Extended X-ray Absorption Fine Structure Studies on Mixed-Phase Zirconia

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The differences among radial distribution functions (RDFs) of monoclinic ZrO_2 , tetragonal ZrO_2 , and mixedphase ZrO_2 have been discussed. A much decreased Zr-Zr peak was found in the RDF of mixed-phase ZrO_2 . The result was explained by Lu Kunquan's equation very well.

1. Introduction

 ZrO_2 is an important catalyst support and also an important ceramic material. The Zr local coordination environment has been studied by extended x-ray absorption fine structure (EXAFS) on zirconia or yttrium-stabilized zirconia.^{1–14} In many literature reports, much decreased Zr–Zr peaks have been found in their ZrO₂-contained samples. The decrease is usually explained by the smaller coordination number or the larger Debye–Waller factor. However, it may not always be the truth. The cancellation of Zr–Zr peaks exists between monoclinic and tetragonal ZrO₂, which is shown in this paper. The purpose of this paper is to remind people to pay enough attention to the mixed-phase cancellation effect, especially during fitting Zr– Zr peaks. Otherwise, the fitting results may not be obtained correctly.

2. Experimental Section

2.1. Sample Preparation. High-surface mixed-phase zirconia (designated as CZ) is prepared by dropping excessive 0.87 mol dm⁻³ NH₄HCO₃ into 3 mol dm⁻³ Zr(SO₄)₂ at a speed of 1–2 drops/min under fast stirring. The precipitate was divided into two parts. One part was washed with distilled water, then dried at 383 K, and calcined at 773 K for 4 h, which produced sample CZ. Sample CZ's N₂–BET surface area is 67 m²/g. The other part was washed with pure ethanol, then also dried at room temperature, and calcined at 773 K for 4 h in air, which produced sample TZ, mainly composed of tetragonal zirconia. Monoclinic ZrO₂ (MZ) was commercially supplied.

2.2. X-ray Diffraction. X-ray diffraction (XRD) results were obtained by BD-86 X-ray diffractometer (Cu K α , 20 mA, 40 kV). The original spectra were smoothed by POWDERX program.¹⁵

Sample CZ can be seen as a mixture of MZ and TZ. To determine the ratio of MZ and TZ in CZ, the XRD peak intensity ratio of MZ (111) (designated as PM1) reflection to TZ (111) (designated as PT) was taken as the relative amount of MZ and TZ.

2.3. EXAFS. X-ray absorption experiments were carried out on the beam line 4W1B at Beijing Synchrotron Radiation



Figure 1. XRD patterns for MZ, CZ, and TZ.

Facility with a ring energy of 2.2 GeV and stored current of 70–110 mA. EXAFS data of samples were collected in transmission mode at room temperature with a Si (111) twocrystal monochromator. The experimental spectra were analyzed with a program from Physical Institute, Chinese Academy of Sciences. The atomic-like absorption coefficient calculated by three-cubed fit was used as spectrum normalization. Zr-centered and k^3 -weighted radial distribution functions (RDFs) were obtained in range of 3.0–12.0 Å⁻¹ by the program UWXAFS¹⁶ from the University of Washington.

3. Results

3.1. XRD Measurement Results. The XRD patterns for MZ, TZ, and CZ are shown in Figure 1. CZ is a mixture of monoclinic phase and tetragonal phase and also a little amorphous phase.¹ For the smaller size of crystal, the XRD peaks in CZ are broader than commercially supplied MZ. The width of PT peaks in TZ and CZ is almost same, which can be explained by similar crystal size in the two samples because of their similar ways of preparation.

Peak area of PT for the TZ sample is 1911. Because the X-ray absorption coefficients for the monoclinic and tetragonal samples are nearly same, the relative amount of MZ and TZ weight fraction can estimated from its peak area. Peak area of PM1 for the MZ sample is 735. For sample CZ, the peak area of PM1 is 335 and the area of PT is 880. The dotted horizontal lines in Figure 1 are chosen as baselines for PT and PM1, that is, MZ's weight fraction, $W_{MZ} = 370/735 = 0.50$, in sample

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Figure 2. Uncorrected Zr K-edge RDF for MZ, CZ, and TZ.



Figure 3. Zr K-edge k^3 -weighted k-space-filtered results for MZ and TZ.

CZ and TZ's weight fraction, $W_{\text{TZ}} = 949/1911 = 0.50$. The amorphous state can be neglected.

3.2. EXAFS Results. The Zr-centered RDFs for MZ, CZ, and TZ are shown in Figure 2. From Figure 2, the peak at 1.69 Å in MZ's RDF and the peak at 1.59 Å in TZ's RDF correspond to Zr–O shells. The peak at 3.03 Å in MZ's RDF and the peak at 3.25 Å in TZ's RDF correspond to Zr–Zr shells (for MZ, it also includes Zr–O shells, but the contribution is small and does not affect the following discussion). For sample CZ, the intensity of the Zr–O peak, which is located at 1.60 Å, is just between that of MZ and TZ. However, for CZ's Zr–Zr peak near 3.0 Å, the intensity is much reduced, which cannot be explained by a decrease of the Zr–Zr shell's coordination number.

4. Discussion

According to the equation recommended by Lu Kunquan,¹⁷ if sample γ consists of phase α and β , then

$$\chi(\gamma) = W_{\alpha}\chi(\alpha) + W_{\beta}\chi(\beta) \tag{1}$$

For sample CZ,

$$\chi(CZ) = W_{MZ}\chi(MZ) + W_{TZ}\chi(TZ)$$
(2)

As mentioned above, $W_{MZ} = 0.50$ and $W_{TZ} = 0.50$.

The total χ (CZ) of all shells can directly obtained from eq 2. The χ (MZ) and χ (TZ) are shown in Figure 3. The calculated χ (CZ) according eq 2 (designated as M5T5) and the experimental χ (CZ) (designated as CZ) k^3 -weighted k-space results



Figure 4. Zr K-edge χ (CZ) from calculated and experimental results.



Figure 5. Zr K-edge RDFs for CZ from calculated and experimental results.

are shown in Figure 4, and Fourier transformation results in *R*-space are shown in Figure 5.

Thus, for the mixed-phase sample, CZ, its EXAFS result is easily explained by Lu's equation. Figure 5 shows evidently the cancellation of Zr-Zr peaks from monoclinic and tetragonal phases.

This cancellation effect can also be found in other people's systems to some extent,^{1,2,4,18} which have been neglected for their small portion of monoclinic phase. Due to the cancellation effect, the existence of monoclinic and tetragonal phase is not apparent in CZ's RDF, though it is shown in CZ's XRD pattern clearly.

For one shell, if *A* expresses the amplitude of one coordination shell, then

$$\chi(k) = A(k) \sin[2kR + \delta(k)] \tag{3}$$

The phase shift $\delta(k)$ is related to absorption atoms' type and scattering atoms' type. For oxide M_XO_Y , the first nearest shell is always the M–O shell; the second nearest shell is mostly the M–M shell (the contribution of the second M–O shell is usually very small). So, $\delta(k)$ of the first M–O shell and that of the M–M shell is similar for different phases because their absorption and scattering atoms' type is same.

Thus, the difference of $[2kR + \delta(k)]$ between phase α and phase β is

$$\Delta \varphi(k) = 2k\Delta R, \quad \Delta R = |R_{\alpha} - R_{\beta}| \tag{4}$$

When $\Delta \varphi(k) = \pi$, the $\chi(k)$ in eq 3 from phase α and phase β will cancel each other to the biggest extent. At this time,

$$k_{\text{cancel}} = \frac{\pi}{2\Delta R} \tag{5}$$

In phase α and phase β , for the corresponding shell, if the k_{cancel} is between 3 and 12 Å⁻¹, where $A_{\alpha}(k_{\text{cancel}})$ and $A_{\beta}(k_{\text{cancel}})$ is often big enough (k^3 -weighted), under this condition, the cancellation effect should be considered.

For most oxides M_XO_Y , the coordination distances of the first M–O shells have nearly same value in different phases, so it is rarely to see the cancellation of the M–O shell, whereas for the M–M shell, they often have larger differences. So for M–M shells, they are more easily able to cancel each other in RDFs.

From Figure 2, the uncorrected R_{Zr-Zr} for MZ is 3.03 Å, and that for TZ is 3.25 Å. So, $\Delta R_{Zr-Zr} = 0.22$ Å and

$$k_{\text{cancel}}(\text{Zr}-\text{Zr}) = \frac{\pi}{2\Delta R_{\text{Zr}-\text{Zr}}} = 7.1 \text{ Å}^{-1}$$

 $k_{\text{cancel}}(\text{Zr}-\text{Zr})$ falls between 3 and 12 Å⁻¹, which means the cancellation of the Zr–Zr peak in MZ and TZ is big enough.

5 Conclusion

When doing EXAFS study about ZrO_2 -contained system, if the much decreased Zr-Zr peak in RDF was found, besides smaller coordination number and the bigger Debye–Waller factor, it may also be caused by the cancellation effect of $\chi(k)$ from the monoclinic and tetragonal ZrO_2 . This cancellation effect may exist in other mixed-phase materials, which should be taken into consideration as well.

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