Application of Dynamic Photoluminescence Spectroscopy to the Study of the Active Surface Sites on Supported Mo/SiO_2 Catalysts. Features of Anchored and Impregnated Catalysts

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Abstract: A dynamic photoluminescence technique has been applied to investigate the active surface species on two different types of Mo/SiO_2 catalysts, which contain lower Mo content (0.01–0.1 wt % Mo) and differ in molybdenum dispersion. Phosphorescence spectra of the Mo/SiO_2 catalysts, which are attributed to the radiative decay processes from the charge-transfer excited triplet state of tetrahedral dioxo–molybdenum species, appear at ~440 nm at 298 K and shift to 470 nm at 77 K. The decay curves of the phosphorescence of the anchored and impregnated Mo/SiO_2 catalysts indicate that the anchored catalysts possess only one type of Mo emitting site, while the impregnated ones contain at least two. These results are confirmed by photoluminescence quenching by O_2 or CO, in which the phosphorescence of the anchored catalysts is completely quenched but that of the impregnated samples is only partially quenched. With the anchored catalyst the absolute quenching rate constants of the charge-transfer excited triplet are determined first to be 7.6×10^7 g of catalyst/mol·s for O_2 and 4.2×10^6 of catalyst/mol·s for CO, respectively. The phosphorescence spectra of the anchored catalysts obtained at different excitation wavelengths are found to be the same, being quite different from that of impregnated catalysts, where the phosphorescence spectra change in their position with excitation energies. These results indicate that the dynamic photoluminescence technique is useful for investigation not only of active surface species on metal oxides supported on a carrier at very small concentrations but also of their reactivity in the excited states.

A fundamental problem in catalysis is to identify and characterize surface active sites and surface reactions that can be induced by thermal activation (catalysis), light (photocatalysis), or both. Highly dispersed supported transition-metal oxide catalysts seem to be useful to study these problems, because it is relatively easy to identify the surface active sites and to follow the surface reactions. In addition to these problems, the transition-metal oxides include species that span the range from discrete molecules to extended semiconductor structures.[1]

In recent years, the preparation and the characterization of supported transition-metal oxide catalysts such as Mo, V, and Cr have been extensively studied and much information has been reported on the chemical state of the active surface sites and its influence upon the catalytic properties.[2-12] However, the widely used conventional methods such as XRD, IR, and Raman spectroscopy, as well as adsorption and desorption, are very often not sensitive enough for supported oxide catalysts with low metal oxide concentrations (typical concentration below 0.1 wt %). At these low concentrations, unusual catalytic properties due to support effects have been observed, resulting in a change in their catalytic and/or photocatalytic activities and selectivities.[2-4]

Tench and Pott showed first that the photoluminescence studies of oxides are useful in the study of the surface structure and the excited states of the oxides, because of the high sensitivity and nondestructive nature of luminescence methods.[13] Bard et al.[14] and Brus et al.[15] have shown that the photoluminescence of semiconductor particles is very sensitive to surface effects or adsorbed species and concluded that the photoluminescence can be used as a probe of electron-hole surface processes. Later, many workers made photoluminescence measurements not only of bulk metal oxides and sulfides but also of highly dispersed metal oxide catalysts.[16-36] Recently, we have shown that measurements of the lifetimes of phosphorescence, as well as the phosphorescence intensity and shape of the associated band, give very useful information about the characteristics of the active surface sites on supported catalysts with much lower metal oxide loading than 0.5

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† University of Osaka Prefecture.
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(1) Fox, M. A.; Cardona, R.; Gaillard, E. *J. Am. Chem. Soc.* **1987**, *109*, 6347.
(2) Massoth, F. E. *Adv. Catal.* **1987**, *27*, 265.
(3) Delmon, B.; Grange, P.; Poncelet, G. *Preparation of Catalysts II*; Elsevier: Amsterdam, 1979.
(4) Kazansky, V. B. *Proc. Int. Congr. Catal., 6th* **1976**, *1*, 50.
(5) Wang, L.; Hall, W. K. *J. Catal.* **1982**, *77*, 232.
(6) Haber, J.; Kozlowska, A.; Koztsowski, R. *J. Catal.* **1986**, *102*, 52.
(7) McDaniel, M. P.; Johnson, M. M. *J. Catal.* **1986**, *101*, 446.
(8) Rodrigo, L.; Marcinkowska, K.; Adnot, A.; Roberge, P. C.; Kaliaguine, S.; Stencel, J. M.; Makovsky, L. E.; Diehl, J. R. *J. Phys. Chem.* **1986**, *90*, 2690. Rodrigo, L.; Marcinkowska, K.; Roberge, P. C.; Kaliaguine, S. *J. Catal.* **1987**, *107*, 8.
(9) Jeziorowskii, H.; Knozinger, H.; Grange, P.; Gajarldo, P. *J. Phys. Chem.* **1980**, *84*, 1825.
(10) Yang, T.; Lunsford, L. H. *J. Catal.* **1987**, *103*, 55.
(11) Carlson, T.; Griffin, G. L. *J. Phys. Chem.* **1986**, *90*, 5896.
(12) Narayana, M.; Zhan, R. Y.; Kevan, L. *J. Phys. Chem.* **1985**, *89*, 636.
(13) Tench, A. J.; Pott, G. T. *Chem. Phys. Lett.* **1976**, *26*, 590.
(14) Becher, W. G.; Bard, A. J. *J. Phys. Chem.* **1983**, *87*, 4888.
(15) Rossetti, R.; Brus, L. *J. Phys. Chem.* **1982**, *86*, 4470.
(16) Meyer, G. J.; Lisensky, G. C.; Ellis, A. B. *J. Am. Chem. Soc.* **1988**, *110*, 4918, and their earlier series.
(17) Chestnoy, N.; Harris, T. D.; Hull, R.; Brus, L. E. *J. Phys. Chem.* **1986**, *90*, 3399, and their earlier series.
(18) Kazansky, V. B.; Pershin, A. N.; Shelimov, B. N. *Proc. Int. Congr. Catal., 7th* **1980**, B-1210.
(19) Coluccia, S.; Tench, A. J. *J. Chem. Soc., Faraday Trans. 1* **1984**, *80*, 1173.
(20) Iwamoto, M.; Furukawa, H.; Matsukami, K.; Takanaka, T.; Kagawa, S. *J. Am. Chem. Soc.* **1983**, *105*, 3719.
(21) Occelli, M. L.; Psaras, D.; Suib, S. L. *J. Catal.* **1985**, *96*, 363.
(22) Che, M.; Tench, A. J. *Adv. Catal.* **1982**, *31*, 77; *Ibid.* **1983**, *32*, 1.
(23) Anpo, M.; Tanahashi, I.; Kubokawa, Y. *J. Phys. Chem.* **1980**, *84*, 3440.
(24) Anpo, M.; Tanahashi, I.; Kubokawa, Y. *J. Chem. Soc., Faraday Trans. 1* **1982**, *78*, 2121.
(25) Anpo, M.; Kubokawa, Y. *Rev. Chem. Intermed.* **1987**, *8*, 105.
(26) Kubokawa, Y.; Anpo, M. *Adsorption and Catalysis on Oxide Surfaces*; Che, M., Bond, G. C., Eds.; Elsevier: Amsterdam, 1985; p 127.
(27) Anpo, M.; Mihara, K.; Kubokawa, Y. *J. Catal.* **1986**, *97*, 272.
(28) Anpo, M.; Nakaya, H.; Kodama, S.; Kubokawa, Y.; Domen, K.; Onishi, T. *J. Phys. Chem.* **1986**, *90*, 1633.

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Table I. Characterization of Mo/SiO_2 Oxide Catalysts with Various Methods

methods	samples: anchored Mo/SiO_2	samples: impregnated Mo/SiO_2
color after preparation (before calcination)	brown	yellow
Mo solubility in H_2O	no	complete
color after solubility test with H_2O	brown	white
Mo solubility in $HF–H_2SO_4$	partial	complete
mean oxidation degree of Mo ions[a] after H_2 reduction at 873 K	4	2–3
Mo dispersion,[b] %	80–100	ca. 30
rate of photoinduced metathesis reaction of C_3H_6 at 298 K[c]	37.0 nmol/ g-catalyst-m	22.0 nmol/ g-catalyst-m
rate of photoinduced metathesis reaction of C_3H_6 at 298 K[d]	76.0 nmol/ g-catalyst-m	23.0 nmol/ g-catalyst-m

[a] Mean oxidation degree i.e., average valence state of reduced molybdenum ions (x)] was determined from the equation $x = 6–2N_{H_2}/N_{Mo^{6+}}$, where N_{H_2} is the amount of hydrogen consumed during the thermal reduction of the sample at 773 K, and $N_{Mo^{6+}}$ is the total number of molybdenum ions in the sample. [b] The electron-transfer reaction, $Mo^{5+} + O_2 \rightarrow Mo^{6+}–O_2^-$, was used to measure the Mo^{5+} dispersion by ESR spectroscopy. Under conditions precluding bulk oxidation (77 K, 10^{-1} Torr), O_2 is adsorbed on catalysts previously thermally reduced by H_2. The Mo^{5+} signal decreases as the O_2^- signal appears. Mo^{5+} dispersion was calculated from the ratio of the integrated intensities of the Mo^{5+} ESR signal.[40,44] [c] Mo content of anchored Mo/SiO_2 oxide, 0.01 wt % Mo content of impregnated Mo/SiO_2 oxide, 0.013 wt %; initial pressure of C_3H_6, 5.0 Torr; excitation wavelength, 280 nm. [d] Mo content of anchored Mo/SiO_2 oxide, 0.043 wt %; Mo content of impregnated Mo/SiO_2 oxide, 0.053 wt %; initial pressure of C_3H_6, 5.0 Torr; excitation wavelength, 280 nm.

Table II. λ_{max} Position (in nm) of the Phosphorescence and Its Excitation Spectrum of Anchored and Impregnated Mo/SiO_2 Oxide Catalysts

	Mo, wt %	max positn of excitn spectrum at 77 K	max positn (rel yield) of phosphores spectrum: at 77 K	max positn (rel yield) of phosphores spectrum: at 298 K
anchored Mo/SiO_2 catalyst	0.07	290.1	467.2 (12.8)	437.1 (0.45)
impregnated Mo/SiO_2 catalyst	0.1	292.4	470.5 (13.8)	440.2 (0.52)

wt % metal.[31,33]

On the other hand, recently, Anpo et al. found the UV irradiation of molybdenum oxide supported on porous Vycor glass in the presence of C_3H_6 induces propene metathesis to produce equimolar C_2H_4 and $2-C_4H_8$ with a high quantum yield (higher than 4.0) and that the charge-transfer excited triplet state is closely associated with the photoinduced metathesis reaction.[24-26] Kazansky et al. also confirmed that photoinduced metathesis of propene occurs on molybdenum oxide supported on silica.[37] More recently, we reported that anchored Mo/SiO_2 oxide catalysts, prepared by the reaction between $MoCl_5$ and surface silanol groups on silica, exhibit a higher activity for the photoinduced metathesis reaction of propene.[36] Methanol oxidation,[38] which is known to be structure sensitive, responds similarly. Higher selectivity in methyl formate formation has been attributed to a better dispersion and a stronger interaction with the support than with the impregnated Mo/SiO_2 oxide catalysts.[38-46] We have also found that when titanium oxide is anchored onto porous Vycor glass (PVG), the photoluminescence intensity and the photocatalytic activity are much higher than those of bulk TiO_2 or of supported TiO_2 catalysts prepared by impregnation, the extent being dependent on the higher dispersion of Ti ions, the coordinative unsaturation of surface Ti ions, or both.[33-35] It is anticipated that the samples prepared by the anchoring method, i.e., by a controlled chemical reaction, possess catalytic properties different from catalysts prepared by impregnation.[33-35]

It is, therefore, interesting to compare the structure and nature of surface active sites on the well-defined anchored Mo/SiO_2 oxide catalysts to those of impregnated catalysts, by applying a highly sensitive photoluminescence technique, including its dynamics. Such information about the transition-metal oxides as models for the molecule to solid-state translation seems very important in understanding whether the degree of aggregation can influence catalytic or photocatalytic activity of the oxides, since it is suggested that the charge-transfer excited state of the supported oxide catalysts plays a significant role not only in photocatalytic (and/or photoinduced) reactions but also in thermal catalytic reactions on the supported oxide catalysts.[22,47,48]

Experimental Section

a. Preparation of the Mo/SiO_2 Catalysts. Silica (Spherosil XOA 400, 400 m^2/g; Rhone Poulenc, France) supported molybdenum catalysts were prepared—by the anchoring (or grafting) method:[38-46,49-51] molybdenum pentachloride, either in gas phase or diluted in cyclohexane, reacts with the surface OH groups on SiO_2 in strict air- and water-free conditions. They are then dried in air at room temperature. Samples prepared by either of those two methods are similar, and in the following we shall only present the results obtained with samples prepared from gaseous $MoCl_5$. By impregnation: an aqueous solution of ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ is put in contact with the SiO_2 support. After the preparation, the anchored catalysts differ from catalysts prepared by the impregnation method. As shown in Table I, they have different coloration, solubility in water and in $HF–H_2SO_4$, and Mo^{5+} dispersion, which is determined by monitoring the charge-transfer reaction (1) between prereduced Mo^{5+} ions and added O_2 molecule by EPR:[40]

$$Mo^{5+} + O_2 \rightarrow Mo^{6+}–O_2^-{}_{(ads)} \qquad (1)$$

Table I also involves the rates of the photoinduced metathesis of C_3H_6 on the Mo/SiO_2 catalysts at 298 K. In the photoinduced metathesis reaction, where methylene-type carbene is photoformed and acts as a chain carrier in the metatheis reaction, equal molar amounts of C_2H_4 and $2-C_4H_8$ were formed.[36] Much higher yield of the photoinduced metathesis reaction on the anchored Mo/SiO_2 oxide than that on the impregnated Mo/SiO_2 oxide is attributable to the much higher dispersion of Mo species. The samples were then dried in air at ~350 K with continuous stirring and calcined in oxygen overnight at 773 K. Before the photoluminescence measurements, the samples were pretreated as follows: they were heated in air at ~873 K for 7 h, degassed at 773 K for 3 h, heated at 773 K under 20 Torr oxygen for 3 h, and finally degassed at 423 K for 1 h.

b. Apparatus and Procedure. The photoluminescence spectra were recorded at 77 and 298 K with a Shimadzu RF-501 spectrofluoropho-

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(29) Anpo, M.; Kawamura, T.; Kodama, S.; Maruya, K.; Onishi, T. *J. Phys. Chem.* **1988**, *92*, 438.

(30) Anpo, M.; Tanahashi, I.; Kubokawa, Y. *J. Phys. Chem.* **1986**, *86*, 1.

(31) Anpo, M.; Suzuki, T.; Tanaka, F.; Yamashita, S.; Kubokawa, Y. *J. Phys. Chem.* **1984**, *88*, 5778.

(32) Anpo, M.; Suzuki, T.; Yamada, Y.; Che, M., *Proc. Int. Congr. Catal., 9th* **1988**, *4*, 1513. Anpo, M.; Sunamoto, M.; Fujii, T.; Che, M.; Patterson, H. *Res. Chem. Intermed.* **1989**, *11*, 245.

(33) Anpo, M.; Aikawa, N.; Kubokawa, Y.; Che, M.; Louis, C.; Giamello, E. *J. Phys. Chem.* **1985**, *89*, 5017.

(34) Anpo, M.; Aikawa, N.; Kubokawa, Y.; Che, M.; Louis, C.; Giamello, E. *J. Phys. Chem.* **1985**, *89*, 5689.

(35) Anpo, M.; Shima, T.; Fujii, T.; Suzuki, S.; Che, M. *Chem. Lett.* **1987**, 1997.

(36) Anpo, M.; Kondo, M.; Kubokawa, Y.; Louis, C.; Che, M. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 2771. Anpo, M.; Kondo, M.; Kubokawa, Y.; Louis, C.; Che, M. *Chem. Express* **1987**, *2*, 61.

(37) Shelimov, B. N.; Elev, I. V.; Kazansky, V. B. *J. Catal.* **1986**, *98*, 70.

(38) Louis, C.; Tatibouet, J. M.; Che, M. *J. Catal.* **1988**, *109*, 354.

(39) Louis, C.; Che, M.; Bozon, Verduraz, F. *J. Chim. Phys.* **1982**, *79*, 803.

(40) Louis, C., Doctor Thesis, Paris, 1985.

(41) Louis, C.; Chem, M. In *Reactivity of Solids*; Series Material Science Monograph; Barret, P., Dufour, L. C., Eds.; Elsevier: Amsterdam, 1985; B. 1057.

(42) Che, M.; Bonneviot, L.; Louis, C.; Kermarec, M. *Mater. Chem. Phys.* **1985**, *13*, 210.

(43) Che, M.; Louis, C.; Tatibouet, J. M. *Polyhedron* **1986**, *5*, 123.

(44) Louis, C.; Che, M. *J. Phys. Chem.* **1987**, *91*, 2875.

(45) Che, M.; Dyrek, K.; Louis, C. *J. Phys. Chem.* **1985**, *89*, 4526.

(46) Louis, C.; Che, M. *J. Phys. Chem.* **1987**, *91*, 2875.

(47) Krenzke, L. D.; Keulks, G. W. *J. Catal.* **1980**, *61*, 361.

(48) Ward, M. B.; Lin, M. J.; Lunsford, J. H. *J. Catal.* **1977**, *50*, 306.

(49) Iwasawa, Y.; Hyomen, 161. *Tailored Metal Catalysts*; Iwasawa, Y., Eds.; D. Reidel: Dordrecht, Holland, 1984.

(50) Yermakov, Yu.; Kuznetsov, B. N.; Zakharov, V. A. *Catalysis by Supported Complexes*; Elsevier: Amsterdam, 1981.

(51) Boehm, H. P.; Knozinger, H. In *Catalysis*; Anderson, J. R., Boudart, M., Eds.; Springer Verlag: West Berlin, 1983; Vol. 4, p 39.

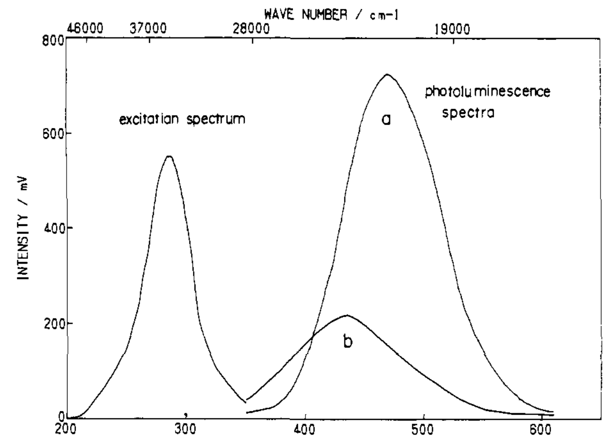

Figure 1. Photoluminescence spectra of the anchored Mo/SiO$_2$ oxide catalyst (0.07 wt % Mo) at 77 (a) and 298 (b) K, and its excitation spectrum. (Excitation wavelength, 280 nm; slit width of excitation, 8.0 nm, excitation spectrum was monitored at 520-nm emission band at 77 K.)

tometer (with a resolution of 0.05 nm) with color filters to eliminate scattered light. For detailed analysis of the spectra, photoluminescence spectra were collected on a NEC-PC9801VM computer through a GP-IB (IEEE-488) interface by applying an AD converter (Advantest digital multimeter TR-6846) and RS-232C. In this system, the accuracy is less than 5 cm^{-1}. The apparatus for lifetime measurements consists of a N$_2$ laser having ~5-ns pulse width, a monochromator, lenses, and a Hamamatsu R955 photomultiplier. The output signal was digitized by an Iwatsu TS8123 storage scope and transferred into a NEC-PC9801 computer through a GP-IP (IEEE-488) interface. ESR measurements were carried out at 77 K with a JEOL ME-1 (X-band) spectrometer. Mn^{2+} ions in MgO powders were used for g values and sweep calibration. The absorption spectra were recorded at 298 K with a Shimadzu UV-210 A double-beam digital spectrophotometer equipped with the conventional components of a reflectance spectrometer. The Mo content of the catalysts was determined by plasma emission spectrometry after dissolution of the sample in a hot HF-HNO$_3$-HClO$_4$ medium. The amounts of O$_2$ or CO molecules adsorbed onto the catalyst at 77 K were determined by measuring the pressure change in a constant volume by using a Pirani pressure gauge (ULVAC). The details of the experiments have been described in our previous papers.[23-36,52-56]

Results

1. Comparison of the Photoluminescence Spectra of the Anchored and Impregnated Mo/SiO$_2$ Catalysts. 1.1. Temperature Dependence of the Photoluminescence Spectra.

Figure 1 shows typical photoluminescence spectra obtained at 77 (a) and 298 (b) K of the anchored (0.07 wt % Mo) Mo/SiO$_2$ oxide catalyst with their corresponding excitation spectra. The excitation has been attributed to the charge-transfer process associated with the molybdenyl bond.[18,24-27,37,57-60,61,62]

$$(\mathrm{Mo}^{6+}{=}\mathrm{O}^{2-}) \underset{h\nu'}{\overset{h\nu}{\rightleftharpoons}} (\mathrm{Mo}^{5+}{-}\mathrm{O}^{-})^{*} \tag{2}$$

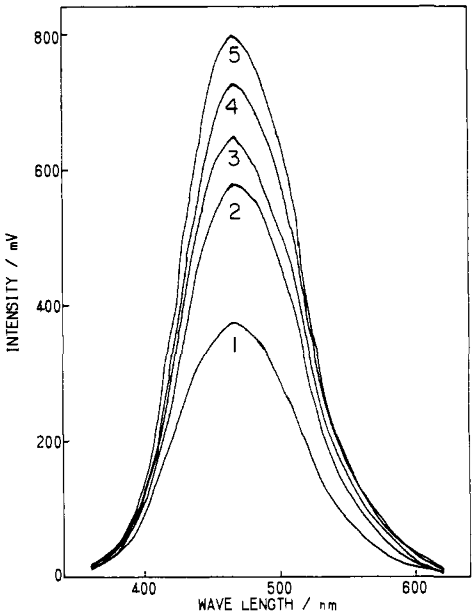

Figure 2. Effect of the excitation energy upon the position of the phosphorescence spectrum of the anchored Mo/SiO$_2$ oxide catalyst (0.07 wt % Mo) at 77 K. (Excitation wavelength (in nm): 1, 262.5; 2, 268.0; 3, 272.5; 4, 282.5; 5, 288.5.)

Table III. Exact Wavelengths at $\lambda_{\max}$ of the Phosphorescence and the Yields of the Phosphorescence of the Anchored (0.07 wt % Mo) and the Impregnated Mo/SiO$_2$ Oxide (0.013 wt % Mo) Catalysts at 77 K

			phosphorescence	
	line no.	excitation wavelength, nm	wavelength, nm	yields, mV
anchored catalyst[a]	1	262.5	466.5	56.7
	2	268.0	467.0	74.3
	3	272.5	467.0	83.4
	4	282.5	466.6	118.0
	5	289.5	467.0	120.5
	6	304.5	466.4	96.1
impregnated catalyst[b]	1	270.5	466.4	105.3
	2	280.0	467.0	149.7
	3	292.5	467.5	162.9
	4	297.0	469.2	149.3
	5	302.5	475.4	91.4
	6	305.0	481.0	61.2

[a] Excitation power was 20 A, 800 mV. [b] Excitation power was 20 A, 920 mV.

As shown in Table II, there is no remarkable difference between the excitation spectra of the anchored and impregnated Mo/SiO$_2$ catalysts, both of which possess a maximum at ~290 nm. For both catalysts, the excitation band was less intense and broader at 298 K and it was difficult to determine whether there is any band shift.

The photoluminescence spectrum usually consists of two bands. One corresponds to the fluorescence arising from radiative decay of the excited singlet: for Mo supported on PVG it is at ~340 nm.[24,26,30] The silica used in this work induced an emission at around 320–340 nm that masked this Mo fluorescence. The other band corresponds to phosphorescence arising from the charge-transfer excited triplet state associated with the molybdenyl bond. The phosphorescence band position of impregnated or anchored Mo/SiO$_2$ catalysts at 298 K at ~440 nm agrees with that observed by Anpo et al.[24,26,30] on impregnated Mo/PVG (450 nm) and by Iwasawa et al.[57-60] on Mo/SiO$_2$ (1.7 wt % Mo) prepared by chemical fixation or impregnation (440 nm). On the other hand, the band position at ~470 nm at 77 K is in agreement with

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(52) Ono, T.; Anpo, M.; Kubokawa, Y. *J. Phys. Chem.* **1986**, *90*, 4780.

(53) Anpo, M.; Yamada, Y.; Kubokawa, Y.; Coluccia, A.; Zecchina, A.; Che, M. *J. Chem. Soc., Faraday Trans. 1* **1988**, *84*, 751. Anpo, M.; Yamada, Y. *Mater. Chem. Phys.* **1988**, *18*, 465.

(54) Anpo, M.; Kondo, M.; Kubokawa, Y.; Coluccia, S.; Louis, C.; Che, M. *J. Chem. Soc., Faraday Trans. 1* **1989**, *85*, 609.

(55) Anpo, M.; Suzuki, T.; Tanahashi, I.; Kondo, M.; Kubokawa, Y., Shokubai, 68.

(56) Fournier, M.; Louis, C.; Che, M.; Chaquin, P.; Masure, D., submitted to *J. Catal.*

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

(58) Iwasawa, Y.; Ogasawara, S. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3709.

(59) Iwasawa, Y.; Sato, Y.; Kuroda, H. *J. Catal.* **1983**, *82*, 289, and Iwasawa, Y.; Shokubai, 191.

(60) Iwasawa, Y. *Adv. Catal.* **1987**, *35*, 187.

(61) Forzatti, P.; Attardo, C.; Trifiro, F. *J. Chem. Soc., Chem. Commun.* **1979**, 747.

(62) Mahay, A.; Kaliaguine, S.; Roberge, P. C. *Can. J. Chem.* **1982**, *60*, 2719.

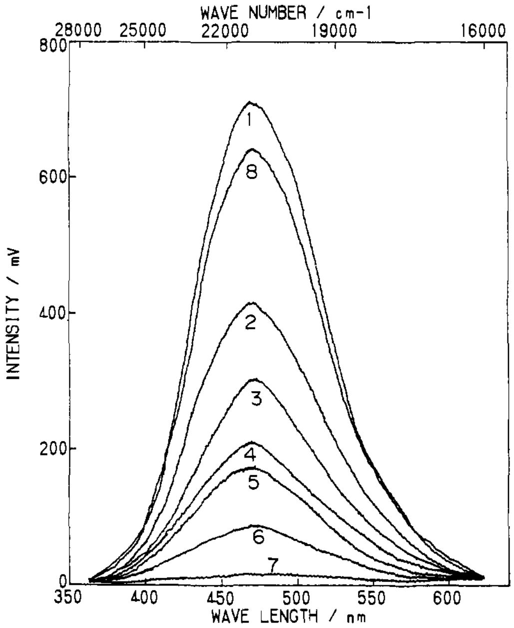

Figure 3. Effect of the addition of oxygen upon the yields of the phosphorescence of the anchored Mo/SiO_2 oxide catalyst (0.07 wt % Mo) at 77 K. (Excitation wavelength, 280 nm; amounts of adsorbed O_2 at 77 K (in 10^{-6} mol/g of catalyst): 1, 0.0 (under vacuum); 2, 4.3; 3, 9.5; 4, 18.8; 5, 29; 6, 57.6; 7, 85; 8, after evacuation of the previous sample (7) at 298 K for 20 min.)

the results obtained by Kazansky et al.[63,64] and Anpo et al.[52] on impregnated Mo/SiO_2 catalysts (470 nm).

As shown in Table II and Figure 1, for both types of Mo/SiO_2 samples, the phosphorescence obtained at 77 K slightly shifted toward higher wavelengths, while its intensity drastically increased as compared to those obtained at 298 K. Such features have been found with other highly dispersed metal oxides such as V_2O_5/PVG, V_2O_5/SiO_2, etc.,[20,23,25,26] being attributable to the fact that the lifetime of the excited triplet state is markedly affected by temperature-dependent radiationless processes; i.e., radiationless deactivation from the triplet state is less efficient at 77 than at 298 K, leading to an increased phosphorescence intensity. Furthermore, at this temperature, the contribution of the electronic population in the lower state of the excited triplet (p_{21} state) is more important than that of the higher lying triplet (p_{31} state), resulting in a red shift.[65]

1.2. Excitation Energy Dependence of the Photoluminescence Spectra. Figure 2 shows the phosphorescence spectra at 77 K of the anchored (0.07 wt % Mo) Mo/SiO_2 oxide catalyst obtained with different excitation energies. Table III summarizes the exact wavelengths at the phosphorescence maxima and the yields of their phosphorescence. Figure 2 and Table III clearly show that the maximum at 467.0 nm (21 414 cm^{-1} = 2.654 eV) of the phosphorescence spectrum of the anchored sample does not depend on the excitation energy. In contrast, as shown in Table III, for the impregnated catalyst the maximum of phosphorescence changes from 466.4 to 481.0 nm when the excitation wavelength decreases from 305.0 to 270.5 nm, in good agreement with those obtained recently by Kaliaguine et al.[8]

Iwasawa et al.[57-60] found similar results. These results suggest that the phosphorescence spectrum is sensitive to the preparation method. Such features also suggest that the anchored Mo/SiO_2 catalysts involve only one type of molybdenum emitting site, while the impregnated Mo/SiO_2 catalysts possess more than one type of emitting site on the surface, even though their Mo content was ~5 times lower. Coluccia et al.[66] and Anpo et al.[53] also found that the photoluminescence of degassed SrO at 77 K depended upon the excitation energy and explained it in terms of three different types of emitting sites with different radiative efficiencies.

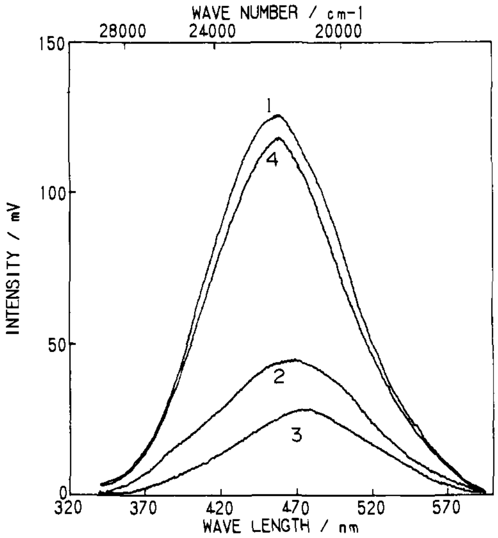

Figure 4. Effect of the addition of oxygen upon the yields of the phosphorescence of the impregnated Mo/SiO_2 oxide catalyst (0.013 wt % Mo) at 77 K. (Excitation wavelength, 280 nm; amounts of adsorbed O_2 at 77 K (in 10^{-6} mol/g of catalyst): 1, 0.0 (under vacuum); 2, 24.6; 3, 119 or excess; 4, after evacuation of the previous sample (7) at 298 K for 20 min.)

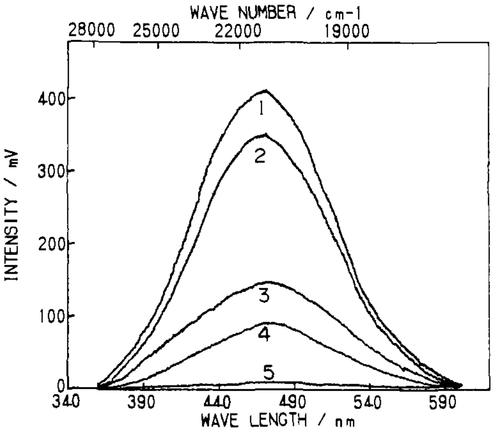

Figure 5. Effect of the addition of CO upon the yields of the phosphorescence of the anchored Mo/SiO_2 oxide catalyst (0.043 wt % Mo) at 77 K. (Excitation wavelength, 280 nm; amounts of adsorbed CO at 77 K (in 10^{-6} mol/g of catalyst): 1, 0.0 (under vacuum); 2, 21; 3, 198; 4, 421; 5, excess.)

2. Quenching of Phosphorescence by Added O_2 or CO Molecules. The different emitting sites were investigated further by observing the effect of added gases on the phosphorescence spectra of the Mo/SiO_2 catalysts. O_2 and CO are well-known as efficient quenchers of excited triplet states. Figures 3 and 4 show the results of oxygen quenching at 77 K on anchored (0.07 wt % Mo) and impregnated (0.013 wt % Mo) Mo/SiO_2 oxide cattalysts, respectively. From Figures 3 and 4, it is clear that the yield of the phosphorescence of the anchored Mo/SiO_2 catalyst is ~7 times higher than that of the impregnated catalyst and that oxygen completely quenches the phosphorescence of the anchored samples. For the impregnated catalysts, the quenching is not complete, even though their Mo concentration is ~5 times lower than that of the anchored catalysts. About 20% of the phosphorescence remains unquenched in the presence of excess oxygen. Figure 5 shows phosphorescence quenching by CO molecules at 77 K on the anchored Mo/SiO_2 catalyst (0.043 wt % Mo). Thus, the addition of CO onto the Mo/SiO_2 catalysts led to results similar

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(63) Shelimov, B. N.; Pershin, A. N.; Kazansky, V. B. *J. Catal.* **1980**, *64*, 426.

(64) Kazansky, V. B. *Kinet. Katal.* **1982**, *24*, 1338.

(65) Blasse, G. *Struct. Bonding* (*Berlin*) **1980**, *42*, 1. Blasse, G.; Boon, L. *Ber. Bunsenges. Phys. Chem.* **1984**, *88*, 929.

(66) Coluccia, S. In *Adsorption and Catalysis on Oxide Surfaces*; Che, M., Bond, G. C., Eds.; Elsevier: Amsterdam, 1985; p 59.

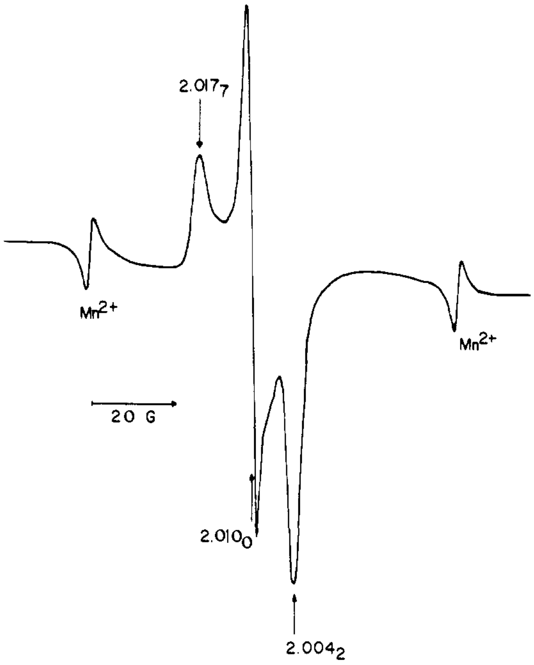

Figure 6. ESR spectrum of the photoformed O_2^- anion radicals on molybdenum oxide supported on porous Vycor glass at 77 K. (In order to obtained a strong ESR signal, the transport porous Vycor glass (major composition, SiO_2 = 96%) was used as a support. UV irradiation (λ > 280 nm) was carried out at 77 K for 30 min in the presence of O_2 (5 × 10^{-5} mol/g of catalyst.)

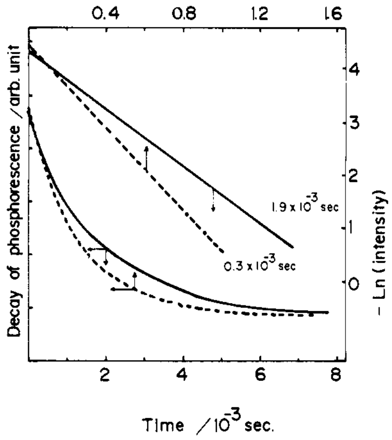

Figure 7. Decay of the phosphorescence of the anchored Mo/SiO$_2$ oxide catalyst (0.07 wt % Mo) under vacuum (solid line) at 77 K (straight solid line corresponds to its logarithm) and in the presence of the added oxygen at the same temperature (dotted lines) (straight dotted line corresponds to a logarithm of the decay curve). (Decay was monitored at the 460-nm emission band; amount of adsorbed O_2 at 77 K, 31.5 × 10^{-6} mol/g of catalyst.)

to those for oxygen (vide infra).

When the quenching is complete, the number of CO or O_2 molecules is larger than that of molybdenum ions contained in the samples, suggesting that part of the CO or O_2 is physisorbed on silica. At those low Mo concentrations, only about 0.1–0.2% of the silica is covered with Mo. It should be emphasized that with the impregnated Mo/SiO$_2$ catalyst, the peak position of the remaining phosphorescence in the presence of oxygen changes a bit from that of the original phosphorescence (Figure 4). The same phenomenon in the phosphorescence quenching was observed at 298 K. Furthermore, with impregnated catalysts, the ratio between the unquenched and the original phosphorescence intensities increases with the molybdenum content. On the other hand, for anchored catalysts, only the sample with the highest Mo content (0.37 wt % Mo) led to incomplete quenching, since ~30% of the phosphorescence remains unquenched at both 77 and 298 K in presence of excess O_2.

As described previously,[22,23,30,53] two mechanisms of phosphorescence quenching by addition of quencher molecules such as CO or O_2 are possible: (1) dynamic (collisional or weak-interaction) quenching, whereby quencher molecules diffuse on the surfaces and interact with the emitting sites in their metastable excited state; or (2) quenching via the formation of adsorbed complexes between the adsorbed molecules and the excited active emitting sites with different pathways. These two mechanisms might operate in the quenching processes to give a nonradiative deactivation pathway (to enhance the intersystem crossing to the ground state) and/or destructive radiative pathways via the formation of adsorbed complexes such as O_2^- on the active emitting sites.

For both anchored and impregnated Mo/SiO$_2$ catalysts, the former mechanisms seems to be predominant, since the reversible nature in the quenching (i.e., a recovery of the phosphorescence after the evacuation of the sample at room temperature for 20–30 min) suggests that the added O_2 molecules interact weakly with the active surface sites on the Mo/SiO$_2$ catalysts, except for a small fraction that irreversibly adsorbed, as seen in Figures 3 and 4. It was found that the phosphorescence of each catalyst seems to depend on the exposure time of the catalyst to the excitation in the presence of O_2, and as shown in Figure 6, in this system the formation of O_2^- anion radicals is confirmed by EPR. The g values ($g_1 = g_{zz}$ = 2.017$_7$, $g_2 = g_{yy}$ = 2.010$_0$, and $g_3 = g_{xx}$ = 2.004$_2$) of the signal suggest that the photoformed O_2^- anion radicals are adsorbed on Mo^{6+} sites of the catalyst.[22] It should be noted that quenching with added CO molecules is, at least partly, associated with the destruction of the emitting sites, i.e., with the photoreduction of the molybdenyl species to produce CO_2 and reduced Mo ion.[18,36,63] According to recent studies, the reaction of CO with the charge-transfer excited triplet state of molybdenum species can lead to the formation of molybdenum species having a oxidation state around 2+ for samples with smaller Mo loading (0.01–0.1 wt % Mo)[36,67] and 4+ for samples with Mo loadings higher than 0.1 wt % Mo.[67]

The results of phosphorescence quenching experiments indicate that, with anchored catalysts with Mo contents lower than 0.37 wt %, the molybdenum emitting sites are all accessible, located on the surface, and essentially in the same symmetry. In contrast, with impregnated catalysts, incomplete quenching suggests that the emitting sites are not all on the surface, in agreement with their lower Mo dispersion.[38-48] Different types of emitting sites are thus suggested to be involved in the phosphorescence. As an exception, the anchored sample with 0.37 wt % Mo has a behavior similar to that of impregnated samples because of its lower Mo dispersion.

Iwasawa et al.[51,52] also observed similar quenching phenomena on the addition of O_2 and CO at 298 K: on a chemically fixed Mo/SiO$_2$ catalyst (1.7 wt % Mo), the photoluminescence was completely quenched, whereas on an impregnated Mo/SiO$_2$ sample (1.7 wt % Mo), about 30–40% of the emission remained unquenched. This difference in behavior was explained in terms of only one type of emitting site for the chemically fixed sample, while for the impregnated catalysts at least two types of emitting sites were involved.

3. Comparison of the Phosphorescence Decay Processes for Anchored and Impregnated Mo/SiO$_2$ Catalysts. There is no report of direct measurement of the decay curves of the phosphorescence for supported molybdenum oxide catalysts. Figure 7 shows the decay of the phosphorescence at 77 K of an anchored Mo/SiO$_2$ catalyst (0.07 wt % Mo) under vacuum (solid lines) and in oxygen (dotted lines). After cutoff of the excitation radiation, the phosphorescence of the anchored catalyst decays as a single exponential proved by the straight lines in the logarithmic plots of the phosphorescence intensity versus time. This indicates that the phosphorescence involves only one emitting site, in agreement with the results obtained with the quenching experiments and the phosphorescence spectra with different excitation energies.

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(67) Elev, I. V.; Shelimov, B. N.; Kazansky, V. B. *J. Catal.* **1988**, *113*, 256.

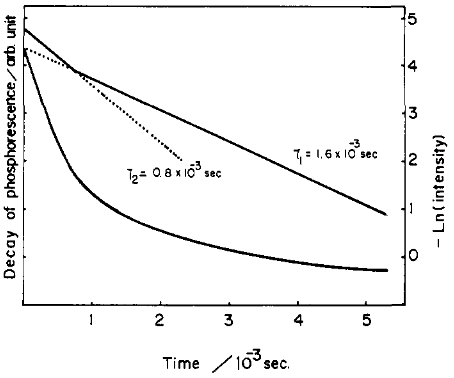


Figure 8. Decay of the phosphorescence of the impregnated Mo/SiO_2 oxide catalyst (0.1 wt % Mo) under vacuum at 77 K (solid curve) (bent solid lines correspond to a logarithm of the decay curve). (Decay was monitored at the 460-nm emission band; deconvolution of the decay curve was carried out by using the equation, $I = A \exp(bt) + C \exp(dt)$, where I is that intensity of the phosphorescence at time t, and A, b, C, and d were all constants. The lifetime of the faster decay component was given as $\tau_1 = -1/b$ and that of the slower decay component, $-1/d$.)

The lifetime at 77 K of the charge-transfer excited triplet state, for the anchored catalyst determined from the single-exponential decay, is 1.9×10^{-3} s under vacuum and $\sim 0.3 \times 10^{-3}$ s in presence of 31.5×10^{-6} mol/g-catalyst amount of oxygen (1.1×10^{-3} s in the presence of 85.2×10^{-6} mol/g-catalyst amount of CO). As shown in Figure 9 (vide infra), the lifetimes was found to decrease with the amount of adsorbed O_2 or CO. Thus, the shorter lifetimes determined in the presence of quenchers clearly suggest that phosphorescence quenching is due to the collisional (or dynamic) mechanism as mentioned above, i.e., interaction between the charge-transfer excited triplet state and the oxygen molecule, leading to a nonradiative deactivation pathway for the absorbed photon energy.

Figure 8 shows the phosphorescence decay of the impregnated Mo/SiO_2 catalyst (0.1 wt % Mo) at 77 K under vacuum. The plot of the logarithm of the total phosphorescence intensity versus time shows that the phosphorescence consists of two components with different lifetimes, i.e., $\tau_1 = 1.6 \times 10^{-3}$ s and $\tau_2 = 0.8 \times 10^{-3}$ s, respectively. This is the first report showing that the decay curve of the charge-transfer excited triplet state of the supported Mo oxide catalyst is deconvoluted by two components. Kazansky has reported that the lifetime in vacuo of the charge-transfer excited triplet state of impregnated Mo/SiO_2 catalysts (up to 1–2 wt % Mo) is 2×10^{-3} s at 77 K.[64] He did not report whether the phosphorescence decay was a single exponential or not, but the latter value is consistent with the longer of the two lifetimes obtained with our impregnated Mo/SiO_2 catalysts. By use of a procedure similar to that described above, at 298 K the lifetime of the anchored sample with 0.07 wt % Mo was measured to be 75×10^{-6} s. The decay of the phosphorescence for the impregnated sample with 0.1 wt % Mo was not a single exponential and gave the following lifetimes: 68×10^{-6} and $\sim 7 \times 10^{-6}$ s at 298 K.

Phosphorescence lifetimes depend on several parameters such as the rate constant of radiationless energy transfer, of radiative energy transfer, and of quenching by gas-phase molecules, which are all temperature dependent. As a result, the lifetime is shorter at 298 K than at 77 K, and as seen in Figure 1 and Table II, the phosphorescence intensity is much lower. For both temperatures of 298 and 77 K, the longer of the two lifetimes observed for the impregnated Mo/SiO_2 catalyst is slightly shorter than that of the anchored catalysts. Such differences in the lifetimes seem to reflect the fact that the strength of the interaction between Mo ions and the surface of the SiO_2 might be slightly different between the anchored catalysts and the impregnated catalysts because of different preparation methods. In other words, some strong chemical bonds between Mo and SiO_2 surfaces are formed for the anchored catalysts, but for the impregnated catalysts they are rather weak. Indeed, Mo ions supported by impregnation were completely soluble in $HF-H_2SO_4$ solution, but with the anchored samples, the Mo ions were only partially soluble (Table I). Further work is needed in order to elucidate the relationship between the lifetime of the excited state of active surface sites on the support surfaces and the chemical nature of their interaction with the supports.

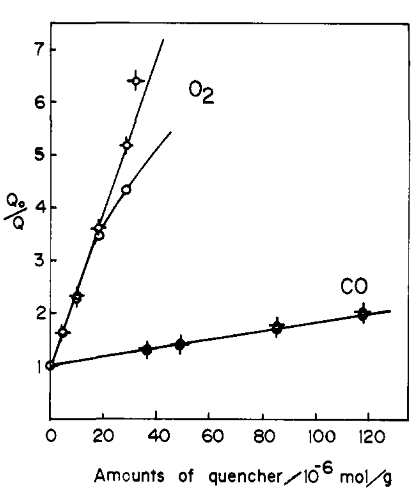
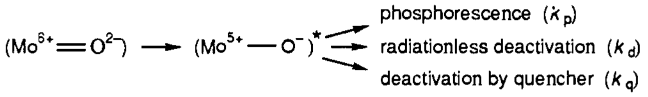


Figure 9. Stern–Volmer plots of Q_0/Q values for the yields of phosphorescence (○) and the corresponding lifetimes (⊕) of the anchored Mo/SiO_2 oxide catalyst (0.07 wt % Mo) versus the amounts of adsorbed O_2 or CO at 77 K. (Lifetime of the catalyst under vacuum was 1.9 ms at 77 K.)

4. Absolute Quenching Rate Constant of O_2 and CO Molecules. As described above, the phosphorescence of the Mo/SiO_2 catalysts is easily quenched by added O_2 or CO. Therefore, the photophysical processes on the Mo/SiO_2 catalysts in the presence of quencher molecules can be described as follows,[22,28,30,53] especially for the anchored Mo/SiO_2 catalysts where there is only one type of emitting site, all located on the surface:



Thus, the following Stern–Volmer equation is obtained for both the yields and the lifetimes of the phosphorescence from the anchored Mo/SiO_2 catalysts by using the steady-state treatment:[68]

$$Q_0/Q = 1 + \tau k_q[Q] \qquad \text{(I)}$$

where Q_0 and Q are yields of the phosphorescence of the supported Mo oxide in the absence and in the presence of quencher molecules, respectively, and τ, k_q, and [Q] are the lifetime of the charge-transfer excited triplet state of the molybdenum oxide in the absence of quencher, the quenching rate constant, and the concentration of quencher on the catalyst surfaces, respectively. In fact, as shown in Figure 9, with the anchored Mo/SiO_2 oxide catalyst (0.07 wt % Mo), Q_0/Q for O_2 or CO is a linear function of O_2 or CO pressure, although there are deviations from linearity at larger values of Q_0/Q obtained for the yields of phosphorescence for O_2. The Stern–Volmer plots for the change of the lifetimes of phosphorescence are also good linear functions, suggesting that dynamic quenching, in which quencher molecules interact with the excited triplet state, mainly operates in this quenching. Deviations from linearity in the Stern–Volmer plots for the yields of phosphorescence in the presence of O_2 might be attributable to a difficulty in measuring the yield of weak phosphorescence. However, it is clear that, in the region of Q_0/Q less than 3–4, for both O_2 and CO the quenching efficiency is dependent on the amount of quencher adsorbed on the surfaces and, in turn, the equilibrium pressure of the added quencher molecules.

From the Stern–Volmer plots of the phosphorescence quenching of the anchored Mo/SiO_2 oxide (0.07 wt % Mo) by added O_2 or CO, and the lifetime determination in the absence of quencher,

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[68] Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings: Menlo Park, CA, 1978.

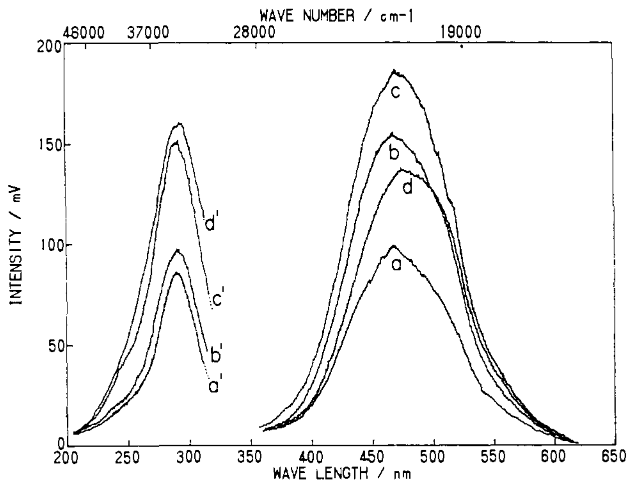


Figure 10. Phosphorescence spectrum and its excitation spectrum of the anchored Mo/SiO$_2$ oxide catalysts with different Mo contents. (Phosphorescence spectra were measured at 77 K under the excitation at the 280-nm band. Spectra of a, b, and c are the same scale, spectrum d is reduced $^1/_2$. Excitation spectra were monitored at the 540-nm emission band. Spectra of a′, b′, c′, and d′ are all in the same scale. The contents of Mo ions (in wt % Mo): a, 0.01; b, 0.02; c, 0.07; d, 0.37.)

the absolute quenching rate constants for O$_2$ and CO at 77 K are first determined to be 7.6×10^7 g of catalyst/mol·s for O$_2$ and 4.2×10^6 g of catalyst/mol·s for CO, respectively. These values are smaller than those for the charge-transfer excited triplet state of the anchored V/SiO$_2$ oxide catalyst (k_q at 77 K was to be 3.2 $\times$ 10^8 g of catalyst/mol·s), its lifetime (~6 ms at 77 K) being much longer than that of the anchored Mo/SiO$_2$ oxide.[28]

The rate constant of O$_2$ for the charge-transfer excited triplet state of the anchored Mo/SiO$_2$ oxide is found to be 18 times larger than that of CO. This suggests that the reactivity of O$_2$ to the charge-transfer excited triplet state of the Mo/SiO$_2$ oxide is much higher than that of CO. Further work is in progress with various quencher molecules such as N$_2$O and C$_3$H$_6$ in order to clarify the general character controlling their reactivity.

5. Effect of the Mo Content upon the Phosphorescence Spectrum of Anchored Mo/SiO$_2$ Oxide Catalysts. Figure 10 shows the effect of the Mo content upon the wavelengths of the phosphorescence and its excitation spectrum (absorption spectrum) at 77 K for the anchored Mo/SiO$_2$ oxide catalysts. For Mo contents increasing from 0.01 to 0.07 wt % Mo, the band position of both the phosphorescence and its excitation spectrum scarcely changes, and the phosphorescence intensity increases with the Mo content (a–c). For the catalyst with 0.37 wt % Mo (higher Mo content), the band position of both the phosphorescence and its excitation spectrum shifts toward longer wavelengths (d), and the extent of an increase in the phosphorescence intensity is rather small as compared to the increase of Mo content.

A similar fact was observed for the impregnated molybdenum oxides supported on porous Vycor glass,[26,31] where a decrease in the phosphorescence intensity as well as the band shift toward longer wavelengths occurred for the samples with Mo contents above 0.035 wt %, i.e., at Mo contents substantially lower than those of the anchored catalysts. Such a phosphorescence behavior may be explained by a decrease in the Mo dispersion when the Mo content of the sample increases. Indeed, the interactions between neighboring Mo ions, which become substantial with increasing Mo content, induce a more efficient radiationless energy transfer, which leads to the decrease in the phosphorescence intensity. This might be the reason why the pure bulk MoO$_3$ oxide does not exhibit phosphorescence even at temperatures lower than 77 K. The band shifts arise from the change in the Mo environment induced by Mo–Mo interactions. This is in agreement with our previous observations in UV reflectance,[56] i.e., the absorption band width increases and the band shifts toward longer wavelengths when the size of the polyoxomolybdate increases (i.e., when Mo–Mo ions interaction increases). As described in our previous paper,[52] such phenomena clearly are associated with the translation of the molybdenum oxide species from a highly dispersed molecular state's level to an aggregated bulk oxide structure state. Such features in the spectral change are of special interest in connection with the size quantization effects on the oxide catalysts.[69,70]

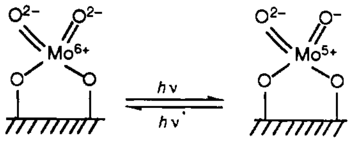
Discussion

In previous work,[31,39] we have shown that the absorption energy and, therefore, the electronic energy levels depend not only on the Mo symmetry but also on further environment, i.e., on the size of the polyoxo–molybdate. Hence, the fact that the anchored Mo/SiO$_2$ oxide catalysts (except for the catalyst with highest Mo content) involve only one type of emitting site means that the Mo sites possess the same symmetry and the same environment. Indeed, the complete quenching by addition of O$_2$ or CO indicates that the molybdenum emitting sites of the anchored Mo/SiO$_2$ oxides are all accessible. Therefore, they must be located on the surface of the SiO$_2$ support and have the same environment. This is confirmed here by the evidence of only one lifetime in the phosphorescence decay.

In contrast, the impregnated Mo/SiO$_2$ oxide catalysts possess at least two different types of molybdenum emitting sites, as shown by the evidence of incomplete quenching by an excess quenchers, a shift of the peak position of the unquenched phosphorescence, two lifetimes in the phosphorescence decay, and a shift of the peak position of the phosphorescence when the excitation energy changes. These results mean that either they have the same symmetry but different further environment or their symmetry is different. The incomplete quenching at 298 and 77 K in the presence of excess O$_2$ or CO suggests that the emitting sites are not all located on the surface. Therefore, the further environment and/or symmetry is not the same. These results seem to be in agreement with a recent study on Mo/SiO$_2$ oxide,[52] where the presence of Mo aggregates as X-ray amorphous or surface polymolybdates (the presence of crystalline MoO$_3$ is negligible for the catalysts with Mo contents less than 1.0 wt %) due to their lower dispersion is characterized by using XRD, FT-IR, and laser Raman techniques.[52] Thus, on increasing the interactions between Mo–Mo ions, an isolated molybdenum species changes into molybdenum aggregate clusters, as mentioned above.

The difference between the longer lifetime of the impregnated catalyst (i.e, 1.6×10^{-3} s at 77 K and 68×10^{-6} s at 298 K) and that of the anchored catalyst (i.e., 1.9×10^{-3} s at 77 K and 75 $\times$ 10^{-6} s at 298 K) may be due to a slightly different environment of the molybdenum species on the surfaces, i.e., the lower dispersion for the impregnated catalysts. This lower dispersion might result from the weaker interaction of Mo ions with the SiO$_2$ surfaces, as mentioned above. The shorter lifetime of the impregnated catalyst (i.e., 0.8×10^{-3} s at 77 K and 7×10^{-6} s at 298 K) probably arises from the molybdenum species located inside the Mo aggregates (Figure 11). Indeed, it seems to correspond to the unquenched emitting sites, i.e., to the species nonaccessible by O$_2$ or CO molecules. Furthermore, this shorter lifetime may be due to a more efficient radiationless energy transfer owing to the proximity of interacting Mo ions.

Kazansky et al.[4,18,64] and Iwasawa et al.[57–60] observed the phosphorescence at ~440 nm at 298 K, in agreement with the present results, with the chemically fixed mononuclear molybdenum oxide species on SiO$_2$ and attributed to radiative decay from the charge-transfer excited triplet state of tetrahedral dioxo–molybdenum species (II):



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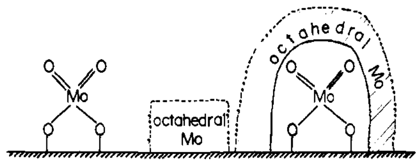
(69) Brus, L. E. *J. Phys. Chem.* **1986**, 90, 2555; *J. Chem. Phys.* **1983**, *79*, 5566; *Ibid.* **1984**, *80*, 4403.

(70) Anpo, M.; Shima, T.; Kodama, S.; Kubokawa, Y. *J. Phys. Chem.* **1987**, *91*, 4305. Anpo, M. *Res. Chem. Intermed.* **1989**, *11*, 67.

anchored catalyst



impregnated catalyst

Figure 11. Models describing the different Mo sites involving isolated tetrahedral Mo species and aggregated Mo and/or polymolybdate species (which are constituted from octahedral Mo species) on the SiO_2 surfaces. (Only the isolated tetrahedral Mo species are emitting.)

In fact, UV/visible diffuse reflectance spectroscopy of the mononuclear molybdenum oxide with an absorption peak at ~290 nm ($t_1 \rightarrow 3t_2$) shows that the Mo ions are located in tetrahedral positions. The observed IR absorption band at ~916 cm^{-1} is assigned to a stretching frequency of the Mo=O bond of the oxomolybdenum species with two terminal oxygen atoms in tetrahedral symmetry (II), as shown in reaction 3.[4,18,57-60,63,64] According to recent studies using EXAFS and XANES made by Iwasawa et al.,[60] the tetrahedral Mo species on the chemically fixed Mo/SiO_2 oxide catalysts have two Mo=O double bond oxygens with the Mo-O distance of 1.68 Å and the two Mo—O single-bond oxygens bonds (with surface) having an Mo-O bonding distance of 2.09 Å. Kazansky et al.[4,18,64] proposed the same model for Mo^{6+} on impregnated Mo/SiO_2 oxide catalysts, by analogy with the V^{5+} symmetry of V/SiO_2 oxide catalysts.

Furthermore, previous experimental[24,36] and theoretical[71] works have revealed that propene metathesis reaction is photoinduced on the Mo/SiO_2 oxide catalysts only if surface Mo species having a dioxo structure with two Mo=O double bond oxygens are present on the catalysts. As shown in Table I, it has been found that the metathesis yields at 298 K with the same Mo/SiO_2 oxide catalysts as the present work change as the yields of the phosphorescence of the catalyst observed at 298 K. In addition, there are several other indications that support a significant contribution of the tetrahedral dioxo-molybdenum species to the observed phosphorescence. It has also been reported that only molybdate compounds such as $CaMoO_4$ and $CdMoO_4$ containing a molybdate tetrahedral species exhibit photoluminescence but not molybdate octahedral compounds.[65,72] Thus, there is no doubt that the emitting sites of the Mo/SiO_2 oxide catalyst are isolated tetrahedral Mo species (aggregates of tetrahedral Mo do not exist in nature) and not octahedral Mo species.

From the discussion mentioned above, it appears that the earlier and the present results can be rationalized in terms of the models shown in Figure 11. On anchored catalysts there is only one type of emitting site (one decay component), i.e., the isolated Mo tetrahedral species, which can be entirely quenched by addition of O_2 or CO molecules. It is possible that octahedral species are also present, especially for the catalysts with higher Mo contents. Those species may be located on the support surface and separated from the tetrahedral species, so there is no interaction between tetrahedral and octahedral species. The presence of octahedral Mo species, in addition to the tetrahedral Mo species, may explain why the phosphorescence yields do not increase linearly with Mo content.

On impregnated catalysts, there are at least two types of emitting sites (two decay components). One is efficiently quenched by the added O_2 or CO molecules, but the other is not. Since the previous discussion led to the identity of the emitting sites as a Mo tetrahedral species, it may be assumed that a part of the sites is physically covered with aggregated Mo and/or polymolybdate species that are constituted from octahedral Mo species but not tetrahedral ones and, therefore, cannot be quenched by added O_2 or CO molecules, while the other part is not covered and located on the surfaces, similar to that with anchored catalysts, and thus can be efficiently quenched. It can be simply postulated that there are two tetrahedral Mo species and that some of them are isolated on the surface. With further increased Mo content, two-dimensional surface polymolybdate species would also participate in the production of the crystalline MoO_3 on SiO_2, as indicated in the previous paper.[52] The possibility of the formation of calcium or sodium molybdate as the second tetrahedral Mo species for the impregnated samples might be pointed out. However, the experimental results obtained for the supports, which had been well washed by acid solutions, and a lack of coincidence of the wavelength of the phosphorescence of the sample and that of $CaMoO_4$ suggest that the contribution of calcium or sodium molybdate to the second phosphorescence is unlikely in these samples.[65]

Kazansky suggested that the lowest triplet state in the octahedral complex, which results in an efficient radiationless deactivation, is consistent with the absence of photosphorescence for the octahedral Mo species.[65] At this stage, it appears necessary to confirm this hypothesis of the short lifetime of the octahedral Mo species owing to the investigation of the photoluminescence of polyoxo-molybdates of various sizes and conformations with both octahedral and tetrahedral Mo species in order to directly probe the model proposed. Studies are being carried out along those lines.

It is worth mentioning that Anpo et al.[32] using an EPR technique have already suggested that, on the impregnated V/SiO_2 oxide catalysts, tetrahedral V species are isolated on the surface and then covered with octahedral V species and then with V_2O_5, with increasing vanadium oxide content. It may be noted though that the V contents are much higher than those of Mo ions in the present work. Thus, the model shown in Figure 11 seems to be widely applicable not only for the supported molybdenum oxide but also for various supported transition-metal oxide catalysts.

Conclusions

While the band position of the excitation and photoluminescence spectra are very similar for the anchored (0.07 wt % Mo) and the impregnated (0.03 wt % Mo) Mo/SiO_2 oxide catalysts, there are several distinct differences: (i) for the anchored catalyst (0.07 wt % Mo), the position of the phosphorescence band is independent of the excitation energy, whereas the band position changes for the impregnated catalyst (0.1 wt % Mo), (ii) O_2 or CO molecules can completely quench the phosphorescence of the anchored catalysts but not that of the impregnated catalysts, and (iii) the decay curves of the phosphorescence involves one lifetime for the anchored catalysts and two components for the impregnated catalysts.

These results have been interpreted in terms of only one type of tetrahedrally coordinated molybdenum emitting site on the anchored Mo/SiO_2 oxide catalysts, i.e., Mo ions are in the same symmetry and located on the surface in the same environment, as it has been expected from its preparation mechanism. In contrast, the impregnated Mo/SiO_2 oxide catalysts contain at least two different types of the tetrahedrally coordinated molybdenum emitting sites with different environments, i.e., one on the SiO_2 surfaces and the other probably covered with octahedral Mo species that do not luminesce.

The absolute quenching rate constants of O_2 and CO molecules for the charge-transfer excited triplet state of the anchored Mo/SiO_2 oxide catalyst were first determined to be 7.6×10^7 g of catalyst/mol·s for O_2 and 4.2×10^6 g of catalyst/mol·s for CO molecules at 77 K, respectively. Thus, dynamic photoluminescence studies provide useful information not only on the chemical nature and properties of the active surface sites on both impregnated and anchored Mo/SiO_2 oxide catalysts with much lower Mo content

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(71) Rappe, A. K.; Goddard, W. A., III *J. Am. Chem. Soc.* **1982**, *104*, 297, 3287.

(72) Kroger, F. A. *Some Aspects of the Luminescence of Solids*; Elsevier: Amsterdam, 1948.

but also on the reactivity of the charge-transfer excited triplet state of the catalyst toward O_2 and CO molecules.

Finally, it is worth mentioning that this information on the charge-transfer excited state of the metal oxides is very important to elucidate the true nature not only of the photoinduced and/or photocatalytic reactions but also of catalysis on the metal oxides, because it has been suggested that the charge-transfer excited state could also be obtained by thermal activation in the catalytic systems on metal oxides.[22,47,48]

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Dynamic Aspects of the Stereochemistry of Metalated Oxime Ethers. An ab Initio Study of the Pathways for Coordination Isomerization, for Syn/Anti Isomerization, and for Racemization of the Lithium Ion Pairs from Acetaldoxime[1]

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Abstract: The pathways to isomerization between the chiral lithium ion pairs of acetaldoxime carbanion have been explored. The configuration of each ion pair is classified using two descriptors. In equilibrium structures one descriptor suffices to describe the configuration of each structure, but both descriptors are necessary for the recognition and consideration of all a priori possible pathways for racemization. Coordination isomerizations and racemizations of the syn- and the anti-configured ion pairs are discussed as special cases of the more general eight-minima scenario representing the epimers of two coordination isomers and their enantiomers, and the syn/anti isomerization is treated separately. This eight-minima scenario is described by a graph representation that reflects that the pathways for any pair of isomerizations $X \rightleftarrows Y$ and $X' \rightleftarrows Y'$ are enantiomerically related. Of all of the possible one-step isomerizations in this scenario only racemizations have the potential to involve achiral transition states since the enantiomerically related pathways $X \rightleftarrows X'$ might be identical. A systematic search for the transition-state structures for coordination isomerization and racemization is described on the basis of the symmetry properties of the imaginary vibrational modes of the achiral structures. Entirely chiral pathways for racemization exist if the corresponding achiral structure is a second-order saddle point and one of the imaginary modes fulfills the so-called IPD condition. The optimal geometries of all reasonable achiral structures have been characterized by vibrational normal mode analysis. In cases where the achiral structure is a second-order saddle point, the adjacent transition states have been located. The racemization of the η^2-NO-bond coordinated anti-configured ion pair involves entirely chiral pathways, but the potential energy surface in the bifurcating region is extremely flat. The syn/anti isomerization most likely involves rotation of the HO group around the CN axis, and the transition-state structure for this pathway has been located. All of these processes occur with only small barriers and should be facile. Thus, any of the structures is readily available as a reaction intermediate or as a building block for ion-pair aggregates. Mechanistic implications are discussed with regard to possible face selectivity of the electrophile entry. The small barrier to coordination isomerization has significant consequences for the design of strategies for regio- and stereoselective CC-bond formation at the α-carbon of diastereoisomeric metalated oxime ethers.

The introduction of metalated enolate equivalents by Wittig,[3] Stork,[4] and Hauser[5] resolved many of the problems associated with the classical methods for the regioselective formation[6] of a new carbon–carbon bond at the α-position of a carbonyl group. Metalated nitrogen derivatives of aldehydes and ketones have since become well established as an important class of intermediates in modern synthetic chemistry.[7,8] Metalated imines,[9–14] hydrazones,[15–19] and oxyimines[20–30] are typically generated by low-temperature deprotonation with a strong metalorganic base in

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(3) (a) Wittig, G.; Frommeld, H. D.; Suchanek, P. *Angew. Chem.* **1963**, *75*, 978. (b) Wittig, G.; Reiff, H. *Angew. Chem.* **1968**, *80*, 8. (c) Wittig, G.; Hesse, A. *Org. Synth.* **1970**, *50*, 66.

(4) (a) Stork, G.; Dowd, S. R. *J. Am. Chem. Soc.* **1963**, *85*, 2178. (b) Stork, G.; Benaim, J. *J. Am. Chem. Soc.* **1971**, *93*, 5938. (c) Stork, G.; Dowd, S. R. *Org. Synth.* **1974**, *50*, 66.

(5) Henoch, F. E.; Hampton, K. G.; Hauser, C. R. *J. Am. Chem. Soc.* **1969**, *91*, 676.

(6) (a) Stork, G. *Pure Appl. Chem.* **1975**, *43*, 553. (b) D'Angelo, J. *Tetrahedron* **1976**, *32*, 2979.

(7) Reviews: (a) Hickmott, P. W. *Tetrahedron* **1982**, *14*, 1975. (b) Mukaiyama, T. *Pure Appl. Chem.* **1983**, *55*, 1749. (c) Evans, D. *Stereoselective Reactions of Chiral Metal Enolates*. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: Orlando, FL, 1984; Vol. 3, p 1. (d) Enders, D. Alkylation of Chiral Hydrazones. In ref 7c, p 275.

(8) Reviews: (a) Fraser, R. R. *Stud. Org. Chem.* (*Amsterdam*) **1984**, *5B*, 65. (b) Gompper, P.; Vogt, H. H.; Wagner, H. U. *Z. Naturforsch.* **1981**, *36B*, 1644.

(9) (a) Ferran, H. E., Jr.; Roberts, R. D.; Jacob, J. N.; Spencer, T. A. *J. Chem. Soc., Chem. Commun.* **1978**, 49. (b) Lee, J. Y.; Lynch, T. J.; Mao, D. T.; Bergbreiter, D. E.; Newcomb, M. *J. Am. Chem. Soc.* **1981**, *103*, 6215.

(10) (a) Meyers, A. I.; Williams, D. R.; Druelinger, M. *J. Am. Chem. Soc.* **1976**, *98*, 3032. (b) Meyers, A. I.; Poindexter, G. S.; Brich, Z. *J. Org. Chem.* **1978**, *43*, 892. (c) Meyers, A. I.; Williams, D. R. *J. Org. Chem.* **1978**, *43*, 3245.

(11) Houk, K. N.; Strozier, R. W.; Rondan, N. G.; Fraser, R. R.; Chuaqui-Offermanns *J. Am. Chem. Soc.* **1980**, *102*, 1426.

(12) (a) Fraser, R. R.; Chuaqui-Offermanns, N.; Houk, H. N.; Rondan, N. G. *J. Organomet. Chem.* **1981**, *206*, 131. (b) Fraser, R. R.; Bresse, M.; Chuaqui-Offermanns, N.; Houk, K. N.; Rondan, N. G. *Can. J. Chem.* **1983**, *61*, 2729.

(13) Meyers, A. I.; Mihelich, E. D. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 270.

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