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The Identification of Radial Structure Peaks of EXAFS Fourier Transform of NiO Dispersion Phase

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Abstract: A comparison of backscattering amplitudes and APCFT of XAFS of dispersed and crystalline NiO were used to identify radial structural peaks. The results show that there are coordination peaks in the FT function of dispersed phase corresponding to the first, third and forth Ni-Ni coordination shells in the crystalline NiO, although their area may very different depending on the loadings of NiO. But there are no peak corresponding to the second Ni-Ni coordination shell of NiO. It is to say that the second Ni-Ni shell in crystalline NiO disappears as in spinel and the other Ni-Ni coordination shells may still exist when NiO disperses on the surface of support. It also implies that the structure of surface-dispersed NiO has both similarity and difference to NiAl_2O_4 or NiO.

1. Introduction

XAFS can give abundant structural information quantitatively, moreover, the information about coordination species can be obtained qualitatively in some cases, too. In general, little attention is paid to the later one which is the base of the former. If the radial structural peaks are not been assigned correctly, it is impossible to get the true quantitative information. Especially, for the case that the system has several coordination shells with close distances, it is more important to distinguish the radial peaks and to develop the qualitative studies on coordination atom species. In this paper, comparison of backscattering amplitudes [1] (including $(N/R^3)e^{-2\sigma^2/4\lambda^2}$), APCFT [2] (Amplitude and phase shift corrected Fourier transform) method were carried out on NiO/ $\gamma\text{-Al}_2\text{O}_3$ dispersion system to discriminate its structure peaks.

2. Results and Discussion

NiO has the structure of NaCl type. Its radial peaks have been assigned very well yet [1]. When NiO is dispersed on the support, the diffraction pattern of NiO disappears. But most Ni-Ni coordination peaks corresponding to crystalline NiO still exist (the position shifts slightly and intensity decreases) except the second Ni-Ni coordination shell (Ni-Ni(2) corresponding to the second Ni-Ni in NiO). Figure 1 shows the Fourier transform of Ni-K edge of NiO/ $\gamma\text{-Al}_2\text{O}_3$ system. At the position corresponding to Ni-Ni(2) peak of NiO there is no radial peak, meantime, at its left, a little radial peak appears, which doesn't change with the loading when it is less than maximum dispersion amount. The coordination type of this peak will be discussed below.

Figure 2 shows the XAFS oscillating curves and the backscattering amplitudes functions of the structural peaks of NiO/ $\gamma\text{-Al}_2\text{O}_3$ corresponding to Ni-Ni(1) and Ni-Ni(2) in crystalline NiO respectively. The Figure 2-A shows that the maximum of backscattering amplitudes, frequencies and phase of oscillating curves of samples are agreed to those of Ni-Ni(1) in NiO, although the amplitudes reduce with decrease of NiO loading. The case of Ni-Ni(3), Ni-Ni(4) is similar to that also. But the situation of Ni-Ni(2) coordination is different. When the content of Ni decreases, especially for the new radial peak mentioned above, the maximum of backscattering amplitudes shift to low K markedly and the frequency and phase of oscillating curves are different to NiO obviously either. It shows that the coordination shell in the dispersed phase is not corresponding to Ni-Ni(2) in crystalline phase. Maybe the peak is due to coordination shell of lighter atom.

Figure 1: The Fourier transform of $k^3\chi$ (Ni-K edge) of NiO/ $\gamma\text{-Al}_2\text{O}_3$

a: NiO
b: 0.225 gNiO/g $\gamma\text{-Al}_2\text{O}_3$
c: 0.143 gNiO/g $\gamma\text{-Al}_2\text{O}_3$
Maximum dispersion amount: 0.19 gNiO/g $\gamma\text{-Al}_2\text{O}_3$ (obtained from XRD)

APCFT was carried out on the standard amplitude and phase shift obtained from corresponding Ni-Ni coordination shells of crystalline NiO. A part of results was shown in Figure 3. The absolute values and imaginary parts of Fourier transforms of Ni-Ni(1,3,4) coordination peak at near same position. The peaks of imaginary parts are also symmetric. The absolute values and imaginary parts decrease with the decrease of NiO content regularly. But the situation of Ni-Ni(2) coordination shell is different either. For the samples in which NiO is dispersed, the peaks of imaginary parts and absolute values misfit. The mentioned peak can be fit quite well by Ni-O coordination. The results show further that when NiO is dispersed on the support, the Ni-Ni coordination shell corresponding to the Ni-Ni(2) in crystalline NiO disappears but a part of Ni-Ni coordination shell corresponding to Ni-Ni(1), even Ni-Ni(3) coordination shell in NiO may remain still. The mentioned peak may belong to Ni-O coordination. It is reasonable since in fact there is Ni-O coordination shell in this position in crystalline spinel or NiO. In spinel there is a part of Ni-Ni(1) coordination shell but no Ni-Ni(2) corresponding to NiO. The dispersion system has formed a structure which has both similarity and difference to NiAl_2O_4 or NiO. It is very consistent with the monolayer dispersion mode[3].

Figure 2: XAFS(solid line) and the backscattering amplitude(dotted line) $(N/R^2)e^{-2\sigma^2/4\lambda}$ term is included) curves corresponding to different Ni-Ni coordination shells.

A: Ni-Ni (1) coordination shell

B: Ni-Ni (2) coordination shell

Large amplitude: crystalline NiO

Middle amplitude: dispersed and crystalline NiO

Small amplitude: dispersed NiO

Figure 3: Comparison between imaginary part (solid line) and the absolute value (dotted line) of APCFT of different Ni-Ni coordination shells

A: Ni-Ni (1) coordination shell

B: Ni-Ni (2) coordination shell

High peak: crystalline NiO

Middle peak amplitude: dispersed and crystalline NiO

Low peak: dispersed NiO

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