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Dynamic Behavior and Nature of Active Sites Directly Observed by Means of Photoluminescence Spectroscopy

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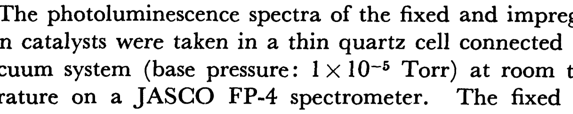
Synopsis. The dynamic behavior and properties of the active sites (Types I, II, and III) of SiO_2-supported Mo catalysts during a redox reaction with H_2 or O_2 (in connection with a general two-stage redox mechanism) were observed directly by means of a photoluminescence technique.

It has been demonstrated that photoluminescence is a sensitive technique for obtaining useful information on the surface structures and environments of solid catalysts.[1,2] The tetrahedral dioxo-Mo^{6+} structure of the fixed Mo catalysts (a supported molecular catalyst) has been found to have a spectroscopically uniform nature, but it was found by means of photoluminescence[2] that there were at least three different molybdenum species (Types I, II, and III) in a conventional impregnation catalyst ($Mo/SiO_2=1.7$ wt%). However, it does not naturally follow that the behavior of an individual molybdenum site during a catalytic reaction reflects the static, spectroscopic nature. The reactivities of all the active sites, with different environments, distributed on the SiO_2 surface could not be followed by conventional methods, such as adsorption, kinetics, UV diffuse reflectance spectroscopy, or IR spectrometry. In the present paper the direct observation of the dynamic behavior and the energy aspect of active sites will be reported in connection with the catalysis of Mo catalysts involving a two-stage redox mechanism; the following reaction sequence was chosen as a model process of the catalytic oxidation:



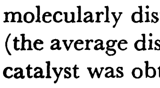
(1)

(2)

where H_2O was removed from the system by means of a liq.N_2 trap.

Experimental

The photoluminescence spectra of the fixed and impregnation catalysts were taken in a thin quartz cell connected to a vacuum system (base pressure: 1×10^{-5} Torr) at room temperature on a JASCO FP-4 spectrometer. The fixed Mo catalysts with the tetrahedral dioxostructure,



$$\begin{matrix}\rangle\mathrm{Si{-}O} & & \mathrm{O}\\ & \mathrm{Mo} & \\ \rangle\mathrm{Si{-}O} & & \mathrm{O}\end{matrix}$$

(XPS B.E.(eV): Mo $3d_{3/2}=235.7$, $3d_{5/2}=232.7$), were synthesized by taking advantage of the facile reaction between $Mo(\pi\text{-}C_3H_5)_4$ and OH groups of silica surface, as has previously been described;[2] $Mo/SiO_2=1.7$ wt%. The molybdenum ions fixed on silica were found to be molecularly distributed, with no interaction with one another (the average distance of Mo–Mo: *ca.* 20 Å). The impregnation catalyst was obtained by a conventional impregnation method using an aqueous ammonium paramolybdate solution.

Results and Discussion

The photoexcitation ($3t_2\leftarrow t_1$) of the charge transfer band of a $Mo^{6+}{=}O^{2-}$ bond in the fixed catalyst (Curve 1 of Fig. 1) and an impregnation catalyst (Curve 1 of Fig. 2) was followed by a strong luminescence from the lowest triplet T_1 state, as has previously been reported.[2] The fixed Mo^{6+} catalyst showing Spectrum 1 of Fig. 1

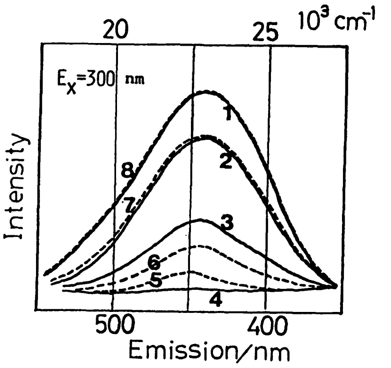


Fig. 1. Behavior of luminescence of the fixed Mo catalyst in the following consecutive redox processes; 1: oxidized catalyst, 2: after reduction of 1 with H_2 (50 Torr) at 723 K for 5 min, 3: H_2 (723 K, 17 min), 4: H_2 (733 K, 1 h), 5: after oxidation of 4 with O_2 (40 Torr) at 473 K for 5 min, 6: O_2 (513 K, 5 min), 7: O_2 (673 K, 5 min), 8: O_2 (823 K, 15 min).

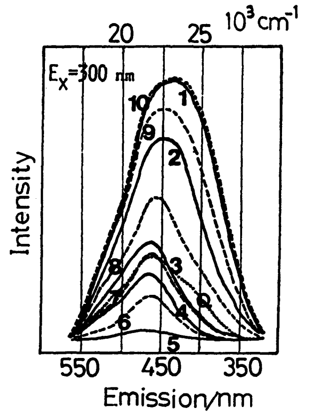
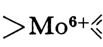


Fig. 2. Behavior of emission of the impregnation catalyst in the following consecutive steps; 1: oxidized catalyst, 2: after reduction of 1 with H_2 (50 Torr) at 673 K for 10 min, 3: H_2 (723 K, 1 h), 4: H_2 (723 K, 45 min), 5: H_2 (863 K, 2.5 h), 6: after oxidation of 5 with O_2 (40 Torr) at 463 K for 15 min, 7: O_2 (513 K, 10 min), 8: O_2 (563 K, 10 min), 9: O_2 (563 K, 20 min), 10: O_2 (823 K, 15 min), Q (quenching by CO_2): after exposure of catalyst (curve 1) to CO_2 (293 K, 280 Torr).

contained no Mo^{5+} ion, according to ESR at 77 and 295 K. The quadrivalent molybdenum with the oxostructure and the bivalent molybdenum showed no emission. Thus, the luminescence observed at 22.9 10^3 cm^{-1} directly illustrates the behavior of the tetrahedral  $>\mathrm{Mo}^{6+}\begin{array}{l}\diagup\!\!\diagup\mathrm{O}\\ \diagdown\!\!\diagdown\mathrm{O}\end{array}$ species (Type I). Figure 1 shows the variation in the emission of the fixed catalyst in the course of Reactions 1 and 2. The peak position and the shape were invariable during the redox process. On the other hand, the heterogeneous reactivity of the molybdenum species in the impregnation catalyst was observed in Fig. 2. The same emitting species (Type I) as that of the fixed catalyst reacted with hydrogen more rapidly than the molybdenum species (Type II), with an emission of 21.8 10^3 cm^{-1}. Type III, whose luminescence (21.8 10^3 cm^{-1}, Curve Q in Fig. 2) is not quenched by CO, CO_2, O_2, H_2, *etc.*, was also reduced with H_2 at 720 K. The order of ease of the reduction for molybdenum was Type I>Type II≫Type III. The reduced species of the Type I-molybdenum was less reactive in the oxidation (2) (in contrast to the reduction (1)) than the other two types, although the difference among three types was not so large as the difference observed in the reduction, judging from the shapes of the emission spectra. The tetrahedral dioxomolybdenum structure obtained by the straightforward fixation of molybdenum using a reactive Mo $(\pi\text{-}C_3H_5)_4$ complex may be highly distorted and/or located on a coordination-unsaturation site of the SiO_2 surface; these structural factors would raise the T_1 state and also increase the covalency of the Mo=O double bond as active sites. The more the covalency of the Mo=O site, the more the hydrogen pulling step may be promoted.[2-4] The fixed catalyst was kinetically found to be much more active than the impregnation catalyst in the hydrogen-abstraction step in the oxidations of hydrogen,[5] ethyl alcohol,[2] and propylene.[3] Photoluminescence clearly monitored the behavior of active sites during reaction, where the fixed catalyst was found to have an active molybdenum of Type I with a uniform nature, which gave an emission of a relatively high energy.

References

1) G. T. Pott and W. H. J. Stork, Catalysis Rev., **12**, 163 (1975); G. T. Pott and B. D. McNicol, *Discuss. Faraday Soc.*, **52**, 121 (1971); S. Coluccia, M. Deane, and A. J. Tench, Proc. 6th Int. Congr. Catalysis (London, 1976), The Chemical Society, London (1977), Vol. **1**, p. 171; S. Coluccia, J. F. Hemidy, and A. J. Tench, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2763 (1978); A. M. Gritscov, V. A. Shvets, and V. B Kazansky, *Chem. Phys. Lett.*, **35**, 511 (1975); C. Yun, M. Anpo, and Y. Kubokawa, *J. Chem. Soc., Chem. Commun.*, **1977**, 665.

2) Y. Iwasawa, Y. Nakano, and S. Ogasawara, *J. Chem. Soc., Faraday Trans. 1*, **74**, 2968 (1978); Y. Iwasawa and S. Ogasawara, *ibid.*, **75**, 1465 (1979).

3) Y. Iwasawa, T. Nakamura, K. Takamatsu, and S. Ogasawara, *J. Chem. Soc., Faraday Trans. 1*, **76**, 939 (1980).

4) G. K. Boreskov, *Proc. 5th Int. Congr. Catal.*, **2**, 981 (1972).

5) Y. Iwasawa, unpublished data.