Fine structure in phosphorescence spectra of silica–alumina

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Fine structure is clearly observed in the phosphorescent emission spectra of silica–alumina binary oxides evacuated at high temperature (1073 K) and excited by 300 nm light, although it is not observed in silica or alumina alone.

Photoluminescent spectroscopy directly reflects the characteristics of photoexcited species, and has been applied to structural analysis of surfaces of metal oxides. Most metal oxides exhibit only a broad band,[1–4] since there are many photoexcited sites and/or deactivation pathways. Fine structure in photoluminescence spectra are clearly observed only in a few cases of highly dispersed metal (V,[5–10] Mg[11,12]) oxides on silica.

The fine structure reveals vibrational levels of the ground state and provide some important information for the luminescent site. For vanadium oxide species, the fine structure in the emission spectrum was proposed to be due to the terminal V=O bond in the pseudotetrahedral oxovanadium group.[5–8] However, recently this fine structure was claimed to be from V–O bonds involving basal plane oxygen ions and not from the V=O bond.[10] On the other hand, the luminescent site magnesium oxide species dispersed on silica[11,12] is not fully understood, this being the first example of observation of fine structure in a non-transition metal oxide system, which is believed to possess no doubly bonded terminal oxygens.

In the present study, we found that silica–alumina binary oxide evacuated at high temperature is also luminescent and exhibits similar fine structure in its phosphorescent emission spectra as do the vanadium and magnesium species despite the fact that silica–alumina is not a supported system and contains no doubly bonded oxygen.

The silica–alumina samples employed were Japan Reference Catalysts[13,14] (JRC-SAH-1 and JRC-SAL-2) which were supplied by the committee on Reference Catalyst, Catalysis Society of Japan. The alumina contents were 28.6 and 13.8 mass% and the specific surface areas were 511 and 560 m^2 g^{-1}, respectively. Silica and alumina were also JRC samples, JRC-SIO-4 and JRC-ALO-4 (surface areas, 347 and 177 m^2 g^{-1}). The samples were recalcined in air at 773 K for 5 h. Before recording spectra, the samples were treated with 60 Torr oxygen for 1 h at 1073 K, followed by 1 h evacuation at 1073 K to clean the surface, and then transferred *in situ* to the optical cell (quartz tube, 5 mm diameter). The amount of the sample in the cell was *ca.* 150 mg. Photoluminescence spectra were recorded at 77 K with a Hitachi F-3010 fluorescence spectrophotometer using a UV filter ($\lambda_{\text{transmittance}} > 300$ nm) to remove scattered light from the UV source (Xe lamp), where the fluorescence emission was cut off mechanically to record phosphorescence spectra.

Fig. 1 shows the phosphorescent emission spectra of silica, alumina, and silica–alumina samples evacuated at 1073 K and excited by 300 nm light. Silica exhibits a broad band centred at 450–480 nm, and alumina shows a broad band centred at 520 nm accompanied by a shoulder at 450 nm; for both silica and alumina the band intensities were very weak. By contrast, silica–alumina samples exhibit fine structure spectra centred at 520 nm. Although this characteristic feature of the emission spectrum does not change upon varying the aluminium content, the band intensity of the SAL-2 sample is higher than that of the SAH-1 sample. This vibronically structured emission spectrum was reversibly varied upon water adsorption to give a broad spectrum which had been assigned to hydroxy groups on the surface.[12] High temperatures such as 1073 K were required for the silica–alumina samples to exhibit the fine structure. The same treatment was also required in the case of Mg.[11,12]

The fine structure spectra of silica–alumina samples evacuated at 1073 K are most clearly observed under excitation by 300–330 nm light. While neither silica nor alumina alone show a band at *ca.* 300 nm in the excitation spectra (Fig. 2), the silica–alumina samples exhibit a band at *ca.* 300 nm. This band is more prominent in SAL-2 (lower Al content) than in SAH-1 (higher Al content).

The vibrational energy which is estimated from the fine structure in the emission spectra (Fig. 1) is 900–1000 cm^{-1}. In IR spectroscopy, such a wavenumber is typical of a metal–oxygen–metal linkage, *e.g.* ν(Si–O–Al) in zeolites.[15,16] Since silica–alumina samples exhibit characteristic emission spectra in contrast to silica or alumina, the emission site is due to the Al–O–Si linkage.

The larger band intensities in Figs. 1 and 2 of the SAL-2 sample with lower Al content suggest that a high dispersion of Al is required to obtain fine structure. The reactivity to water molecules, which results in the disappearance of the fine structure, establishes that the luminescent sites exist on the

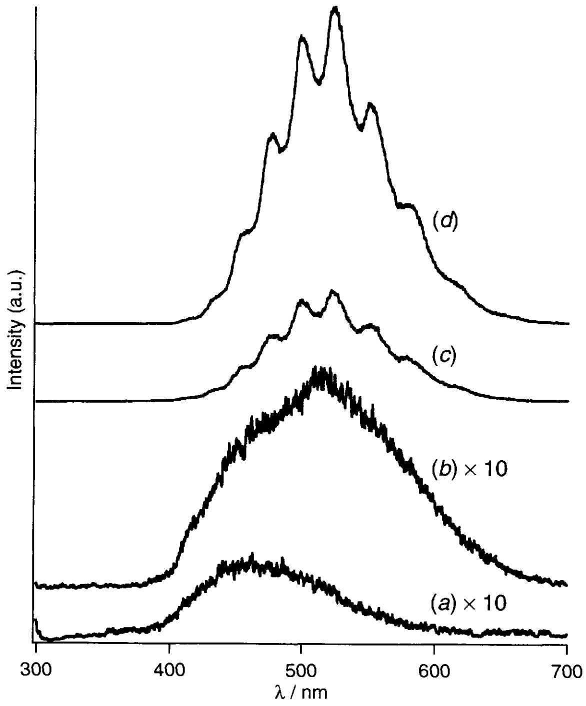

Fig. 1 Phosphorescent emission spectra of samples excited at λ = 300 nm; (*a*) SIO-4, (*b*) ALO-4, (*c*) SAH-1 and (*d*) SAL-2

surface. Such sites are also coordinatively unsaturated, since evacuation at high temperature is needed for the recovery of the fine structure. Therefore, the luminescent site which exhibits this spectrum is a coordinatively unsaturated site belonging to the heterobond linkage Al–(O–Si)$_3$ on the surface.

It is commonly accepted that the coordinatively unsaturated Al ion on the surface of silica–alumina evaucated at high temperature is positively charged, a so-called Lewis acid site.[17] Therefore, the electrons of oxygens bound to the Al ion might transfer to the Al ion under photoexcitation. When the excited electron is retransferred to oxygen during the deactivation process, the vibration of Al–O–Si linkage would be observed as fine structure in the phosphorescent emission spectrum. This suggestion for the photoexcitation and deactivation mechanism could also be applied to the Mg–O–Si linkage in the highly dispersed magnesium on silica.[11,12]

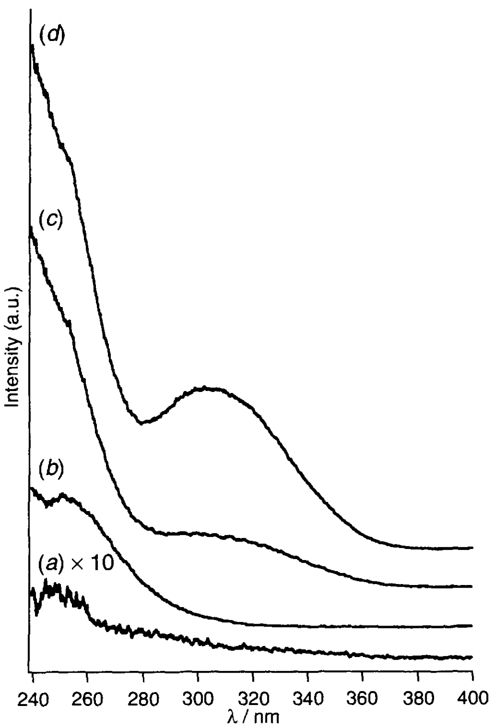

Fig. 2 Phosphorescent excitation spectra of samples recorded by monitoring emission at 520 nm; (*a*) SIO-4, (*b*) ALO-4, (*c*) SAH-1 and (*d*) SAL-2

We conclude that coordinatively unsaturated sites belonging to the heterobond linkage metal–(O–Si)$_3$ on the silica surface is the active species producing fine structure in phosphorescence spectra for Mg or Al on silica. It is also suggested that other heterolinkages on silica have a potential ability for photoexciting and exhibiting luminescence spectra containing fine structure.

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