

EXAFS Characterization and Pentane Isomerization Activity of a Pt-Modified Sulfated Zirconia Catalyst

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Introduction

In the late 1970s, sulfated zirconia (SZ) was reported to activate light alkanes at low temperature, similar to super acids [1, 2]. These catalysts, however, suffer fast deactivation, which is thought to result from the formation of carbon deposits [3], loss of acid sites [4], or removal of sulfur [5]. A number of transition metals, especially Pt, are added to SZ, resulting in catalysts with higher activity and better stability. The state of Pt and its role as a modifier, however, is not well understood [6].

The effectiveness of Pt as an activity promoter and as a stability promoter is highly dependent on the method of preparation. The important parts include the method of sulfiding and sulfur concentration of zirconia, the calcination temperature, the Pt precursor, and the oxidation and reduction of Pt. In this study, we report on a synthesis procedure for the preparation of Pt on SZ with sustained high activity for isomerization of n-pentane. A key preparation step is the high-temperature calcination of sulfated zirconia prior to Pt addition. For SZ calcined at lower temperature, Pt is an ineffective promoter. The extended x-ray analysis fine structure (EXAFS) analyses of the catalysts at various stages of preparation provide evidence that metallic Pt is required for stable performance and is present only on SZ calcined at high temperature.

Methods and Materials

Zirconium hydroxide was precipitated from an aqueous solution of zirconyl chloride by the addition of 30% NH₄OH. The solid was recovered by vacuum filtration, followed by H₂O washing until the solution was Cl free. The zirconium hydroxide gel was dried at 100°C, and the catalyst was sulfated by incipient wetness impregnation with 0.5 M H₂SO₄. The catalyst was dried at 100°C and calcined at either 550 or 650°C. The Bronauer, Emmett, and Teller (BET) surface area and elemental S analysis were 145 m²/g and 4.4% S for SZ₅₅₀ and 120 m²/g and 2.1% S for SZ₆₅₀. Following calcination, Pt was added by incipient wetness impregnation with Pt(NH₃)₄Cl₂. After drying at 100°C, the catalysts were reduced in H₂ at 300°C for 2 hours. The conversion of n-pentane was obtained in an

atmospheric-pressure, fixed-bed reactor at 250°C and a weighted hourly space velocity (WHSV) of 0.6 h⁻¹.

X-ray absorption [x-ray absorption near-edge structure (XANES) and EXAFS] measurements were performed at the MR-CAT undulator beamline. It was equipped with a liquid-nitrogen-cooled, double-crystal Si(111) monochromator used in conjunction with a Rh-coated mirror to minimize harmonics. Measurements were made in a controlled-environment fluorescence cell at room temperature following reduction treatment at elevated temperature. Standard procedures were used to analyze the data by using experimental references.

Results

The n-pentane isomerization activity of Pt-free SZ with time on stream (TOS) declined exponentially. While the initial conversions were 55% and 80% for SZ₅₅₀ and SZ₆₅₀, respectively, the conversion was less than 5% for both after only 20 minutes. For both catalysts, the selectivity toward iso-pentane was 85%. Addition of Pt to the SZ₅₅₀ did not change the initial activity and decreased the deactivation rate only slightly (e.g., the conversion decreased to 20% after 20 minutes). The addition of Pt to SZ₆₅₀ gives a catalyst with lower initial activity (ca. 40% n-pentane conversion) but results in a catalyst that does not deactivate with TOS (for the duration of the test). The selectivity for the latter was identical to that of the Pt-free SZ. While the catalytic performance of the two catalysts was dramatically different, characterization of the Pt by x-ray diffraction (XRD), H₂ chemisorption, or x-ray photoelectron spectroscopy (XPS) showed little difference.

Figures 1 and 2 show the EXAFS spectra for the Pt on SZ₅₅₀ and SZ₆₅₀ catalysts, respectively, and the fits of the Pt coordination shell are given in Table 1. The EXAFS fits indicate that on SZ₅₅₀ there are four Pt-S bonds at a distance of 2.33 Å. Figure 3 shows the XANES spectra of Pt on SZ₅₅₀ along with reference compounds. The XANES fit of Pt on SZ₅₅₀ indicates that Pt is present in the +2 oxidation state. The state of Pt on SZ₅₅₀ is PtS with no metallic Pt.

The EXAFS fit of Pt on SZ₆₅₀ indicates that there is metallic Pt with a Pt-Pt coordination number of 9.3. In

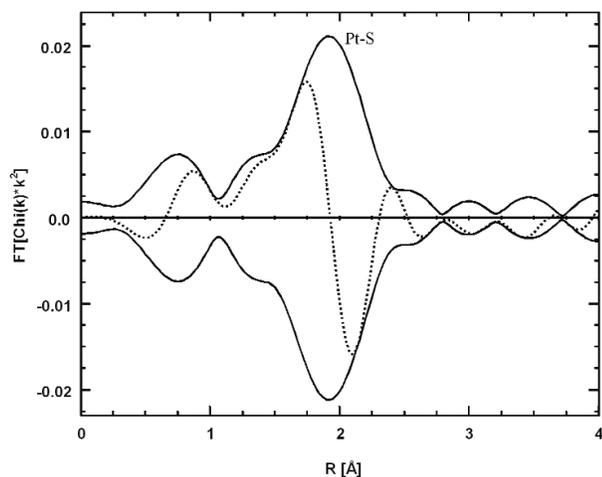


FIG. 1. Fourier transform of SZ_{550} reduced (k^2 , $\Delta k = 3.01$ - 10.45 \AA^{-1}); solid: transform magnitude; dotted: imaginary part.

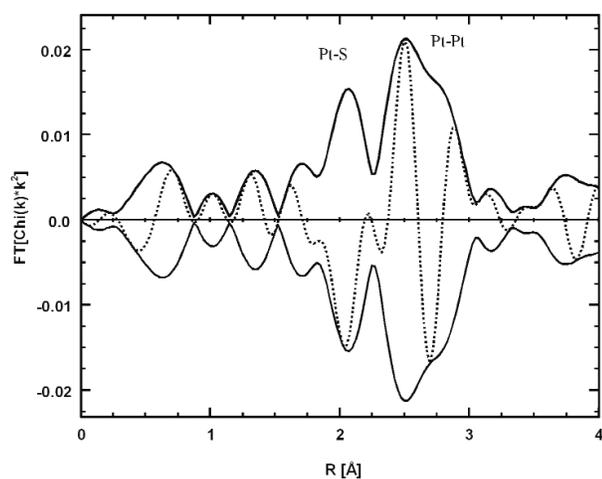


FIG. 2. Fourier transform of SZ_{650} reduced (k^2 , $\Delta k = 2.75$ - 13.80 \AA^{-1}); solid: transform magnitude; dotted: imaginary part.

addition, a fraction of the Pt is coordinated to Pt-S. A fit of the XANES spectra suggests that approximately 75% of the Pt is reduced while 25% is Pt^{+2} .

Pt particles of similar coordination number are approximately 40-50 Å. However, since these particles do not chemisorb significant amounts of H_2 , it is likely that sulfur largely poisons the surface of the metallic particles.

In order to confirm that the S is coordinated to the surface of the metallic particles and to determine if there are any exposed metallic Pt atoms, the reduced catalyst was oxidized at 150°C with 4% O_2 . The

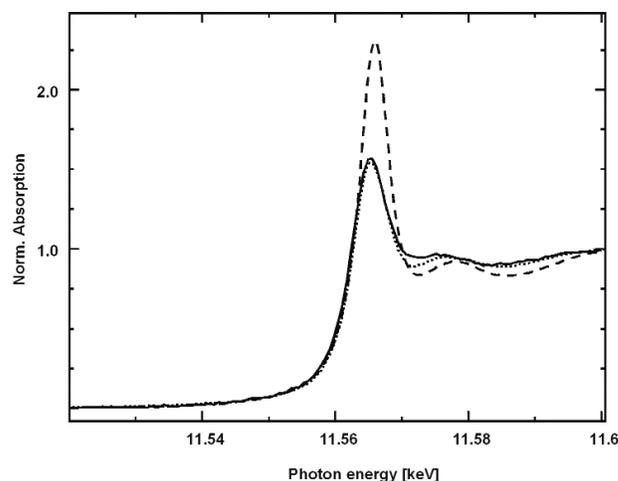


FIG. 3. Normalized XANES Spectra (SZ_{550} reduced: solid; Na_2PtCl_4 reference: dotted; H_2PtCl_6 reference: dashed).

EXAFS analysis of the oxidized catalyst (Table 1) indicates that the metallic particle is partially oxidized, as evidenced by a reduction in the Pt-Pt coordination number. In addition, all of the Pt-S bonds are lost, and a fraction of the Pt is coordinated to Pt-O. The XANES fits indicate that the fraction of metallic Pt has decreased to 50%, while the amount of Pt^{+2} has increased to 50%. These results suggest that in the reduced catalyst, there are few exposed metallic Pt sites that react with O_2 to oxidize the surface S, which desorbs at 150°C.

Discussion

Sulfate ions on zirconia are well known to generate acidic sites capable of activating paraffins at relatively low temperature. Increasing the calcination temperature of the Pt-free sulfated zirconia from 550 to 650°C results in a significant decrease in the amount of S species. Despite the difference in amount of S, both catalysts are highly active and selective for isomerization of n-pentane. In addition, both readily deactivate with TOS. Upon addition of Pt, there is little change in the performance of Pt on SZ_{550} . Pt is present as PtS, which is not capable of dissociating H_2 . Pt on SZ_{650} is present as moderately small metallic Pt particles with a large fraction of the surface poisoned by S. While S largely covers the surface, there appears to be a small fraction of metallic surface that is free of S and remains active for dissociation and reaction with H_2 . It is likely that this hydrogenation activity is responsible for the stable activity performance of the catalyst. In order to obtain an active metallic phase, it is necessary to remove the labile S coordinated to the zirconium oxide before the addition and reduction of Pt.

TABLE 1 EXAFS Fit Results (k^2 : $\Delta k=3.0-12.1 \text{ \AA}^{-1}$ and $\Delta r=1.84-2.92 \text{ \AA}$)

Sample	Treatment	Scattering Path	CN	R (\AA)	DWF ($\times 10^3$)	E_0 (eV)
ZS ₅₅₀	H ₂ /250°C	Pt-S	4.1	2.33	3.0	1.0
ZS ₆₅₀	H ₂ /250°C	Pt-Pt	9.0	2.76	1.0	-2.3
		Pt-S	1.0	2.32	3.3	2.6
ZS ₆₅₀	H ₂ /250°C + O ₂ /150°C	Pt-Pt	7.8	2.76	1.0	-0.4
		Pt-O	1.2	2.05	3.3	-2.3

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References

- [1] X.M. Song and A. Sayari, Catal. Rev.-Sci. Eng. **38**(3), 329 (1996).
- [2] Z. Gao, Y.D. Xia, W.M. Hau, and C.X. Miao, Top. Catal., **6**(1-4), 101 (1998).
- [3] R.A. Keogh, D. Sparks, J. Hu, I. Wender, J.W. Tierney, W. Wang, and B.H. Davis, Energy Fuels **8**(3), 755 (1994).
- [4] B.H. Li and R. D. Gonzalez, Ind. Eng. Chem. Res. **35**(9), 3141 (1996).
- [5] B.H. Li and R. D. Gonzalez, Appl. Catal., A **165** (1-2), 291 (1997).
- [6] T. Shishido, T. Tanaka, and H. Hattori, J. Catal., **172**(1), 24 (1997).