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ESR Spectra of Nitric Oxide Adsorbed on ZrO_2, CeO_2, and ThO_2

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Synopsis. ESR spectra of nitric oxide adsorbed on ZrO_2, CeO_2, and ThO_2 were measured at −196 °C, and $g_\perp$, $g_{//}$ and splitting constants were determined.

Nitric oxide is a rare paramagnetic compound stable in the gas phase. However, the ESR spectrum of gaseous NO is not observed with an ordinary X-band spectrometer. Adsorption of NO allows us to observe the adsorbed radical, since the orbital momentum is quenched by the surface fields. The spectra of radicals formed by NO adsorption have been reported only for MgO, ZnO, Al_2O_3, zeolite, Molecular Sieve 4A, TiO_2, SnO_2, and Cr_2O_3–Al_2O_3.[1-10] These spectra have hyperfine structures owing to the nuclear spin of nitrogen, and are easily removed by evacuation for a short time, except for that on Cr_2O_3–Al_2O_3.[10] Lunsford determined the anisotropy of NO radical by utilizing ^{14}NO and ^{15}NO, and discussed its relationship to catalytic activity.[1-5] In the present work, an attempt was made to observe the hyperfine structure for the system of NO on ZrO_2, CeO_2, and ThO_2.

Experimental

Samples. The ZrO_2 sample was prepared by calcination of the powder in air stream at 450 °C for 2 hr. The CeO_2 and ThO_2 samples were made by thermal decomposition of nitrates at 500 °C for 4 hr. Nitric oxide (Takachiho Chemical Ind. Co. Ltd.) was used without further purification.

Measurements. The samples were placed in Pyrex glass ampules for ESR measurements, and dehydrated at 250 °C during a period of 1 hr in a vacuum of 10^{-6} Torr. Nitric oxide was adsorbed at a pressure of *ca.* 5 Torr. ESR measurements were carried out at −196 °C with a JEOL Spectrometer (JES-ME-1X). *g*-Values and hyperfine splitting constants were calculated by comparison with the value for the Mn^{2+} impurity in MgO.

Results and Discussion

The obtained spectra on ZrO_2, CeO_2, and ThO_2 are shown in Figs. 1, 2, and 3, respectively. These spectra were easily removed by evacuation for a short time. They are similar to those obtained for ZnS by Lunsford[2] and TiO_2 by Imelik *et al.*[9] This corresponds to the case in which an unpaired electron of NO (nuclear spin of nitrogen=1) lies in a crystal field such that $g_\perp > g_{//}$. The anisotropy of spectrum is thus determined

TABLE 1. *g*-VALUES AND HYPERFINE SPLITTING CONSTANTS

Material	$g_\perp$	$g_{//}$	a (G)	Δ (eV)
ZrO_2	2.000	1.92	27.5±0.3	0.36
CeO_2	1.993	1.90	28.4±0.3	0.29
ThO_2	1.991	1.95, 1.93	27.6±0.3	0.57, 0.42

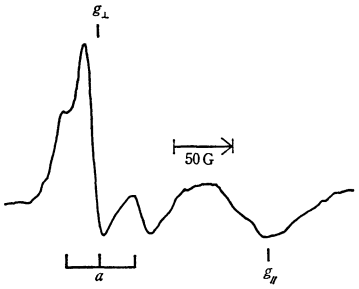

Fig. 1. ESR spectrum of NO adsorbed on ZrO_2.

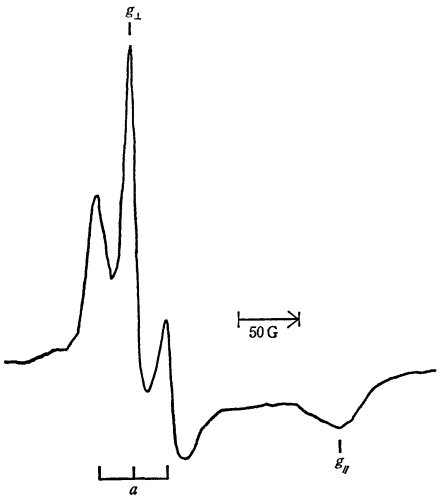

Fig. 2. ESR spectrum of NO adsorbed on CeO_2.

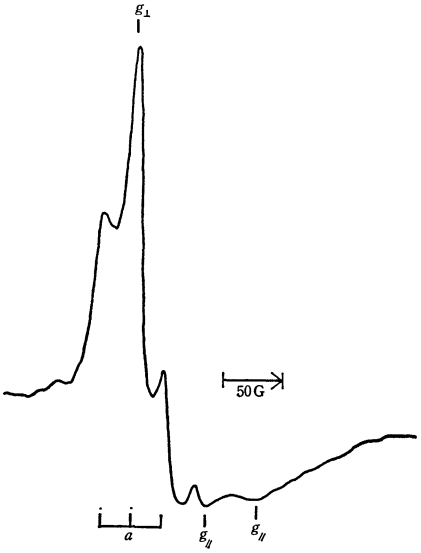

Fig. 3. ESR spectrum of NO adsorbed on ThO_2.

as shown in Table 1.

The spectrum on ThO_2 has two high-field minima as observed on silica–magnesia.[4] The anisotropy of this spectrum remained unchanged when the sample was evacuated at 665 °C under 10^{-6} torr or at 450 °C under 10^{-3} torr. It seems that two types of sites contribute to the adsorption of NO.

The splitting (Δ) of $2p\pi^*$ orbital of NO by the crystal field given by Kanzig and Cohen[11] is as follows,

$$\Delta = \frac{2\lambda}{g_e - g_{//}}$$

where λ is the spin-orbit coupling constant (0.015 eV for NO), and g_e is the g-value of free electron (2.003). The values of Δ for ZrO_2, CeO_2, and ThO_2 are given in Table 1.

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