INVESTIGATION OF THE SOLID– SOLID SURFACE ADSORPTION OF Eu_2O_3 ON AMORPHOUS Al_2O_3

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ABSTRACT

Solid–solid surface adsorption of Eu_2O_3 on amorphous Al_2O_3 have been investigated by Mössbauer spectroscopy, X–ray diffraction analysis and laser Raman spectra (LRS). No X–ray diffraction peak of crystalline Eu_2O_3 can be found for all samples studied. The LRS show that two peaks at 998 and 1051 cm^{-1} assigned to two–dimensional surface europium–oxygen species appear at Eu_2O_3 content of 18.7 wt%. The peak at 1068 cm^{-1} due to the surface species and another peak at 342 cm^{-1} due to crystalline Eu_2O_3 content start to appear for the sample with an Eu_2O_3 content of 36.5 wt%. The dispersity of Eu_2O_3 on the surface of amorphous Al_2O_3 were compared with that of γ $-Al_2O_3$, η $-Al_2O_3$ and SiO_2 gel. The results of these studies indicate that the structure of Eu_2O_3 dispersed onto the support surface depend on the structure of support and that there is an inductive effect of support on the structure of the Eu_2O_3.

Keywords: Mössbauer spectroscopy XRD LRS Eu_2O_3 Amorphous Al_2O_3 Solid–solid surface adsorption

1 INTRODUCTION

Knowledge of the interaction between the active component of a catalyst and its support is particularly important for the preparation of a catalyst with the desired catalytic property. For the supported catalyst, after calcining at a suitable temperature for several hours, the bulk structure of the support would not change, but some kinds of interaction between its surface and the active component would occur. The results of the Mössbauer spectroscopic investigation show that the Mössbauer parameters of supported Eu_2O_3 are significantly different from those of the bulk. It provides a clear evidence of the Eu_2O_3–support interaction for supported europium catalysts[1].

In order to probe the interaction behavior in solid-solid adsorption processes, we have studied the dispersity of Eu_2O_3 on the surface of γ -Al_2O_3[2], η -Al_2O_3 and SiO_2 gel[3] by Mössbauer spectroscopy and X-ray diffraction analysis (XRD), and confirmed the dispersion of Eu_2O_3 on these supports after appropriate treatment. Changes in Mössbauer parameters as a function of the europium content revealed the differences of the interaction between Eu_2O_3 and the individual supports. We are dealing continuously with the study of solid-solid adsorption phenomenon using amorphous Al_2O_3 (a-Al_2O_3) as a support.

2 EXPERIMENTAL

$Al(NO_3)_3 \cdot 9H_2O$ was decomposed to form a-Al_2O_3 at 600 °C in a muffle furnace for 18 h. No XRD peak was observed for this kind of Al_2O_3 and its BET surface area determined was 20.2 m^2/g. Samples of Eu_2O_3 supported on a-Al_2O_3 were prepared according to Ref.[2]. The Mössbauer spectra were obtained at room temperature using conventional equipment. The Mössbauer source was $^{151}SmF_3$ with 1.85×10^9 Bq. The isomer shift values of the ^{151}Eu resonance line are given relative to bulk Eu_2O_3 at room temperature. XRD patterns were measured for all samples using a Siemens diffractometer type D-500 with a Cu target and a Ni filter. LRS of all samples were measured by a Spex Ramanlog Model 1403. The excitation source was the Ar^+ laser with an exciting line of 488.0 nm.

3 RESULTS AND DISCUSSION

Typical Mössbauer spectra of pure Eu_2O_3 supported on a-Al_2O_3 are shown in Fig.1. The corresponding isomer shift (IS) values and line width as a function of the Eu_2O_3 content are listed in Table 1 for all samples.

Table 1

Mössbauer parameters of Eu_2O_3 and of Eu_2O_3 supported on a— Al_2O_3

Sample	Eu_2O_3 content (wt%)	IS (mm/s)	Line width (mm/s)
Eu_2O_3 supported on a-Al_2O_3	1.69	-0.46	2.98
	2.79	-0.40	3.14
	3.87	-0.39	3.22
	4.65	-0.40	3.13
	5.44	-0.39	3.23
	7.92	-0.37	3.19
	10.30	-0.37	3.32
Pure Eu_2O_3	99.99	0.00	3.77

The experimental errors are ±0.02 mm/s and ±0.10 mm/s for IS and line width, respectively

In order to establish the monolayer capacity of Eu_2O_3 dispersed on a-Al_2O_3, a close packed model was assumed by taking the Pauling radii 0.103 nm and 0.140 nm for Eu and O respectively, since the surface area of a-Al_2O_3 was 20.2 m^2/g, when Eu_2O_3

content reached 5.44 wt%, a monolayer converage was achieved.

No XRD peak of crystalline Eu_2O_3 can be found for all samples studies, we assumed that Eu_2O_3 was highly dispersed onto the surface of a-Al_2O_3. Typical LRS of samples studied are presented in Fig.2. Two peaks at 998 and 1051 cm^{-1} assigned to two-dimensional surface europium-oxygen species appear at an Eu_2O_3 content of 18.7 wt%, but no crystalline peak is observed. With increasing Eu_2O_3 content, the 998 cm^{-1} peak disappears, the 1051 cm^{-1} peaks shifts to 1068 cm^{-1} and its intensity slightly increases. Another weak broad peak at 342 cm^{-1} assigned to crystalline Eu_2O_3 starts to appear for the sample with an Eu_2O_3 content of 36.5 wt%. It reveals that there are two-dimensional surface europium-oxygen species and a few Eu_2O_3 crystallites on the surface of the sample. The above-mentioned two peaks become stronger at 53.5 wt% Eu_2O_3. The results show that with increasing Eu_2O_3 content the number of Eu_2O_3 crystallites on the surface increases and its grain size rises. However, these Eu_2O_3 crystallites are still smaller than 5 nm, and can not be detected by XRD.

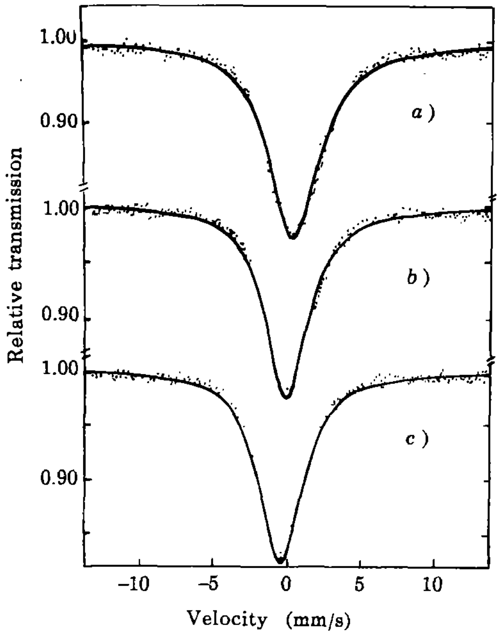

Fig.1 Typical Mössbauer spectra of ***a*)** **PureEu_2O_3,** ***b*)** **Eu_2O_3 (10.3 wt%)/a-Al_2O_3 and** ***c*)** **Eu_2O_3 (2.79 wt%)/a-Al_2O_3 measured at room temperature**

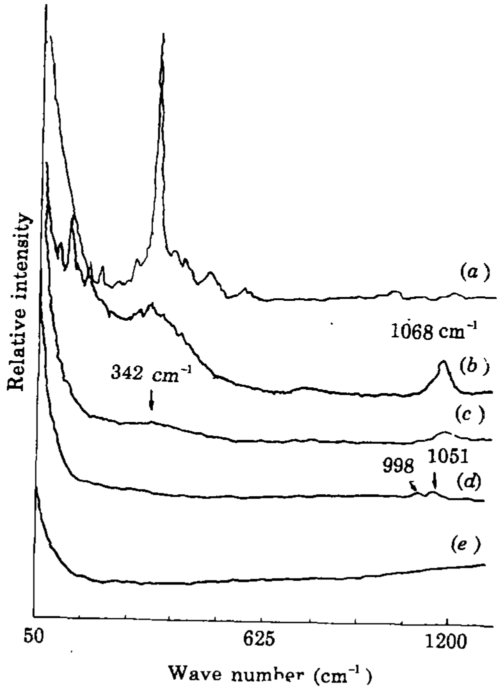

Fig.2 Raman spectra of Eu_2O_3 supported on a-Al_2O_3 and reference materials

a) Pure Eu_2O_3 *b*) 53.5 wt% Eu_2O_3 *c*) 36.5 wt% Eu_2O_3 *d*) 18.7 wt%Eu_2O_3 *e*) Pure a-Al_2O_3

Fig.3 (*a*) shows the IS as a function of Eu_2O_3 content on a-Al_2O_3 measured by Mössbauer spectroscopy. IS progressively increases approaching that of bulk Eu_2O_3 with increasing Eu_2O_3 content. Larger IS means larger electron density at the Eu nuclei and hence a smaller distance between the Eu and O ligand. The interaction between the support and Eu_2O_3 is stronger for the samples with lower Eu_2O_3 contents below 5.44 wt%. With increasing Eu_2O_3 content it tends to disperse on the surface as an additional layer and the Eu_2O_3-support interaction weakens, in which case the electron density at Eu nuclei becomes larger, the distance between the Eu and O ligand becomes smaller and gradually approaches the values of bulk Eu_2O_3.

With increasing Eu_2O_3 content, the line width increases and approaches the value of bulk Eu_2O_3. Since the line width is a measure of the magnitude of the quadrupole splitting, the increasing values of Γ indicate increasing quadrupole splitting, which could result not only from the decreasing Eu-O distances, but also from the formation of lower symmetry units.

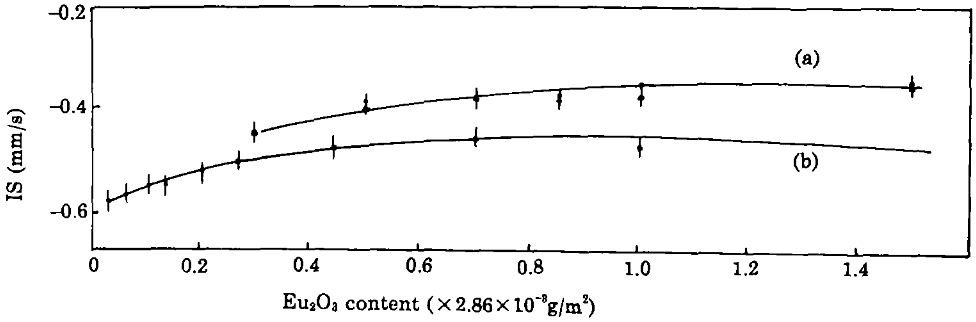

Fig.3 **The comparison of IS value of Eu_2O_3 supported on a- Al_2O_3 (*a*) and on SiO_2 (*b*)**

Thus it can be seen that the dependence of IS and Γ on the Eu_2O_3 content on a-Al_2O_3 is similar to that of Eu_2O_3 on γ-Al_2O_3 and η-Al_2O_3. The only difference is that with increasing Eu_2O_3 content to monolayer coverage, crystalline Eu_2O_3 appears on γ-Al_2O_3 and η-Al_2O_3, but no Eu_2O_3 phase is detected by XRD on a-Al_2O_3. LRS results indicate that only two-dimensional surface europium-oxygen species occur for lower Eu_2O_3 content. Above 53.5 wt% Eu_2O_3, crystalline Eu_2O_3 shows up. This suggests that the support inductive effect on the Eu_2O_3 structure almost disappears at long-range.

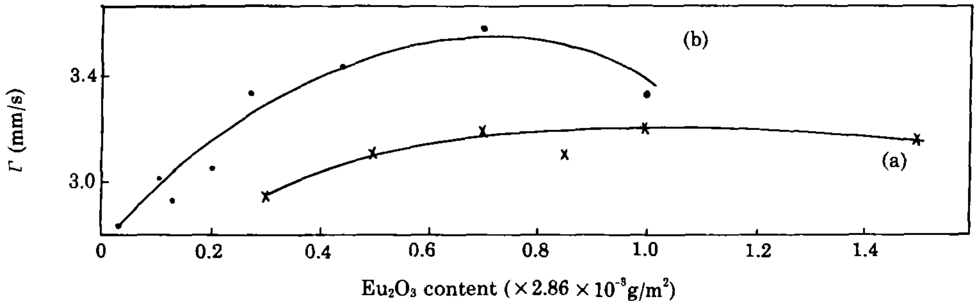

Fig.4 **The comparison of the line width of Eu_2O_3 supported on a- Al_2O_3 (*a*) and on SiO_2 (*b*)**

The differences in the IS for the various supports (shown in Fig.3) result from their distinct electronegativity which is the capacity of attracting electron. A according to Sanderson's model[4], the electronegativity of Al_2O_3 is smaller than that of SiO_2 and hence the tendency to attract electrons is also smaller. This indicates that the Al-Eu interaction is different from that of Si-Eu and their influence on the surrounding electron cloud of Eu atom dispersed on its surface is distinct. Eu_2O_3 dispersed on the Al_2O_3 surface with a larger surrounding electron density of Eu atoms. Thus, in this case the values of IS are larger than those of Eu_2O_3 dispersed on the SiO_2 support. Fig.4 shows the symmetry of the surroundings of the Eu atoms supporting on the SiO_2 surface is lower than that on a-Al_2O_3 surface.

4 SUMMARY

Up to now, Eu_2O_3 dispersion on the surface of the crystalline support γ-Al_2O_3, η-Al_2O_3, the amorphous supports SiO_2 and Al_2O_3 have been studied. The solid-solid surface adsorption of Eu_2O_3 on a-Al_2O_3 and SiO_2 were different from that of on crystalline support. With increasing Eu_2O_3 content, Eu_2O_3 may tend to disperse on the surface in a disordered monolayer configuration or as crystallites with a diameter smaller than 5 nm. The results of these studies indicate that there is a strong interaction between Eu_2O_3 and the support. The first layer structure of Eu_2O_3 on the support surface depends on the structure and properties of the support. This means that there is a support inductive effect on the structure of the supported Eu_2O_3.

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