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The Structural Characteristics of the Dispersed State of CdO/ γ -Al₂O₃ System

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Abstract: A comparison between the FT functions of XAFS of CdO/ γ -Al₂O₃ and NiO/ γ -Al₂O₃ systems was carried out. The results show that their situations are very different. For the former, there is no Cd-Cd coordination peak corresponding to the first Cd-Cd coordination shell in the crystalline CdO and the coordination numbers of the first Cd-O shell decrease to 3.0. But after NiO disperses, Ni-O coordination numbers just decrease a little. The coordination numbers of the Ni-Ni shell corresponding to the first, even the farther Ni-Ni coordination shells of NiO remain partly. Maybe the differences between them are mainly due to the their different radii and the different fitness to the support.

1. Introduction

What are the main factors to the structure of dispersed phase? It is a problem concerned by both theoretical and practical field. Here we make a comparison of dispersed states of CdO and NiO in order to investigate the effect of the radii of ions in oxides. The structure of dispersed NiO has been studied widely [1], so here we focus in the structure of dispersed CdO. CdO has the same structure type, but Cd²⁺ has different cation radius from Ni²⁺.

2. Results and Discussion

CdO/ γ -Al₂O₃ system was prepared by impregnation and calcination at 773K for 8 hours. The specific surface area of γ -Al₂O₃ is 221 m²/g. The threshold (dispersion capacity) obtained by XRD phase quantitative analysis is 0.34 gCdO/g γ -Al₂O₃ (Figure 1-A).

In the |FT| functions of χ k³ for pure CdO and samples, only the nearest Cd-O coordination peaks (Cd-O (1), corresponding to the first Cd-O coordination shell of CdO) appear and the coordination peaks corresponding to the first Cd-Cd coordination shell (corresponding to Cd-Cd (1) in crystalline CdO) disappear for completely dispersed samples, in which loadings are below the threshold. Compared with pure CdO, the peaks are keener and have less area but shift to left. The coordination numbers of Cd-O in dispersed phase decrease to 3.0, and the coordination distances decrease too. In the samples up the threshold, there is residual crystalline phase besides dispersed phase. Accordingly the Cd-O and Cd-Cd coordination peaks of crystalline CdO can be found. The area of Cd-O(1) peaks, especially, of all Cd-Cd peaks and their apparent coordination numbers increase with the increase of CdO loadings (shown in Figure 1-B). Apparently, it is due to the change of fraction of crystalline CdO in the samples.

Fourier filter was carried out on Cd-O(1) and Cd-Cd(1) coordination peaks. The ranges are [1.329~2.327 Å] and [2.659~3.630 Å] for Cd-O(1) and Cd-Cd(1) respectively. The isolation of dispersed phase [2, 3] is according to the following formula and the results are shown in Figure 2.

For Cd-O(1) coordination shell: $[6.0(x-Th)/x] + [N_{Cd-O(dispersed)}Th/x] = N_{Cd-O(apparent)}$ or $(6.0 - N_{Cd-O(apparent)})x = (6.0 - N_{Cd-O(dispersed)})Th$. For Cd-Cd(1) coordination shell: $(12.0 - N_{Cd-Cd(apparent)})x = (12.0 - N_{Cd-Cd(dispersed)})Th$. (x, loading, Th, threshold, both in g/g).

From Figure 1, it can be seen that for the samples with loadings more than the threshold, the curves ($N_{Cd-O(apparent)}$) or N_{Cd-Cd}

Figure 1: A. Residual crystalline amount ~ loadings of CdO in the samples;
B. $N_{apparent}$ ~ loadings of CdO/ γ -Al₂O₃

a. Cd-O coordination (corresponding to first Cd-O coordination shell of CdO crystall)
b. Cd-Cd coordination (corresponding to the first Cd-Cd coordination shell of CdO crystall)

$N_{Cd-O}(\text{apparent}) \sim x$) are just the hyperbolas. The cross points of $N_{Cd-Cd}(\text{apparent}) \sim x$ and the abscissa is 0.34 gCdO/g γ -Al₂O₃, which is just equal to the threshold got from XRD. It is worthy to note also that the $N_{Cd-O}(\text{dispersed})$ always is 3.0, $N_{Cd-Cd}(\text{dispersed})$ is 0, regardless of that it comes from direct XAFS result of perfect dispersed sample or comes from phase isolation of mixed phase samples as shown in Figure 2. The consistency demonstrates that above results are reliable. Apparently, the structure of CdO/ γ -Al₂O₃ is very different from NiO/ γ -Al₂O₃ [1].

Figure 2: The actual coordination numbers of dispersed phases versus loading

A: NiO/ γ -Al₂O₃;

B: CdO/ γ -Al₂O₃;

Upon: Ni-O or Cd-O shell corresponding to the first M-O coordination shell in crystal;

Below: Ni-Ni or Cd-Cd shell corresponding to the first M-M coordination shell in crystal.

(1) Their coordination polyhedra are different. In the dispersed phase, Ni-O coordination numbers just decrease a little, most Ni²⁺ ions remain octahedra coordination mode. In the dispersed phase of CdO on γ -Al₂O₃ surface, the coordination numbers of Cd-O(1) reduce to 3.0 from 6 in crystalline phase and doesn't change with loadings below or above threshold. The coordination distances also decrease about 0.08 Å. Although it can not be excluded that there is the probability of several coordination modes, it is in certain that Cd²⁺ in dispersed phase tends to coordinate to fewer O atoms with shorter distance.

(2) Below the threshold, Ni-Ni(1), and even Ni-Ni(3) coordination increase with the increase of loadings till the maximum (at the threshold) which keeps about 4.0. But CdO in dispersed phase has no Cd-Cd(1) coordination peaks. It may be because of very random distribution of Cd²⁺ in the dispersed phase.

Why these two oxides with same structure type have so marked differences when they are dispersed on same support? Apparently, it must be related to the different radii of Cd²⁺ and Ni²⁺. The parameters of cell of NiO are quite agreed with those of Al₂O₃. In the NiO or spinel, Ni-O distance is close to 2 Å, which is near the Al-O distance. So, when NiO is dispersed, Ni-O and Ni-Ni coordination shells can still remain very order state. But the parameters of cell of CdO (4.659 Å) is different from Al₂O₃ greatly. The coordination distance of Cd-O (2.33 Å) in CdO is much greater than that of Al-O (octahedron, 1.95 Å, tetrahedron, 1.71 Å) in Al₂O₃, although it has same cell type as NiO. So when CdO disperses on γ -Al₂O₃, it is difficult to keep order distribution and the previous coordination polyhedron.

The results indicate that the ion radius maybe an important, even a key factor to affect the structure of a dispersion state for some systems.

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