranging from 36 to 45. The data region from 4.8 to 5.7 Å is dominated by the signal from Re7. These atoms are located in the z-direction. The signal in this region is more consistent with the sheet-like CN than the spherical CN. This is illustrated by comparing the RCS of both models to the data in this data range, where the parameters that do not depend on this region of the data are held at their previously determined values. This refinement results in a statistically higher quality fit by using the sheet-like particle than for spherical particle (RCS of 13 versus 38, respectively). We conclude that the average Re particles are sheet-like, 24-30 Å diameter (as determined by the 1st and 2nd shell CNs of 9.6 ± 0.4 and 3.3 ± 0.5, respectively), and consist of 4 ± 1 layers.

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