Vol.6 No.4 NUCLEAR SCIENCE AND TECHNIQUES November 1995

MÖSSBAUER STUDY ON REDUCIBILITY OF SUPPORTED Eu_2O_3[*]

Wu Xiaohua (吴小华), Hsia Yuanfu (夏元复), H. M. Widatallah[1]
(Department of Physics , Nanjing University, Nanjing 210008)
Shen Jianyi (沈俭一), Guan Bing (关 冰) and Chen Yi (陈 懿)
(Department of Chemistry, Nanjing University, Nanjing 210008)

ABSTRACT

The reduction process of Eu_2O_3 on TiO_2 and other supports is investigated in detail by Mössbauer spectroscopy. The reducibility of Eu_2O_3 is greatly enhanced when it is supported on a surface of support. This is due to the solid-solid interaction between the oxide and the support.

Keywords Mössbauer spectroscopy, Eu_2O_3, Reducibility, Supports, Solid-solid interaction, Catalysis, Surface science, Hyperfine structure study

1 INTRODUCTION

Bulk Eu_2O_3 is difficult to reduce. The reduction temperature is over 1200°C for the oxide to be reduced to metal in hydrogen. However, when Eu_2O_3 is highly dispersed on the surface of some supports, such as γ-Al_2O_3, η-Al_2O_3, α- Al_2O_3, SiO_2 or TiO_2, it was found that the reducibility of the oxide is highly enhanced due to the intensive interaction between the oxide and the support. When γ-Al_2O_3 is used as a support in hydrogen atmosphere, for example, 0.6~0.8 of mass fraction of Eu^{3+} can be reduced to Eu^{2+} in 450~ 500°C[1]. In the previous work, we have comparatively studied the interactions of Eu_2O_3 with various supports as well as its dispersibility on the surface of some supports[2–4]. The importance of Eu_2O_3 as catalyst and promoter reflects the significance of such studies from an applied viewpoint[2]. Although generally, the study of a solid-solid interaction is experimently rather difficult, Mössbauer spectroscopy has been proved to be a very useful tool in this respect. To elucidate the reduction behaviour of supported Eu_2O_3 in the present work, we analyse the change of the hyperfine structure of Eu_2O_3 on TiO_2 and other supports by Mössbauer spectroscopy.

2 EXPERIMENTAL

Eu_2O_3/TiO_2 was prepared by the coprecipitation method. Eu_2O_3 was dissolved in dilute H_2SO_4, then $Ti(SO_4)_2$ was added to the solution. While stirring the mixture, aqueous solution of ammonia was added. This resulted in the coprecipitation of Eu_2O_3

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[*] The Project Supported by National Natural Science Foundation of China

[1] On leave from Khartoum University, Sudan

Manuscript received date: 1995–06–18

and TiO_2. The precipitate was washed by distilled water after filtration until SO_4^{2-} was not detected by saturated $BaCl_2$; then, dried at 120°C for 12 h, finally, placed in a muffle furnace and kept at 500°C for 8 h. Samples with different mass fractions of Eu (0.05, 0.15, 0.30 and 0.60) were obtained, respectively. Samples of Eu_2O_3 supported on γ-Al_2O_3, SiO_2, ZrO_2 were prepared in a similar way.

After reduction at 500°C, each sample was sealed in a hydrogen atmosphere. Mössbauer measurements of the samples were carried out at room temperature, using 1.85 GBq $^{151}SmF_3$ as source. Isomer shift is given relative to bulk Eu_2O_3. The nuclear spins of the ground state and the Mössbauer excited state of euronium are 5/2 and 7/2, respectively. The electric quadrupole interaction causes a partial removal of the degeneracy. The ground state splits into three sublevels with $m_I = \pm 5/2, \pm 3/2$ and $\pm 1/2$ while the Mössbauer excited state splits into four sublevels with $m_I = \pm 7/2, \pm 5/2, \pm 3/2$ and $\pm 1/2$. The allowed transition for M1 is $\Delta m_I = 0, \pm 1$. The electric quadrupole Hamiltonian is given by

$$H_Q = \frac{eQV_{zz}}{4I(2I-1)}[3\hat{I}_z^2 - \hat{I}^2 + (\eta/2)(\hat{I}_+^2 - \hat{I}_-^2)]$$

where Q is the electric quadrupole moment, V_{zz} is the principal component of the EFG tensor; I is the nuclear spin. $\hat{I}$ and $\hat{I}_z$ are the nuclear spin operator and its z-component, respectively; $\hat{I}_+ = \hat{I}_x + i\hat{I}_y$ and $\hat{I}_- = \hat{I}_x - i\hat{I}_y$, $\hat{I}_x$ and $\hat{I}_y$ being the components of $\hat{I}$ in the x-direction and y-direction, respectively; $\eta = (V_{yy} - V_{xx})/V_{zz}$ is the asymmetry parameter of EFG. If $\eta < 0.3$, the Hamiltonian may be considered as a diagonal matrix, thus no mixing of the nuclear levels takes place, and the corresponding energy eigenvalues are given by:

$$E_{m_I} = eQV_{zz}(1+\eta^2/3)^{1/2}\frac{3m_I^2 - I(I+1)}{4I(2I-1)}$$

Consequently, the Mössbauer transition energy is:

$$E = eQ_gV_{zz}(1+\eta^2/3)^{1/2} \times \{\frac{1.34[3m_{I_e}^2 - I_e(I_e+1)]}{4I_e(2I_e-1)} - \frac{[3m_{I_e}^2 - I_g(I_g+1)]}{4I_g(2I_g-1)}\}$$

where the subscripts e and g refer to the excited and ground states, respectively.

In this case, there are only eight allowed Mössbauer transitions, whose relative intensities are proportional to the square of the corresponding Clebsch-Gordan coefficients.

3 RESULTS AND DISCUSSION

The Mössbauer spectra of the Eu_2O_3/TiO_2 sample with 0.15 of mass fraction of Eu are shown in Fig.1 for different reduction temperatures. The bars in the figure indicate the positions of the hyperfine subspectra. The Mössbauer parameters corresponding to Eu^{3+} and Eu^{2+} in the sample are shown in Table 1. The variation of the reducibility with different reduction temperatures in a hydrogen atmosphere is shown in Fig.2.

Because of the large difference between the isomer shifts of Eu^{3+} and Eu^{2+}, it is easy to distinguish them using Mössbauer spectroscopy. Since the $4f^7$ configuration shell of Eu^{2+} is half filled, then the Eu^{2+} content in the oxide is relatively stable. In this respect, Eu is different from other lanthanides. The reduction results in the conversion of some Eu_2O_3 to EuO. At room temperature, the isomer shift of EuO is −13.29 mm/s. As the temperature is lowered below 69 K, this oxide becomes ferromagnetic showing a magnetic hyperfine field. Eu_3O_4, on the other hand, is a mixed valence oxide, with two isomer shifts in a wide temperature range. The room-temperature isomer shifts for Eu^{2+} and Eu^{3+} are −12.6 mm/s and −1.4 mm/s, respectively. The spectra, therefore, should consist of two envelopes, since Eu^{2+} and Eu^{3+} occupy different sites in the absence of any electronic hopping process[5].

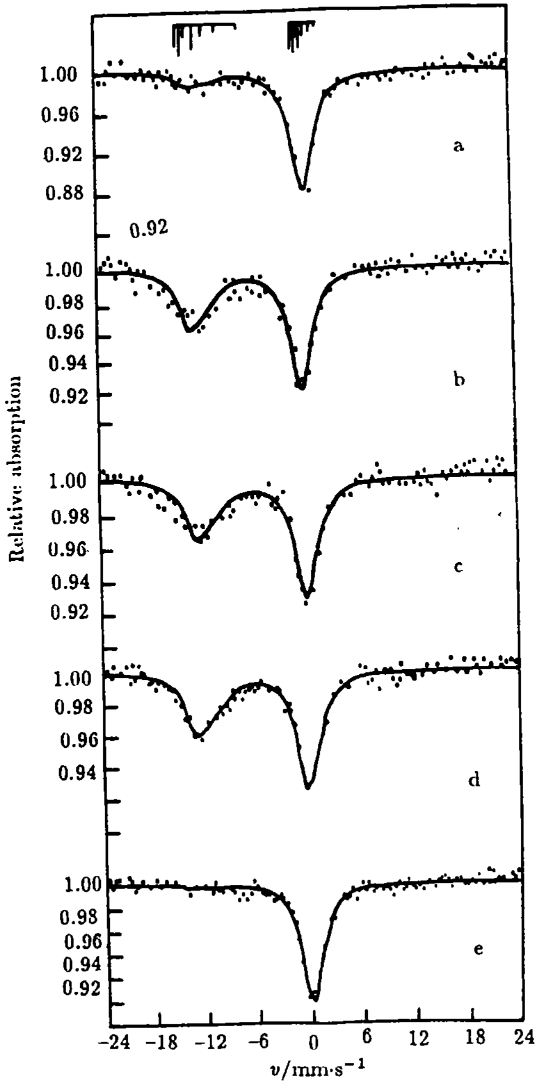

Fig.1 Mössbauer spectra of Eu_2O_3/TiO_2 with 0.15 of mass fraction of Eu reduced at various temperatures in H_2

(a) 450°C (b) 500°C (c) 550°C (d) 600°C

(e) Exposed to air at room temperature after reduction

The quadrupole splitting for Eu^{3+} before reduction was found to be −4.72 mm/s. This value is in good agreement with the literature[5]. After reduction, Eu^{2+} has a very large quadrupole splitting of about −14 mm/s. The two major contributions of the electric quadrupole interaction come from both the lattice and the electronic asymmetry. Since the ground state for Eu^{3+} is $^7F_0$, there are no first-order contributions from the 4f electrons. The second-order contributions, however, come from the excited state. For Eu^{2+}, besides the above contributions, both the reduced Eu cations occupied at different sites and the lattice defects at the oxide-support interface raise the quadrupole splitting.

The isomer shifts of the non-metallic Eu^{3+} components are found to be between −0.5 mm/s and 0.5 mm/s, while those of the non-metallic Eu^{2+} lie in the region from

-11 mm/s to -15 mm/s. The tendency towards positive values for the Eu^{3+} comes from the much higher s-electron density at the nucleus. For Eu^{2+}, a major contribution to the isomer shift comes from the 5d electrons depending on the Eu ionic states.

Table 1
Mössbauer parameters of Eu_2O_3/TiO_2 with 0.15 mass fraction of Eu under different reduction conditions

Reduction condition	Eu^{3+}				Eu^{2+}			
	I.S./ $mm \cdot s^{-1}$	Q.S./ $mm \cdot s^{-1}$	Γ/ $mm \cdot s^{-1}$	A	I.S./ $mm \cdot s^{-1}$	Q.S./ $mm \cdot s^{-1}$	Γ/ $mm \cdot s^{-1}$	A
450°C, H_2, 6 h	-0.67	-4.45	1.50	0.88	-13.92	-13.77	1.50	0.12
500°C, H_2, 6 h	-0.67	-4.64	1.50	0.60	-13.92	-13.72	1.50	0.40
550°C, H_2, 6 h	-0.60	-4.80	1.61	0.60	-13.52	-14.61	1.61	0.40
600°C, H_2, 6 h	-0.60	-4.76	1.58	0.58	-13.70	-14.86	1.58	0.42
Exposure after reduction	-0.60	-4.71	1.46	0.96	-13.70	-14.42	1.46	0.04

I.S.=Isomer shift relative to bulk Eu_2O_3, Q.S.=Quadruploe splitting, Γ=Full width at half maximum, A=Relative area

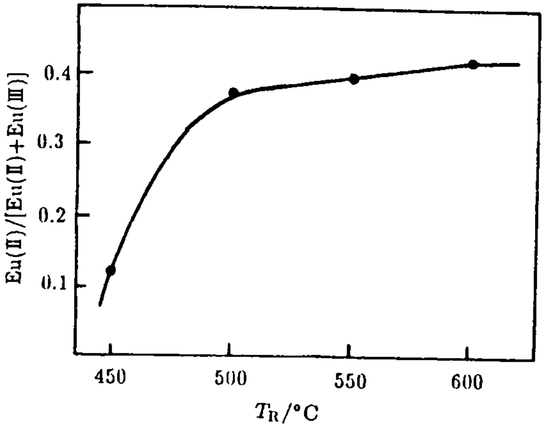

Fig.2 Variation of the reducibility with the reduction temperature T_R in hydrogen for Eu_2O_3/TiO_2 sample with 0.15 of mass fraction of Eu

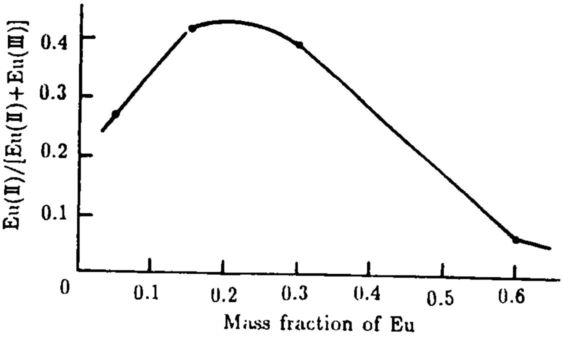

Fig.3 Reducibility for Eu_2O_3/TiO_2 sample with various Eu contents in hydrogen at 500°C

As the temperature is raised from 450°C to 600°C, the reduction mass fraction of Eu^{3+} was found to increase from 0.12 to 0.42. A subsequent air exposure of the sample for a long time has only resulted in the formation of Eu_2O_3, the fact indicated that $EuTiO_3$ has not existed during the reduction process.

The reason why only a partial reduction took place for Eu^{3+} may be attributed to the aggregation of the Eu^{3+} species. This means that only partial Eu^{3+} species interacted with the surface of the TiO_2 support. The fact that the change of Eu_2O_3 content on the TiO_2 surface changes the reducibility serves as an evidence for this argument. Fig.3 shows the reducibility of Eu_2O_3 supported on TiO_2 as a function of the Eu contents.

In the previous work, we have studied the interaction of Eu_2O_3 with other supports, such as Al_2O_3, SiO_2 and amorphous Al_2O_3. We have also studied the reducibility of Eu_2O_3 using different supports[2-4]. The results showed that the strength of the interaction (and hence the reducibility) decreases for Eu_2O_3 with the different supports in the following order: $Al_2O_3 > TiO_2 > SiO_2$. When Eu_2O_3 is dispersed on ZrO_2, the reduction becomes very difficult in the above temperature range, indicating that the interaction is very weak[6].

4 CONCLUSION

When Eu_2O_3 is dispersed on the surface of a support such as TiO_2 and γ-Al_2O_3, the reducibility is greatly enhanced. This is due to the solid-solid interaction of Eu_2O_3 with its support. The large difference in the isomer shifts of Eu^{2+} and Eu^{3+} presents Mössbauer spectroscopy as a convenient method for studying the reducibility. The large quadrupole splitting value of reduced Eu^{2+} species can be attributed to the lattice defects at the interface.

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