JOURNAL OF CATALYSIS 72, 288–293 (1981)

X-Ray Absorption Spectroscopy of Pt–Re/Al_2O_3 Catalysts

D. R. SHORT,[1] S. M. KHALID, AND J. R. KATZER

Center for Catalytic Science and Technology and Department of Chemical Engineering,
University of Delaware, Newark, Delaware 19711

AND

M. J. KELLEY[2]

Center for Catalytic Science and Technology and Department of Chemical Engineering,
University of Delaware, Newark, Delaware 19711

Received February 12, 1981; revised August 11, 1981

The state of Re in reduced Pt–Re/Al_2O_3 catalysts has been a subject of controversy for some years. X-ray absorption spectroscopy at the Stanford Synchrotron Radiation Laboratory was used to examine two laboratory-prepared, commercial-type catalysts after reduction. Data from the Re L_{III} absorption edge show that Re is neither zero valent nor significantly associated with Pt. The data also suggest that the Re is in the 4+ valence state.

INTRODUCTION

The advantages of Pt–Re/Al_2O_3 over Pt/Al_2O_3 for naphtha reforming were reported more than a decade ago (*1*, *2*). Since then a multitude of studies have produced conflicting evidence as to whether in the reduced catalyst the Re is chiefly present as an alloy with Pt (*3–7*), or is separately dispersed, with or without (*8–10*) reduction of both elements. This conflict has remained despite rapid advances in instrumental characterization techniques during the same period (*11*). The catalytic evidence favors separate dispersion: a mixed bed of Pt and Re on separate pellets performs similarly to co-impregnated pellets, with no evidence of Re transfer (*12*).

EXPERIMENTAL

We report here the results of the application of X-ray absorption spectroscopy to two laboratory-prepared commercial-type Pt–Re/Al_2O_3 catalysts. One contained 0.9–0.9 and the other 0.6–0.6 wt% Pt–Re and about 1 wt% Cl^-. The catalysts were obtained as impregnated, calcined extrudates, ground to powder, and pressed into wafers. The wafer thicknesses were chosen to give about 50% X-ray absorption at the transition metal L_{III} edge to be studied. All samples were reduced 16 hr at 758 K in rapidly flowing H_2 in a quartz tube; they were cooled in H_2, removed, and transported under dry N_2. They were then mounted in vacuum-tight X-ray absorption cells, which allowed *in situ,* controlled-atmosphere treatments between 77 and 800 K, and were rereduced in flowing H_2 at 758 K for an additional 2 hr. Some samples were cooled under flowing H_2 and others under He to 77 K, at which temperature the X-ray experiments were carried out under static gas. No difference was found for the He versus the H_2 environment. A standard consisting of Re metal powder mixed with zeolite and pressed into a wafer received the same treatment.

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[1] Presently located at Engineering Technology Laboratory, Experimental Station, E. I. du Pont de Nemours & Company, Inc., Wilmington, DE 19898.

[2] To whom correspondence concerning this paper should be addressed.

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The X-ray absorption spectroscopy was carried out using synchrotron radiation at the Stanford Synchrotron Radiation Laboratory. Each experiment consisted of placing the sample cell containing the pretreated sample in the beam path and of measuring the incident (I_0) and transmitted (I) X-ray intensities as a function of the X-ray photon energy from 300 eV before to 1000 eV beyond the desired L_{III} absorption edge. Each scan required about 30 min; details of the procedure are given elsewhere (*13*).

RESULTS AND DISCUSSION

Figure 1 shows the absorption coefficient for the reduced Re metal mixed with zeolite standard. The incident beam intensity contained a large amount of random noise, including randomly located spikes involving a 10% change in input photon flux. The effect of these fluctuations on incident beam intensity is largely eliminated in taking the ratio (I_0/I) but these fluctuations still complicate and reduce the quality of the information in the absorption spectrum. Deglitching and Fourier filtering techniques were used to minimize the effect of this noise, but the low concentration of Re in the catalyst samples led to low signal levels relative to this noise. We believe that the conclusions reached are firm, but additional information which would have been highly desirable could not be extracted from the spectra.

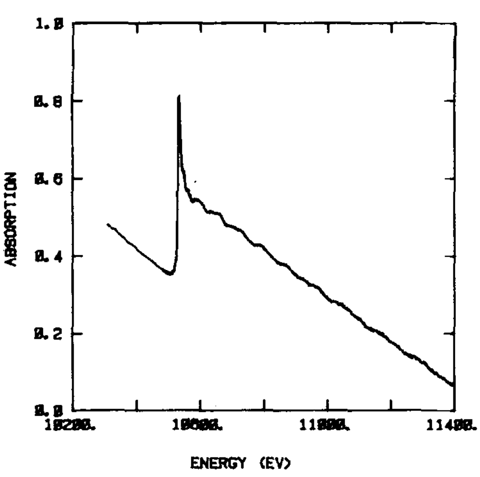

FIG. 1. X-Ray absorption coefficient at the Re L_{III} edge for metal powder mixed with zeolite.

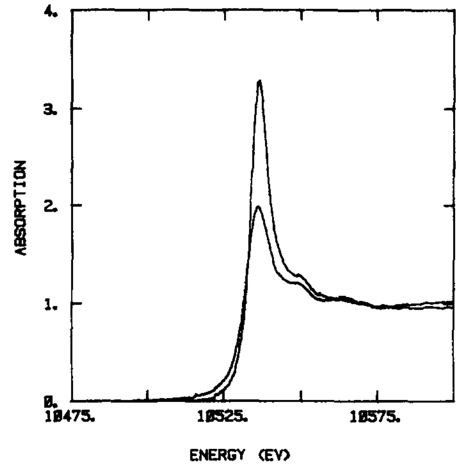

FIG. 2. Comparison of normalized Re L_{III} edge intensities for 0.9–0.9 wt% Pt–Re/Al_2O_3 (upper) and Re powder mixed with zeolite (lower).

Upon analysis of the data, the spectra were normalized to a per Re atom basis, and the background was removed by previously described techniques (*13–16*). The X-ray absorption edge structures of the various samples were compared after the normalization step. The edge peak or white line at the Re L_{III} edge represents energy absorption from the beam by intraatomic electronic transitions from core L_{III} or $2p_{3/2}$ states predominantly to unfilled $5d_{5/2}$ states near the Fermi level. The peak area or transition probability is proportional to the number of unfilled *d* states in the absorbing atom. Transfer of electrons to another atom as a result of covalent or ionic bonding changes the number of unfilled states, so that changes in the white line area can provide information about electron transfer through covalent bonds and about oxidation or valence states in ionic bonding situations (*17–19*).

As Fig. 2 and Table 1 show, the white line intensities (the area under the large peak at the edge) for the two catalyst samples are 1.7–1.9 times greater than that for

TABLE 1

Edge and EXAFS Parameters for Re Mixed with Zeolite and Pt-Re/Al_2O_3 Catalysts at the Re L_{III} Edge

Sample	Normalized white line peak area	First peak distance in transform (Å)	Peak distance plus expected phase shift (Å)	
			Re–Re = 0.12	Re–O ≈ 0.35
Re mixed with zeolite	1.00	2.62 ± 0.08	2.74	—
0.9–0.9 wt% Pt-Re/Al_2O_3	1.9 ± 0.2	1.60 ± 0.08	—	1.94
0.6–0.6 wt% Pt-Re/Al_2O_3	1.7 ± 0.2	1.58 ± 0.08	—	1.92

the Re metal and are nearly equal to one another. The increase in the L_{III} edge peak area observed for the catalysts relative to Re metal indicates that Re is chiefly in a positive-valence (ionic) state in the catalysts rather than in a zero-valence (metallic) state.

The question now arises as to what state or states these might be. Fully answering the question requires measuring the L_{III} edge white line intensity for a number of Re compounds where the valence state is known, so as to provide standards for comparison. We have not done this and we are aware of no such data in the literature. We therefore choose the less desirable alternative of comparing these results with another third-row transition metal where such a variety of compounds has been studied.

Using Pt as a reference, the L_{III} peak area of α-PtO_2 (Pt^{4+}) is 2.1 times that of metallic Pt (Pt^0), as compared with a ratio of 1.1 for Pt^{2+} in $PtCl_2$ relative to the edge intensity of the reduced metal (*17*). The acceptor–donor properties of ligands affect the number of unfilled *d* states and therefore the peak area. However, the similarity of the edge peak area ratios between Pt^{4+} and Pt^0 and between the Re in Pt-Re/Al_2O_3 and Re^0 metal indicates that the valence state of Re is best interpreted as 4+ and that Re has therefore not undergone complete reduction in H_2 at 785 K. Further support for this view is gained from the analysis of the extended fine structure discussed below.

A previous X-ray absorption spectroscopy study of the Re L_{III} edge in reduced Pt-Re/Al_2O_3 catalysts (*20*) concluded that several valence states are present and that the extent of reduction decreases as metal loading is decreased. Metal loadings and procedures for normalizing spectra from different loadings were not reported, so that comparison with our results discussed above is not possible. However, following the more usual practice of defining the edge position as the inflection point of the steeply rising portion of the absorption curve, we found no significant change in edge position, in contrast with the previous result (*20*) in which the edge position was defined as the absorption maximum.

The Fourier transforms of the extended fine structure (EXAFS) portion of the spectra are shown in Fig. 3. Variations in the extent of Fourier filtering and in the range of wavenumber (*K*) employed in the transformation led to modest shifts in the indicated peak positions and peak intensities. The signal-to-noise ratio in our data was such that we are reluctant to base conclusions on other than the principal peak.

The peak positions in Fig. 3 have not been corrected for phase shift and therefore do not lie at their known crystallographic distances. The phase shift for each pair of atoms involves contributions from both the absorbing and the scattering atoms but is a constant independent of the sample in which the atom pair is found (*21*). Therefore in practice, phase-shift values can be accurately determined from Fourier transforms of standard, typically crystalline materials having known atom–atom distances, and these phase shifts can be applied to unknowns having the appropriate atom pairs. The consequence of such a procedure is to add a correction factor to the distances shown in Fig. 3a, thereby increasing them.

For example, the nearest-neighbor distance in Re metal is known to be 2.74 Å; therefore the peak position of 2.62 Å for Re metal mixed with zeolite leads to a phase-shift value of 0.12 Å for a Re–Re atom pair. Vertical lines in Fig. 3a give the first five coordination shell distances for Re metal; the transform clearly indicates the phase-shifted distances of the first four coordination shells. For Pt metal the first shell Pt–Pt phase shift is 0.15 Å (*13*, *18*); for α-PtO_2 the first shell Pt–O phase shift is 0.34 Å (*13*, *22*) whereas the phase shift for the first Pt–Pt coordination distance in the oxide is still 0.15 Å (*13*). The phase shift for the Re–O distance could be expected to be of order 0.35 Å, although we have not determined it from a crystalline oxide standard.

The shape of the first peak is the same for both the 0.9–0.9 and 0.6–0.6 wt% Pt–Re/Al_2O_3 catalysts (Figs. 3b and c), although the peak magnitudes are considerably different. This difference in magnitude could represent real differences in the environment of the Re atoms or could be due to poor data quality; more and higher-quality data are needed to provide an answer.

Table 1 summarizes the first shell peak positions from Fig. 3 and indicates the corresponding atom–atom distances obtained by adding the phase shift. For both Pt–Re/Al_2O_3 samples, the first peak occurs at a significantly shorter distance than does the main peak for the Re metal, and the addition of the metal–metal phase shift (0.12 Å) leads to an unacceptably small value (~1.72 Å) for a Re–Re or Re–Pt distance. The use of our estimated Re–O atom phase shift of 0.35 Å gives a first coordination shell dis-

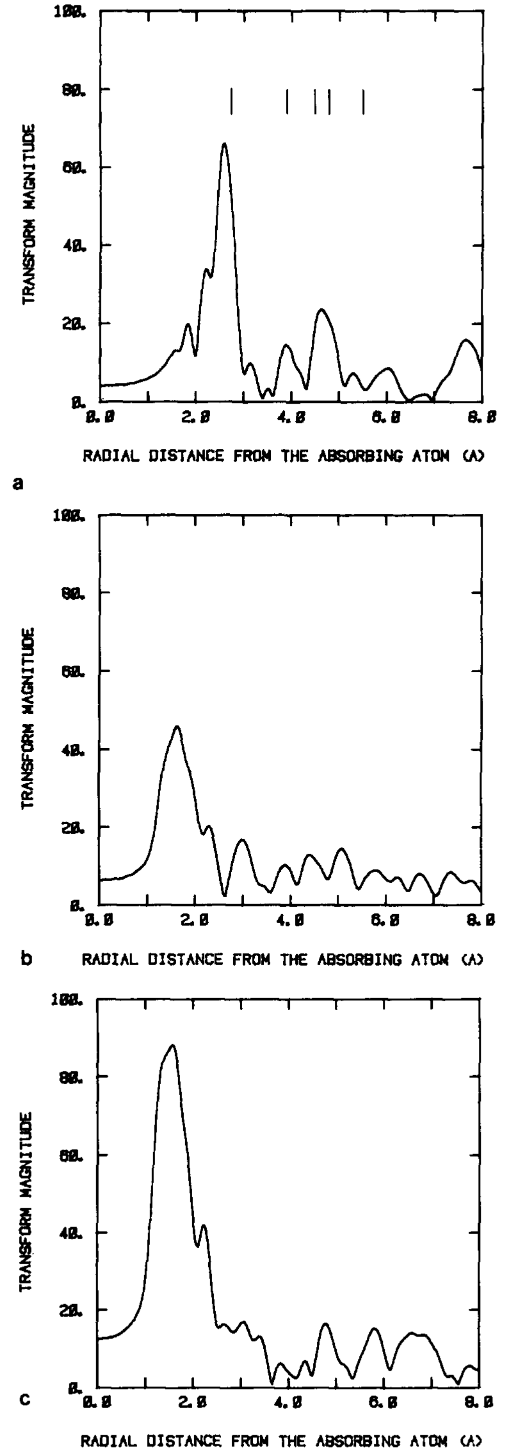

FIG. 3. K^3 weighted Fourier transforms of EXAFS above Re L_{III} edge: (a) metal powder mixed with zeolite; (b) 0.9–0.9 wt% Pt–Re/Al_2O_3; (c) 0.6–0.6 wt% Pt–Re/Al_2O_3.

tance of ~1.95 Å. This is closer to the value of 1.80 Å for the Re–O distance in ReO_2 (*23, 24*) and strongly suggests that it is a Re–O distance and that the Re is unreduced and surrounded by oxygen atoms. On the other hand, these results do not rule out the possibility of Re existing in a dispersed, oxidized form surrounded by Cl^- ions (the catalysts contain 1% Cl^- ion), such as Re Cl_x. However, if the Re had undergone reduction to form either Re metal or a Pt–Re alloy, a strong peak in the region 2.58 to 2.65 Å would have appeared. No such peak is present, strongly suggesting that most if not all of the Re was not reduced by 16 hr at 758 K in flowing, dry H_2 followed by an additional 2 hr at 758 K in flowing H_2 in the EXAFS cell. The bond lengths (indicated in the transform) are consistent with the Re having a 4+ valence and being in an oxide environment. This conclusion agrees with the white line information, reinforcing the conclusion that the Re is not reduced but is in a positive, possibly 4+, oxidation state.

The transformed spectra also indicate that the Re is not present in three-dimensional oxide particles of significant size (>15 Å). Significantly sized three-dimensional rhenium oxide particles should have a strong peak at about 2.49 Å due to the first Re–Re distance in the oxide at 2.61 Å (*23*). The transformed spectra show little evidence for such a peak. Therefore the unreduced Re must be present either as very small rhenium oxide (or chloride) crystallites or more likely as a highly dispersed rhenium oxide layer on the surface of the Al_2O_3, possibly similar to the type of capping layer which is produced when molybdenum salts are impregnated into Al_2O_3 and calcined (*25, 26*).

CONCLUSIONS

This study has clearly shown that the Re at commercially important concentrations in Pt–Re/Al_2O_3 catalysts is not reduced to a significant extent by pure H_2 at the temperature typical for commercial reduction, but remains in the oxide form. The data suggest that the oxidation state of the Re is 4+ and that it is present in a very highly dispersed state on the Al_2O_3. Higher-quality data and standards are required to determine more accurately the oxidation state, coordination number, and higher coordination shell information of the Re, and to establish if reduction produces any secondary effects on the Re and its local environment.

ACKNOWLEDGMENTS

The data incorporated in this work were done at SSRL with the financial support of NSF. We gratefully acknowledge the experimental assistance of the SSRL staff and Ronald J. Emrich of the University of Delaware. We are indebted to John A. Fetchin, American Cyanamid Company, and Robert J. Houston, Chevron Research Company, for preparation of the samples.

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