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Eu_2O_3 在多种 Al_2O_3 载体上固体-固体表面吸附的研究

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摘　要

用穆斯堡尔谱学、X 射线衍射等方法研究了在多种 Al_2O_3 载体上的固体-固体表面吸附。结果表明，Eu_2O_3 在复合载体 Al_2O_3/SiO_2 上的固体-固体相互作用和 Eu_2O_3 在单一载体上分散时的情况有明显差异。用混合模型可成功地解释 Eu_2O_3 在 γ-Al_2O_3 或 η-Al_2O_3 载体表面上的分散。

Study of the Solid-Solid Surface Adsorption of Eu_2O_3 on Various Al_2O_3 Supports

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ABSTRACT

Solid-solid surface interactions of Eu_2O_3 on various oxide suhstrates are investigated with X-ray and Mössbauer experiments. The results indicate that the interaction of Eu_2O_3 on the complex support differs from that having simple support. An incorporation model is used to explain how Eu_2O_3 disperses onto the surface of γ-alumina or η-alumina.

INTRODUCTION

The understanding of the atomic processes on solid surfaces is considerable interest because of its relevance to a variety of technologically important processes such as crystal and thin film growth, surface oxidation, heterogeneous catalysis and so fortb.

We have previously studied the dispersion of Eu_2O_3 onto the surface of γ-Al_2O_3, η-Al_2O_3, SiO_2 gel and amorphous Al_2O_3 by different methods. The changes in X-ray diffraction patterns and Mösshauer parameters as a function of europium content revealed the differences of interaction between Eu_2O_3 and the several substrates studied. Some of the results have heen previously reported [1~3].

In order to elucidate the behavior of Eu_2O_3 in a solid-solid adsorption processes, we expanded our study by using a Al_2O_3/SiO_2 complex substrate and applying the incorporation model proposed by Y. Chen [4]. The mechanism of the dispersion of Eu_2O_3 onto the crystalline supports, γ-Al_2O_3 and η-Al_2O_3, is discussed in this paper.

1 EXPERIMENT

The Al_2O_3/SiO_2 complex substrates were prepared as follows: SiO_2 gel was mixed into Al $(NO_3)_3 \cdot 9H_2O$. The solutions were dried roughly by stirring at 120 ℃. The dried solutions of Al_2O_3/SiO_2 were then treated for 2 h at 300 ℃, 2 h at 500 ℃ and finally for 18 h at 600 ℃. X-ray diffraction patterns show that the Al_2O_3/SiO_2 was amorphous. Its specific surface area of carrier [BET] was determined to be 211.6 m^2/g.

Samples of Eu_2O_3 supported on the Al_2O_3/SiO_2 complex substrates were prepared as previously described [1].

The Mössbauer measurements were performed at room temperature with a conventional Mösshauer spectrometer. The isomer shift values of the ^{151}Eu resonance lines are given relatively to bulk Eu_2O_3 at room temperature.

2 RESULTS AND DISCUSSION

Typical X-ray patterns of the doped Al_2O_3/SiO_2 complex suhstrates are shown in Fig. 1. The diffraction peaks arising from the Eu_2O_3 structure could not be seen until the Eu_2O_3 content mass fraction reaches 75%, a concentration far above the monolayer range. According to the simple electrostatic model [5], 37.6% Eu_2O_3 gives a monolayer. This behavior is different from that found for a single substrate previously reported [1~3].

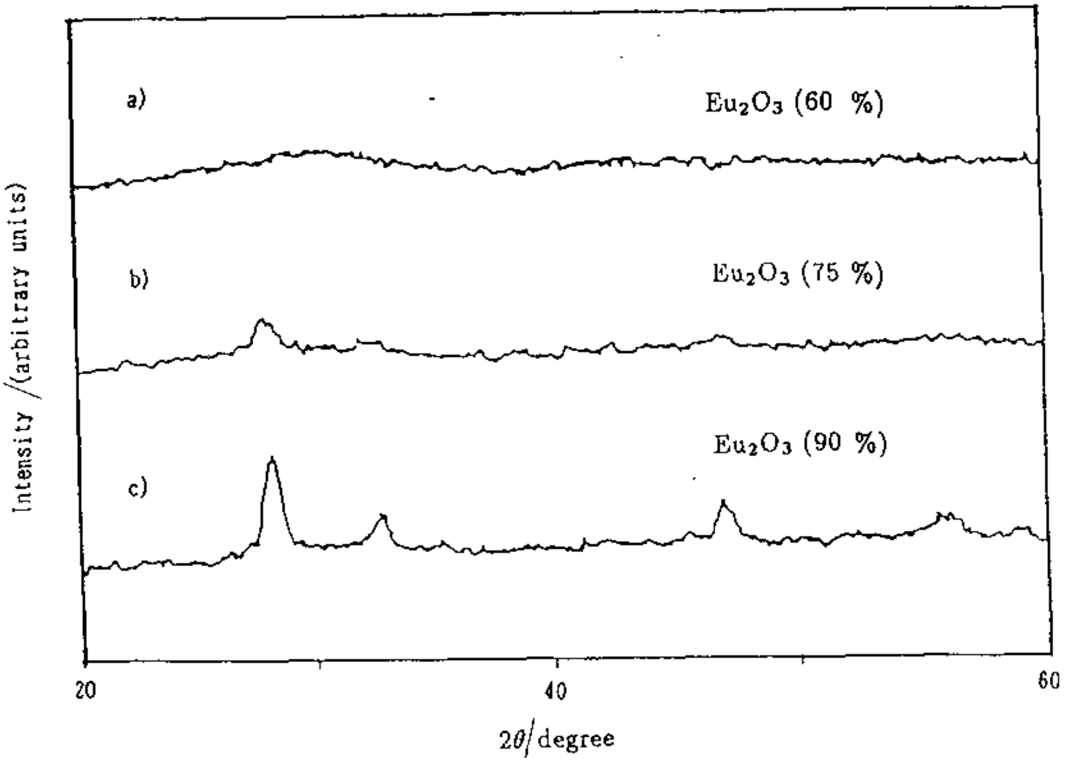

Fig. 1 X-ray diffraction pattern of Eu_2O_3 on Al_2O_3/SiO_2 substrates for different concentration ranges

a) mass fraction of Eu_2O_3 is 60%

b) mass fraction of Eu_2O_3 is 75%

c) mass fraction of Eu_2O_3 is 90%

Typical Mössbauer spectra for different concentrations of Eu_2O_3 on a Al_2O_3/SiO_2 substrate are shown in Fig. 2. The corresponding isomer sbift (IS) values and effective line width as a function of the Eu_2O_3 content are listed in Table 1.

The experimental errosr are ±0.02 mm/s and ±0.10 mm/s for isomer shift and line width respectively.

Table 1 Mössbauer parameters of pure Eu_2O_3 and Eu_2O_3 supported on Al_2O_3/SiO_2

Sample	Mass Fraction of Eu_2O_3 / %	Isomer Shift / mm/s	Line Width / mm/s
Eu_2O_3 supported on Al_2O_3/SiO_2	10.0	−0.44	1.83
	30.0	−0.33	2.08
	45.0	−0.37	2.42
	60.0	−0.30	2.47
	75.0	−0.25	2.54
	90.0	−0.09	2.32
Pure Eu_2O_3	99.99	0.00	2.44

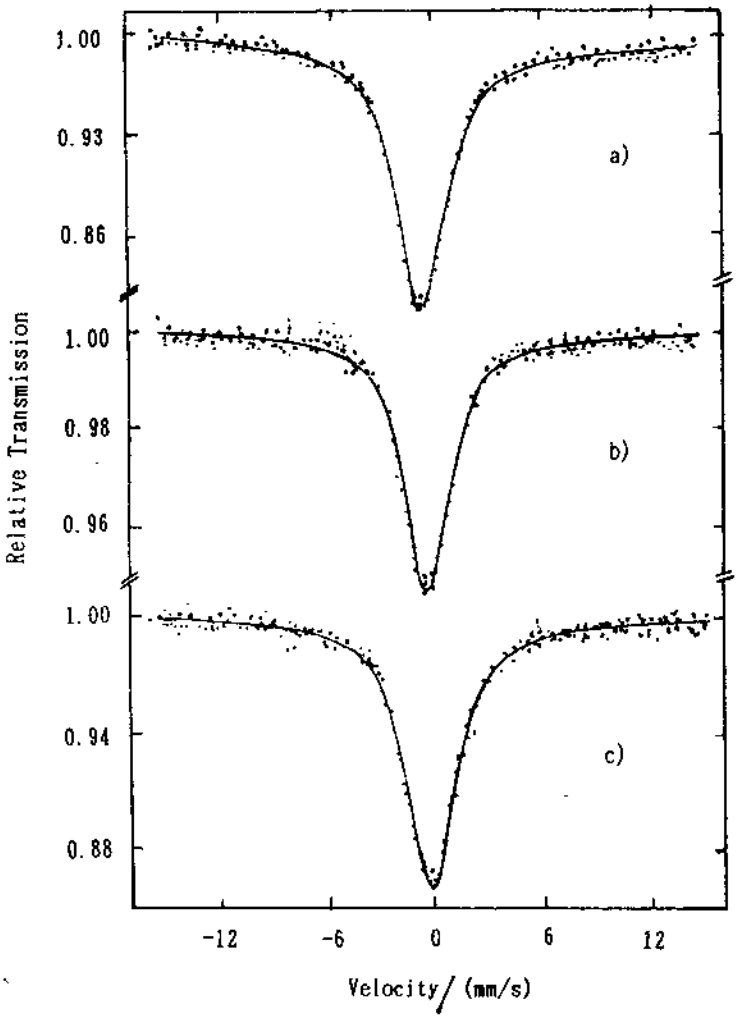

Fig. 2 Mössbauer spectra of Eu_2O_3 on complex Al_2O_3/SiO_2

a) mass fraction of Eu_2O_3 is 10%

b) mass fraction of Eu_2O_3 is 60%

c) pure Eu_2O_3

Fig. 3 shows the IS as a function of Eu_2O_3 content on amorphous Al_2O_3, SiO_2 gel and a Al_2O_3/SiO_2 complex substrate. We noted that the IS of Eu_2O_3/Al_2O_3 is larger than that of Eu_2O_3/SiO_2. The explanation for this difference is that since the electronegativity of Al is smaller than that of Si, the tendency of attracting electrons is smaller. This indicates that the Al-Eu interaction is different from that of Si-Eu and that their influence on the surrounding electron cloud of Eu atom dispersed on its surface is distinct. If Eu_2O_3 disperses onto the Al_2O_3 surface with a larger surrounding electron density of Eu atoms, its values of IS are larger than those of Eu_2O_3 dispersed on the SiO_2 support.

The IS of Eu_2O_3/SiO_2 substrate lies between those of Eu_2O_3/Al_2O_3 and Eu_2O_3/SiO_2 gel (Fig. 3). Together with the X-ray diffraction result, the dispersion of Eu_2O_3 onto its surface seems to show a blent effect.

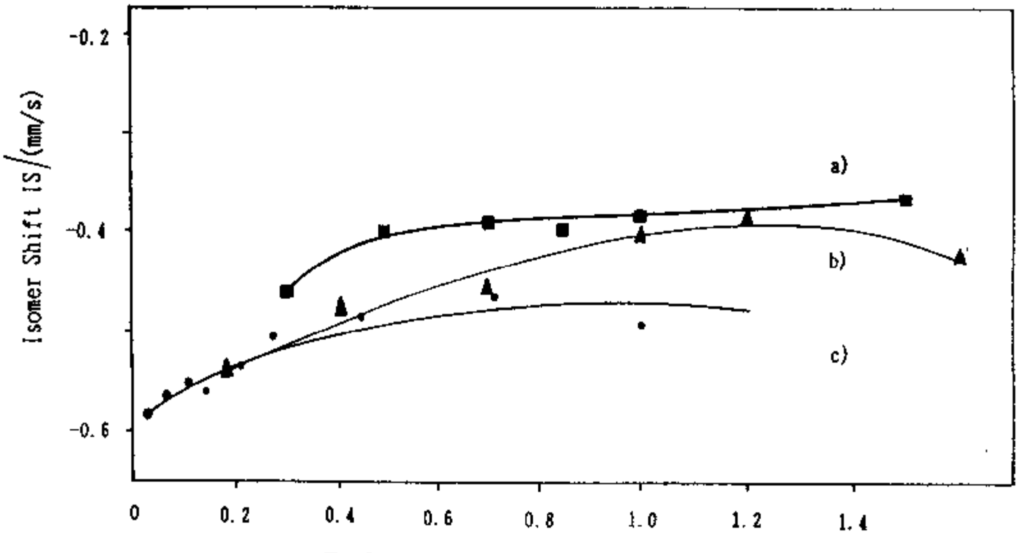

Fig. 3 Comparison of IS value of Eu_2O_3 supported on

a) amorphous Al_2O_3
b) Al_2O_3/SiO_2 complex substrate
c) SiO_2

The dispersion of Eu_2O_3 onto the surface of γ-Al_2O_3, or η-Al_2O_3 had been studied previously. To get a better understanding of the metal oxide/substrate interaction, the surface structure of the substrate is investigated.

For γ-Al_2O_3, the [110] plane is considered to be the preferentially exposed surface. Such an assumption has been supported by the neutron diffraction studies of CD_4 absorbed on γ-alumina. Thus, as a first approximation, the structure of γ-Al_2O_3 can be assumed to consist of particles formed by one dimensional stacking C-D-C-D layers as shown in Fig. 4, with a sequence of C-D-C-D-. The ratio of the exposure probabilities of these two layers is one. The unit mesh of C-and D-can be expressed as $[Al_2O_4]$ and $Al_{4/3}$ $[Al_2O_4]$ respectively. The Al^{3+} cations inside the bracket are octahedrally coordinated, while those outside the bracket are tetrahedrally coordinated [4].

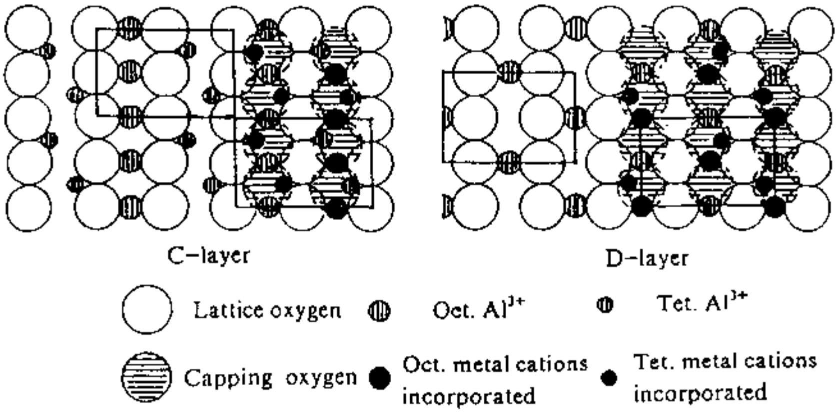

Fig. 4 The structure of C-and D-layers of [110] plane in γ-Al_2O_3 and incorporation of metal cations into C-and D-layers.

Fig. 4 shows the existence of vacant sites on the surface of γ-Al_2O_3. The diameter of Eu^{3+} (0.103 nm) is larger than the diameter of the Al^{3+}, which is about 0.05 nm. So, when Eu_2O_3 disperses onto γ-Al_2O_3, at a loading below its monolayer dispersion capacity, the incorporation of Eu^{3+} into some of the exposed vacant sites is assumed to result in the formation of tetrahedral or octahedral Eu^{3+} cations, and at the same time the associated oxygen anions will stay at the top of the occupied sites. So the excess positive charges can be compensated. Based on these assumptions the dispersion capasity of Eu^{3+} cations is evaluated to be 10.4 cations/nm^2, or 0.28 g/100 m^2. As a consequence of the shielding effect of the capping oxygen anions, half of the vacant sites are actually not available for the incorporaton of other cations. The dispersion capacity of Eu^{3+} cations therefore drops down to 5.2 cations/nm^2, or 0.14 g/100 m^2. Since the BET of γ-Al_2O_3 is 245 m^2/g, Eu_2O_3 reaches the monolayer coverage at 25% Eu_2O_3 concentration. This result is in very good agreement with the 25.5% monolayer capacity obtained experimentally [1].

The structure of η-Al_2O_3 is different from that of γ-Al_2O_3, and its preferentially exposed plane is [111][6]. Using the same model, we can also get satisfactory results to explain Eu_2O_3 dispersion onto a η-Al_2O_3 surface.

3 SUMMARY

The interaction of Eu_2O_3 on different oxide suhstrates has been studied. The results indicate that there were strong interactions hetween Eu_2O_3 and the substrates. There is also an induced effect of the substrate on the structure of the Eu_2O_3 dispersed onto the carrier surface. For the Al_2O_3/SiO_2 complex substrate, it appears that there is an intermediate interaction.

The incorporation model successfully explains how Eu_2O_3 disperses onto the surface of crystalline γ-Al_2O_3 and η-Al_2O_3.

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