

XAFS study of Fe- and Mn-promoted sulfated zirconia

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The local structure around Fe and Mn in Fe, Mn-promoted sulfated zirconia was investigated by means of in-situ XAFS. The Mn atoms are found to be present as MnSO₄ on the surface. The first post-edge peak of the Mn K-edge XANES spectrum was sharpened in a working state, and restored by evacuation. Fe K-edge XANES spectra showed that Fe is in a trivalent state and located at a center of a distorted octahedron. Fe atoms were suggested to be interstitially located into ZrO₂ to form a solid solution. Any procedure did not change the Fe K-edge EXAFS and the shape and edge-positions of the XANES spectra. The reaction gases are in contact with Mn atoms, but not with the Mn atoms of the catalyst.

Keywords. In-situ XAFS, sulfated zirconia, Fe, Mn.

1. Introduction

Recently, Hsu *et al.* discovered that sulfated Fe-Mn-Zr oxide (FMSZ) is much more active for *n*-butane isomerization than the conventional sulfated zirconia (Hsu *et al.*, 1992). The roles of Fe and Mn and their structures, and the difference of acidity from that of sulfated zirconia have not been fully clarified. Wan *et al.* proposed that high-valent Fe oxy species such as tetrahedral Fe (IV) species are present. They speculated that these sites, which form during the calcination of catalysts in air, are responsible for the oxidative dehydrogenation of *n*-butane to butenes (Wan *et al.*, 1991). From XPS, Milbum *et al.* reported that both Fe and Mn are supported on sulfated zirconia in an oxidized state (Milbum *et al.*, 1998). Tábora *et al.* performed EXAFS measurement and speculated that Fe ions were supported on zirconia as small clusters or rafts of oxide (Tábora & Davis, 1995).

In spite of these efforts, the low concentration of Fe (ca 1.5 wt%) and Mn (ca 0.5 wt%) prevents a more detailed characterization. Furthermore, in-situ studies have not been reported. In the present study, the local structures around Fe and Mn at in a working state were investigated by in-situ XAFS measurements.

2. Experimental

2.1. Material

Fe- and Mn-promoted sulfated zirconia (FMSZ) was prepared according to Cheung's method (Cheung *et al.*, 1995). The sulfate ion-treated Zr(OH)₄ (SO₄²⁻/Zr(OH)₄) was prepared by the impregnation of Zr(OH)₄ with 1 M (NH₄)₂SO₄ aqueous solution. The impregnation was carried out at room temperature for 0.5 h with stirring, followed by filtration and drying at 383 K for 6 h. The Zr(OH)₄ was obtained by hydrolysis of ZrOCl₂·8H₂O with 25 mass%

NH₃ aqueous solution at room temperature. The final value of the pH was 8.0 and the aging time was 2 h. The obtained gel was washed with distilled water repeatedly until Cl⁻ was free based on AgNO₃ test. Fe and Mn ions were supported on SO₄²⁻/Zr(OH)₄ by stepwise equilibrium adsorption of 0.2 M Fe(NO₃)₃·6H₂O and 0.043 M Mn(NO₃)₂·9H₂O aqueous solutions. Each equilibrium adsorption was performed at room temperature for 0.5 h with stirring, followed by filtration and drying at 383 K for 6 h. It was then calcined at 873 K for 3 h. The loading amounts of Fe, Mn and S were 1.7, 0.35 and 0.81 wt%, respectively.

2.2. XAFS measurements

The sample was charged in an in-situ XAFS cell with a Kapton window. The recorded XAFS spectra of FMSZ were as follows: pretreated, in a working state (the reacted time was 24 h), evacuated after reaction.

Fe and Mn K-edge X-ray absorption experiments were carried out on the BL7C and BL12C at Photon Factory in High Energy Accelerator Research Organization (KEK-PF; Tsukuba, Japan) with a ring energy of 2.5 GeV and stored current among 250 - 400 mA (Proposal No. 97G041). The X-ray absorption spectra were recorded in a fluorescent mode with Si(111) two-crystal monochromator. The energy was calibrated by the pre-edge position of Cu foil (8980.3 eV).

Data reduction was performed using a FACOM M1800 computer of Kyoto University Data Processing Center. The normalization method has been previously reported in detail (Tanaka *et al.*, 1988). For curve-fitting analysis, backscattering amplitude and phase shift functions of Fe-O were obtained from CoO (Rock salt type, a₀ = 4.260 Å). For Zr atom scatters, they were estimated with FEFF (6.0) (Rehr *et al.*, 1991).

2.3. Catalysis

The isomerization of *n*-butane was performed with an in-situ XAFS cell in a static condition (dead volume: 1,300 cm³). The cell was made of Pyrex glass and was connected with a glass cylinder filled with *n*-butane (54.1 mmol). Prior to a reaction, 700 mg of catalyst was pre-evacuated at 673 K for 1 h. The reaction was performed by leaving exposure of *n*-butane to the catalyst at room temperature. After keeping 24 h at room temperature, Fe and Mn K-edge XAFS spectra were recorded under reaction condition. Then, reaction gases were recovered with a freezing trap cooled by liquid nitrogen and analyzed by GC. The 13% of *n*-butane had converted to *i*-butane, and the reacted *n*-butane was 6.5 mmol. The amounts of Fe and Mn contained in the catalysts were 213 and 32 μmol, respectively. The apparent turnover numbers per Fe and Mn atoms were 32 and 211, respectively.

3. Results and Discussion

3.1. Fe-K edge XANES

Figure 1 shows Fe-K edge XANES spectra of the reference compounds and FMSZ. The chemical shift between Fe²⁺ and Fe³⁺ is observed in the edge positions for FeSO₄ and Fe₂(SO₄)₃. Fe₂(SO₄)₃ was transformed to α-Fe₂O₃ when it was calcined at 873 K. The three spectra of FMSZ are identical to each other, but quite different from those of the reference compounds. It shows that Fe ions are not present on sulfated zirconia as sulfate or as α-Fe₂O₃. The edge positions of the three spectra shows that the valence of Fe atom is invariably trivalent. Because the reacted amount of *n*-butane exceeded

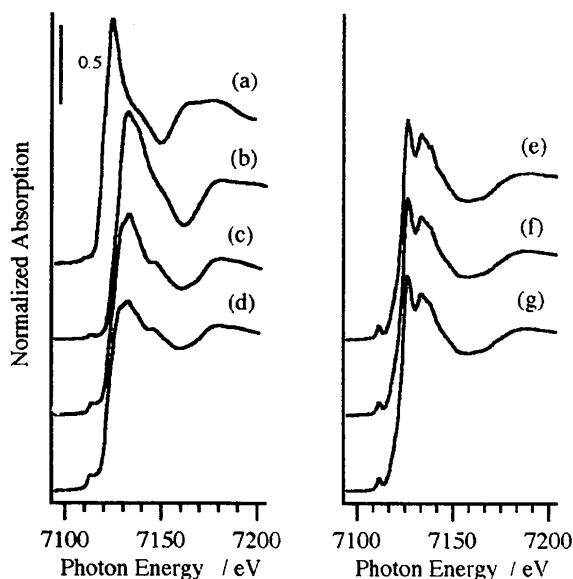


Figure 1. Fe-K edge XANES spectra of FeSO_4 (a), $\text{Fe}_2(\text{SO}_4)_3$ (b), $\text{Fe}_2(\text{SO}_4)_3$ calcined at 873 K (c), $\alpha\text{-Fe}_2\text{O}_3$ (d) and $\text{Fe, Mn-SO}_4^{2-}/\text{ZrO}_2$; pretreated (e), under reaction condition (f), and evacuated after reaction (g).

that of Fe atom contained in the catalyst, it is concluded that reduction of Fe did not occur during reaction.

The pre-edge peak of Fe-K edge XANES is assigned to the $1s\text{-}3d$ transition which is formally dipole-forbidden, but becomes allowed when an Fe atom is at a symmetrically distorted center (Bart, 1986). The pre-edge peak area of FMSZ was slightly larger than that of octahedral Fe^{3+} compounds such as $\alpha\text{-Fe}_2\text{O}_3$, and did not change during reaction. It shows that the symmetry around Fe is distorted more than that of $\alpha\text{-Fe}_2\text{O}_3$, and not affected by reaction gas. However, the pre-edge peak area was smaller than those of Fe-silicate and FePO_4 , both with a tetrahedral Fe symmetry (Bordiga *et al.*, 1996).

These results suggest that Fe in FMSZ is located at the center of a distorted octahedron. Because the reacted amounts of *n*-butane exceeded those of Fe atoms contained in catalyst, *n*-butane does not affect the structure around or the valence of Fe.

3.2. Fe-K edge EXAFS

The Fe-K edge EXAFS spectra of FMSZ are quite similar to each other. Figure 2 shows the Fourier transforms of k^3 -weighted EXAFS spectra in the k range 3 - 14 \AA^{-1} , except for pretreated FMSZ ($\Delta k = 3 - 13 \text{\AA}^{-1}$). Two distinct peaks appeared in the radial structure functions (RSFs) of FMSZ at 1.6 and 3.3 \AA .

The peak at around 1.6 \AA is due to oxygen scatters. The positions of the second peak are higher than that of $\alpha\text{-Fe}_2\text{O}_3$. According to the phase diagram of iron oxide-ZrO₂ system, Fe oxide forms a solid solution with ZrO₂ when the content of iron oxide is up to a few mol% (Jones *et al.*, 1967). In the case of FMSZ, an iron fraction as Fe_2O_3 was 1.8 mol% for ZrO₂. We guess that Fe and Zr oxide formed a solid solution. Therefore, we assigned the second peak of the RSF due to Zr atoms. Because the ion radius of Fe^{3+} (0.67 \AA) is much smaller than that of Zr^{4+} (0.87 \AA). Therefore, the type of solid solution is supposed to be interstitial and not

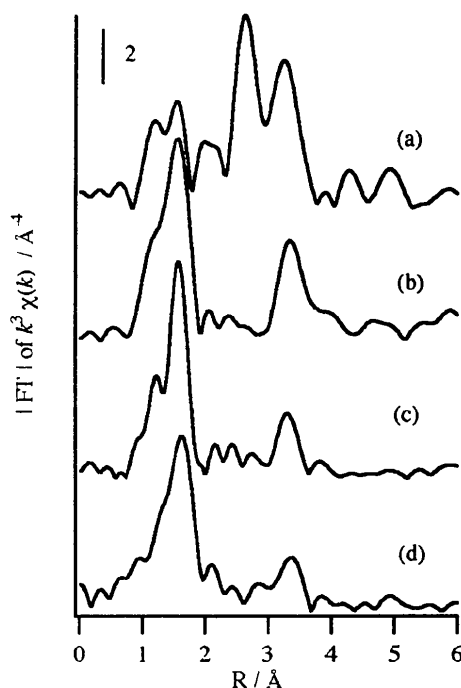


Figure 2. Fourier Transforms for k^3 -weighted Fe-K edge EXAFS spectra of $\alpha\text{-Fe}_2\text{O}_3$ (a), and $\text{Fe, Mn-SO}_4^{2-}/\text{ZrO}_2$; pretreated (b), under reaction condition (c), and evacuated after reaction (d).

Table 1

Results of curve-fitting analysis				
Sample	Shell	C.N.	R / \AA	$\Delta\sigma^2 / \text{\AA}^2$
Fe, Mn-SO ₄ ²⁻ /ZrO ₂ pretreated	Fe-O	3.0	1.86	-0.0048
		2.9	1.99	-0.0075
	Fe-Zr	1.5	3.62	0.0037
under reaction	Fe-O	3.0	1.85	-0.0021
		3.0	1.98	-0.0062
	Fe-Zr	1.5	3.60	0.0070
after evacuation	Fe-O	2.8	1.88	-0.0035
		2.8	2.01	-0.0064
	Fe-Zr	1.9	3.61	0.0090
$\alpha\text{-Fe}_2\text{O}_3$ ^a	Fe-O	3.0	1.91	0.0007
		2.9	2.04	0.0023

^a Taken from reference (Kanai *et al.*, 1992)

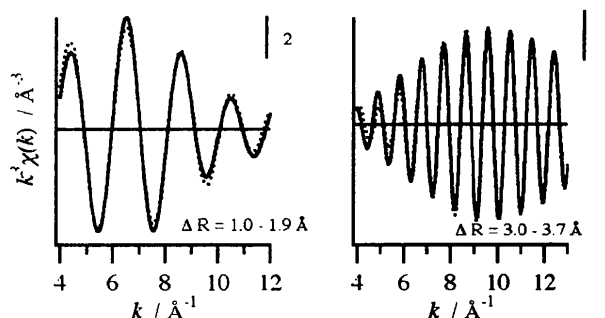


Figure 3
The fits of Fourier-filtered EXAFS of pretreated $\text{Fe, Mn-SO}_4^{2-}/\text{ZrO}_2$. The solid curves were obtained experimentally and dotted ones were the fits.

substitutional. This deduction supports the result that no change was observed in Fe-K edge XAFS throughout reaction.

The first coordination spheres for all the catalysts could not be fitted with a single shell, but could be fitted with two shells of oxygen, similar to α -Fe₂O₃. An Fe atom of α -Fe₂O₃ is surrounded by six oxygen atoms, but the distances between them are not uniform. The bond lengths of three Fe-O pairs are ca. 1.91 Å, and those of three more Fe-O pairs are 2.06 Å (Wyckoff, 1986). EXAFS parameters are not changed during reaction. The curve-fitting results of catalysts are summarized in Table 1. For example, the fits of the Fourier filtered Fe-K edge EXAFS for pretreated FMSZ are shown in Figure 3. The inter-atomic distances between Fe and O atom of the catalysts are similar to those of α -Fe₂O₃. Estimated inter-atomic

distances, coordination numbers and XANES spectra give a conclusion that the Fe atoms of FMSZ are present at a center of an oxygen distorted octahedron. Because FMSZ is an interstitial-type solid solution, coordination number for Fe-Zr shell is much smaller than 12.

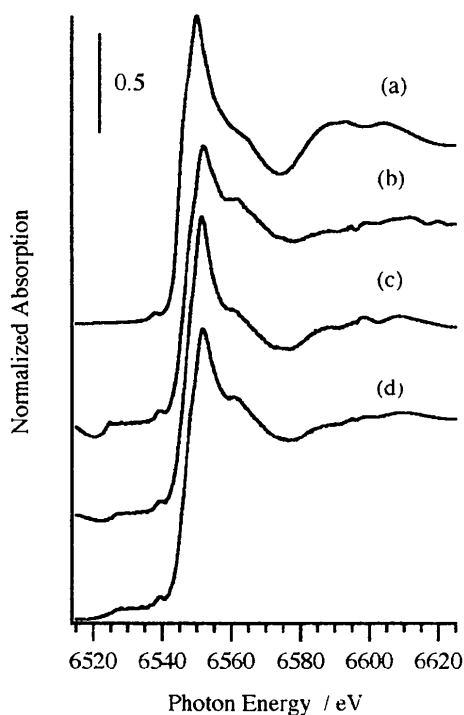


Figure 4
Mn-K edge XANES spectra of MnSO₄ (a), and Fe, Mn-SO₄²⁻/ZrO₂: pretreated (b), under reaction condition (c), evacuated after reaction (d).

3.3. Mn-K edge XANES

Figure 4 shows Mn-K edge XANES spectra of FMSZ and MnSO₄. Each edge-position and the shape of the spectrum are quite similar. It shows that Mn atoms are present as MnSO₄. Since the calcination temperature of FMSZ (873 K) was lower than the decomposition temperature of MnSO₄ (1123 K), the presence of MnSO₄ is very likely.

It should be noted that the post-edge peak of FMSZ changed during reaction. The peak was sharpened under reaction conditions. After evacuation of reacted gas, the post-edge peak had turned back to that of pretreated sample. The reversible change of Mn XANES spectra corresponds to the changes of coordination environment. It indicates that Mn atoms are present on the surface and are directly in contact with *n*-butane, although we can not conclude the Mn is the active species.

4. Conclusion

Fe atoms in Fe, Mn-promoted sulfated zirconia are trivalent and located at a center of oxygen octahedron. Fe and Zr oxides form interstitial-type solid solutions with ZrO₂. The local structure around Fe and the valence of Fe are not influenced by *n*-butane. Mn atoms are present on the surface of sulfated-zirconia as MnSO₄. Under reaction conditions, *n*-butane molecules are in contact with Mn atoms and are desorbed by evacuation.

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