

Pd-Pt Catalysts on Fluorinated Alumina Support Studied by X-Ray Absorption Fine Structure

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Abstract. A series of bi-metallic Pd-Pt catalysts supported on both pristine and fluorinated alumina supports were investigated with x-ray absorption spectroscopy. It was found that Pd and Pt form small alloy particles on the pristine alumina support; the composition and the cluster size of the PdPt bimetallic alloys, and the electronic properties of the metals were significantly altered on the fluorinated support. The remarkable increase in sulfur tolerance of the PdPt metallic clusters supported on the fluorine pretreated alumina can be attributed to an electronic depletion of the metals, large particle size and direct participation of the acid sites in the reaction.

Keywords: Pd-Pt alloy, acidic support, XAFS.

PACS: 61.10.Ht, 61.82.Bg, 71.20.Be

INTRODUCTION

Noble metal catalysts are easily poisoned by sulfur compounds such as H_2S and organic sulfur-containing molecules. Bimetallic Pd-Pt catalysts on acidic supports, such as Al_2O_3 , HY-zeolite, have been reported as excellent aromatic hydrogenation catalysts with high sulfur-tolerance [1]. Additionally, under sulfur-containing reaction atmosphere the Pd-Pt catalysts were reported more active than either pure Pd or pure Pt catalysts [2], but it is not clear whether a real enhancement in sulfur-tolerance is attributed to alloying, electronic effects or acidity. There are a few and contradicting reports on the reason of activity for this family of catalysts [3,4], which makes a more systematic study necessary. Additionally, the properties of bimetallic particles are of great industrial interest.

Recently, several groups have been that adding fluorine into catalysts can lead to dramatic increase in the acidity and the specific performances [5,6]. Fluorinated alumina supported Pd-Pt bimetallic catalysts are expected to have good sulfur tolerance. In order to investigate the mechanism of fluorination effect on the sulfur tolerance, we used XAFS to characterize the local structure and electronic property changes at Pt sites on the fluorinated alumina support before and after sulfur poisoning; the fluorine effect on metal particle properties and the metal-support interaction are discussed in detail.

EXPERIMENTAL

Reduced Pd-Pt (1.1 wt% metal, atomic ratio of Pd:Pt = 8:5) catalysts on the pristine and fluorine(2 wt%)-modified Al_2O_3 supports were prepared by typical incipient wetness impregnation. $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ and PdCl_2 were used as the metal precursors. The $\gamma\text{-Al}_2\text{O}_3$ support has a specific surface area of $270 \text{ m}^2/\text{g}$, and a mean pore diameter of 10.2 nm. The fluorinated Al_2O_3 was prepared by impregnating $\gamma\text{-Al}_2\text{O}_3$ with an aqueous solution of NH_4F drying in air, followed by calcinations at 723 K for 2 h. After the impregnation, the mixture was dried at 393 K, and further calcined at 673 K for 2 h. The reduction and sulfur tolerance test were conducted in situ with 5% H_2/N_2 at 700 K for 1 h and then with H_2S -poisoning at 573 K for 2 h.

The x-ray absorption data were collected in transmission mode under liquid nitrogen temperature (77 K) on the beam line 4W1B of the Beijing Synchrotron Radiation Facility (operating at dedicated mode with energy of 2.2 GeV and typical current of 80-220 mA). Energies were calibrated using an internal Pt foil standard. The EXAFS data analysis was performed by following standard procedure. The structural parameters were obtained by curve-fitting the experimental data with the theoretical functions by nonlinear least squares minimization of the residuals. The data were analyzed using the NSRLXAFS software package [7] together with theoretical

amplitude and phase shift functions from the FEFF code [8].

RESULTS

EXAFS Analysis

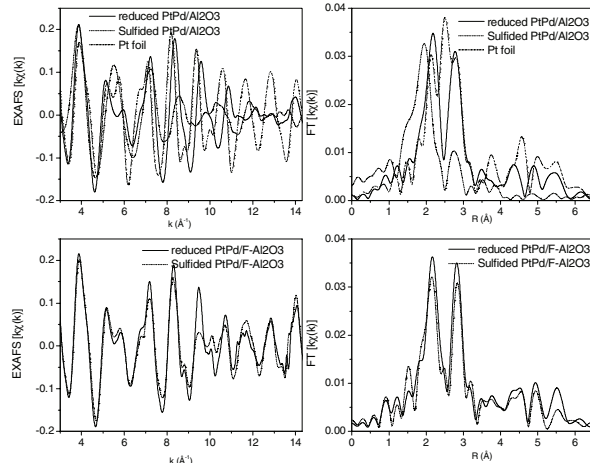


FIGURE 1. Fourier Transforms of k -weighted Pt L_3 edge EXAFS of the reduced and sulfided Pd-Pt catalysts on pristine (bottom) and fluorinated Al_2O_3 (top).

The EXAFS functions $k\chi(k)$ and their Fourier transform magnitudes were shown in Figure 1 for the reduced Pd-Pt/ Al_2O_3 , and Pd-Pt/F- Al_2O_3 samples together with those of the corresponding sulfided catalysts. For the reduced Pd-Pt/ Al_2O_3 , and the Pd-Pt/F- Al_2O_3 (both reduced and sulfided) catalysts, the radial distribution functions show two isolated main peaks. The sharp minimum and the asymmetry of the two peaks indicate that the EXAFS oscillations from the two shells destructively interfere with one another. In order to get accurate structure parameters it is highly preferable to transform the two peaks together and use a fitting approach in the k -space analysis. We also consider any contribution arising from support oxygen interaction with either metal, but the coordination numbers are negligibly small ($N_{\text{M-O}} < 0.1$). Structural parameters derived from best fits are shown in Table 1. The errors of data and fits are roughly estimated from the change of the residual factors to be 15% for N, 0.25% for R, 10% for σ^2 and 4 eV for ΔE_0 . No ambiguities of the theoretical standards are included. The pronounced Pt-Pd coordination numbers indicate that Pt and Pd form an alloy on both pristine and fluorinated Al_2O_3 supports. The Pt-Pd distance being close to the Pt-Pt distance (Table 1) might suggest that Pd and Pt form a solid solution with Pd atoms replacing Pt atoms in the *fcc* structure. But on the fluorinated Al_2O_3 surface the alloy tend to further aggregate and form larger sized clusters, as indicated by the larger total coordination number of Pt site, in the fluorinated sample as compared with that on the pristine support.

Interestingly, the bimetallic Pd-Pt catalyst supported on pristine Al_2O_3 is vulnerable to the sulfur attack, while the Pd-Pt catalyst supported on fluorinated Al_2O_3 has good resistance to sulfur poisoning.

TABLE 1. The coordination parameters of Pt-Pd/ Al_2O_3 catalysts obtained from curve fitting of Pt L_3 edge EXAFS

support	Abs.-Sca.	N	R (Å)	σ^2 (Å ²)	ΔE_0 (eV)
pristine (reduced) (sulfided)	Pt-Pt	5.54	2.75	0.0035	6.2
	Pt-Pd	3.32	2.76	0.0024	
	Pt-S	2.39	2.32	0.0047	
	Pt-Pt	4.06	2.68	0.0090	
Fluorinated (reduced) (sulfided)	Pt-Pt	6.85	2.76	0.0036	7.3
	Pt-Pd	3.19	2.76	0.0041	
	Pt-Pt	7.27	2.77	0.0051	
	Pt-Pd	3.27	2.75	0.0064	

XANES Analysis

Figure 2 displays the Pt near edge structure spectra of both the reduced and the sulfided catalysts. For the bimetallic Pd-Pt catalysts, the Pt edge position shifted about 0.7 eV towards higher energy on the fluorinated Al_2O_3 support with regard to that on the pristine support. Interestingly, the shift of the prominent post-edge peak (Peak *b*) to lower energy was observed for the sulfided Pd-Pt/ Al_2O_3 catalysts, but was not seen in the Pd-Pt catalyst on fluorinated Al_2O_3 . This shift can be explained with the hybridization arising between the Pt- ϵd and continuum S- $3d$ states due to multiple scattering paths connecting these sites [9].

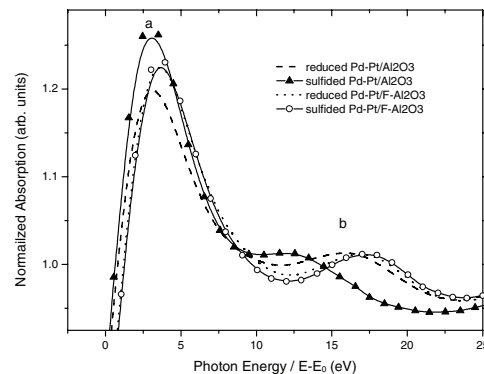


FIGURE 2. XANES evidence of fluoride effect on sulfur tolerance of Pd-Pt catalysts supported over pristine and fluorinated Al_2O_3 .

Whiteline areas of the Pt L_3 -edge are known to be proportional to the number of d -band holes [10]. On the fluorinated support, the depletion of Pt $5d$ electron gets more significant; simultaneously the peak *b* (Figure 2) gets sharper and shifts to higher energy. In the case of the sulfided Pd-Pt/ Al_2O_3 catalyst, sulfur poisoning induces broadening of the d -band for the surface atoms to which the sulfur is coordinated and

the sulfur-metal interactions are mainly due to hybridization of *p*-states of the sulfur overlayer with the substrate *d*-bands. Studies have revealed substantial overlap of sulfur *p*-states with the palladium surface *d*-band giving rise to a strong covalent bond between the adsorbate and the surface [11,12]. Moreover, the adsorbed sulfur withdraws charge from the surface and reduction in the density of *d* states of palladium is observed near the Fermi level [13]. These lead to a change in the reactivity of sulfur-bonded platinum surface that naturally will affect, for instance, probability of dissociation rates and reaction conditions for hydrogen on the poisoned surface [14]. Interestingly, for the sulfided Pd-Pt catalyst on F-treated Al₂O₃, the Pt edge feature does not change much, and the *d*-states charge density of Pt is not affected by the sulfur attack either.

DISCUSSION

The presence of the Pt-Pd pair in the EXAFS of Pt *L*₃-edge indicated the formation of PdPt alloy on both pristine and fluorinated supports. But under the sulfur attack, the Pt-Pd interaction on the pristine alumina crashed, which is consistent with Rousset *et al.*²'s observation that the addition of Pd does not alter the deactivation caused by H₂S above 673 K, although in the mild reaction condition the sulfur resistance of Pt catalysts can be enhanced by the addition of Pd [15]. On the fluorinated alumina, a larger mean alloy cluster size form due to the weakened interaction of bimetallic alloy cluster with fluorinated Al₂O₃ surface. Importantly, the sulfur resistance of Pt catalysts can be greatly enhanced by fluorinated alumina support. Sulfur preferentially adsorbs on sites of the lowest coordination, such as corner and edge sites. The number of such sites increases with decreasing particle size. This is to say, the larger particle size could be beneficial for the sulfur resistance.

The XAFS analysis at the Pt edge revealed a change in the valence states of the Pt atoms when Pd-Pt bimetallic catalyst is supported on the fluorinated alumina. The change in the electronic properties of the metal cluster is often induced by and correlated with the electron richness of the support oxygen atoms through the metal-support interaction [16]. In our case, since fluorine is very electronegative, as it replaces O or OH groups on the alumina surface [17], it increases the acidity of both protonic (Brønsted) and nonprotonic (Lewis) sites on the surface [18,19]. When small metal crystallites are deposited on an acidic support, the metal becomes electron deficient due to the interaction between the metal and acidic sites. The Pt ionization potential increases with increasing acidity through an electrostatic interaction

induced by changes in charge density of the support oxygen ions. The metal thus becomes sulfur-tolerant because the bonding energy between the electron-deficient metal and the electron-acceptor sulfur is weakened.

CONCLUSIONS

Both structure and electronic properties of bimetallic Pd-Pt catalysts were modified by the change in metal-support interaction caused by the fluorine pretreatment of alumina support. The XAFS analysis leads to a model which explains the metal-support interaction as a change in the valence states of the Pt atoms: increase of Pt ionization potential with increasing acidity. This model is based upon an electrostatic interaction induced by changes in charge density of the support oxygen ions. The high sulfur tolerance of noble metals supported on acidic supports should be attributed to the electron-deficient characteristic of noble metals resulting from the interaction with acidic support (electron acceptor).

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