Quantitative analysis of photoluminescence quenching of silica-supported molybdena catalysts. Relation to photocatalytic reduction of nitric oxide by carbon monoxide

Boris Shelimov[a,*], Valeria Dellarocca[b], Gianmario Martra[b], Salvatore Coluccia[b], and Michel Che[c,†]

[a] *Zelinsky Institute of Organic Chemistry, Academy of Sciences, Leninsky prospect 47, 119991 Moscow, Russia*
[b] *Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali, Università di Torino, Via Pietro Giuria 7, 10125 Torino, Italy*
[c] *Laboratoire de Réactivité de Surface, UMR 7609, CNRS, Université Pierre et Marie Curie, 4, Place Jussieu, 75252 Paris Cedex 05, France*

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The quenching effect of NO, O_2, CO, and N_2O on the photoluminescence of Mo^{6+}/SiO_2 has been studied at room temperature as a function of gas pressure. Nonlinear plots of the relative photoluminescence intensity I_0/I (I_0 is the initial intensity under vacuum) vs. pressure of the quenching gases were rationalized assuming that only adsorbed molecules efficiently quench the $(Mo^{5+}–O^-)^*$ excited state and that the fraction of adsorbed quenching molecules can be determined from the classical Langmuir-type adsorption isotherm. The ratio of the quenching rate constants for NO and CO calculated from the computer best fits of the experimental I_0/I–pressure dependence is in agreement with earlier data on the kinetics of the photocatalytic reduction of NO by carbon monoxide on Mo^{6+}/SiO_2.

KEY WORDS: photoluminescence; quenching; silica; molybdena; NO; CO; oxygen; photocatalysis; reduction; oxide; support; adsorption.

1. Introduction

In previous publications [1–3] we have shown that silica-supported molybdena (Mo^{6+}/SiO_2) is an efficient catalyst for converting nitric oxide to N_2 and N_2O in the presence of carbon monoxide under UV irradiation ($\lambda < 360$ nm) at room temperature. The process is a real photocatalytic one, since the turnover number, i.e., the number of NO molecules converted on one molybdenum atom, is much greater than unity. A two-stage redox mechanism for the photocatalytic reduction of NO by CO was proposed. The first stage is a photochemical reaction which includes UV-assisted reduction of the surface Mo^{6+} ions to Mo^{4+} by carbon monoxide via the formation of a transient charge transfer excited state $(\sim Mo^{5+}–O^-)^*$. The second stage is the reoxidation of Mo^{4+} back to Mo^{6+} ions by NO to form N_2O which is further reduced to N_2 on Mo^{4+}. This stage does not require UV irradiation. Both stages can be accomplished separately or combined in one photocatalytic process. This reaction mechanism was supported by kinetic measurements [2,3].

The short-lived excited state $(\sim Mo^{5+}–O^-)^*$ is formed as a result of a charge transfer transition in a surface molybdenyl bond ($\sim Mo^{6+}=O$) induced by absorption of a UV light quantum. $(\sim Mo^{5+}–O^-)^*$ deactivates by emission of a photon (photoluminescence) and a phonon (radiationless decay), or it can be quenched by adsorbed or gaseous molecules. Photoluminescence of silica-supported molybdena was studied in detail by different groups [4–8]. A number of factors can affect the photoluminescence, such as the type of silica support (silicagel, PVG [9,10], mesoporous MCM-41 [11]), preparation method (impregnation with ammonium paramolybdate, grafting of $MoCl_5$ [7] or $Mo(\pi\text{-}C_3H_5)_4$ [4] to the surface OH groups of silicagel), molybdenum loading, etc. The photoluminescence was measured in a wide temperature interval from 300 to 10 K [6]. The maximum in the emission spectrum shifts only slightly from 437–440 to 467–470 nm on going from 300 to 77 K. At the same time, the photoluminescence intensity increases by several orders of magnitude at 77 K, since the lifetime of the $(\sim Mo^{5+}–O^-)^*$ triplet state increases at this temperature.

The quenching of the photoluminescence of Mo/SiO_2 by adsorbed O_2 and CO at 77 K [7] and by gaseous O_2, CO, CO_2, N_2O, propene, and 2-butene at 300 K [4,8] has been reported. The quenching rate constants for CO and O_2 at 77 K were estimated by Anpo *et al.* [7] from the Stern–Volmer dependences. For room-temperature quenching no quantitative information is available. The aim of this work was therefore to measure quantitatively the quenching effect of the molecules (CO, NO, N_2O) that are involved in the photocatalytic reduction of NO with CO on Mo/SiO_2 catalysts as a function of their pressure at room temperature. These data are thought to be necessary for the correct kinetic description of the photocatalytic reaction.

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[*] To whom correspondence should be addressed.

[†] Present address: Institut Universitaire de France.

2. Experimental

Silica-supported molybdena catalysts were prepared by impregnating a commercial KSK-2-5 silicagel or Cab-O-Sil with an aqueous solution of ammonium paramolybdate using the incipient wetness procedure. Molybdenum loadings were 2.5 wt% Mo (0.53 Mo at/nm^2) for KSK-2-5 and 0.23 wt% Mo (0.048 Mo at/nm^2) for Cab-O-Sil. The impregnated catalysts were dried in air at 100 °C overnight.

Prior to the photoluminescence experiments, Mo/SiO$_2$ powder samples were pretreated in a quartz cell connected to a vacuum line supplied with gas containers and a Leybold Thermovac TM-20 Pirani gauge. The catalyst samples were subjected to the following sequence of treatments: (1) evacuation to 10^{-4} torr at room temperature and then at 150 °C for 1 h; (2) raising the temperature at 10 K/min to 800 °C and heating under vacuum for 1 h; (3) heating in oxygen (60 torr) at 800 °C for 1 h followed by evacuation for 1 h; (4) lowering the temperature to 500 °C and heating in oxygen (60 torr) for 0.5 h; (5) final evacuation for 0.5 h at 500 °C; (6) cooling to room temperature.

After the pretreatment procedure, the quartz cell with a catalyst sample was installed in the chamber of a Spex Fluorolog-2 FL212 spectrometer at a fixed position and then connected to the vacuum line through a set of glass tubes without exposing the sample to air. Such an *in situ* arrangement allowed us to improve considerably the reproducibility of the photoluminescence intensity measurements. Photoluminescence spectra were recorded at room temperature either under vacuum or in the presence of O$_2$, NO, CO, or N$_2$O at different pressures (from 0.001 to 50 torr) which were measured by the Pirani gauge (at $P \leq 30$ torr) or by a Hg manometer (at $P > 30$ torr). The bandwidth of the excitation monochromator was set at 0.5 nm, and the bandwidth of the emission monochromator was adjusted to 2.7 nm.

High-purity nitric oxide, oxygen, carbon monoxide (Praxair), and nitrous oxide (Matheson) were used in this study.

3. Results

3.1. Photoluminescence spectra

Photoluminescence excitation and emission spectra of the 2.5 wt% Mo/SiO$_2$ sample after the thermal pretreatment are shown in figures 1 and 2. There are two maxima at about 260 and 330 nm in the excitation spectra whose positions are independent of the emission wavelength (400 or 470 nm, figure 1, curves (a) and (b)). The emission spectra (figure 2) exhibit a maximum at 430 nm with a shoulder at 470 nm. Deconvolution of curve (a) shows that it consists of two Gaussian lines (c) and (d) with maxima at 423 and 472 nm. The amplitudes of lines (c) and (d) are comparable, but line (d) is markedly broader than line (c). The shape of the emission spectra and positions of the maxima in figure 2 are very close for excitation wavelengths of 330 (curve (a)) and 260 nm (curve (b)).

The two excitation maxima in figure 1 can be related to the presence of different types of molybdenum surface species capable of emitting light under UV irradiation. The presence of different types of light-emitting sites in impregnated Mo/SiO$_2$ was reported earlier [4,7]. However, taking into account the fact that the emission spectrum does not change in shape, but only in intensity, upon changing the excitation wavelength, we can conclude that the excitation spectrum could rather be

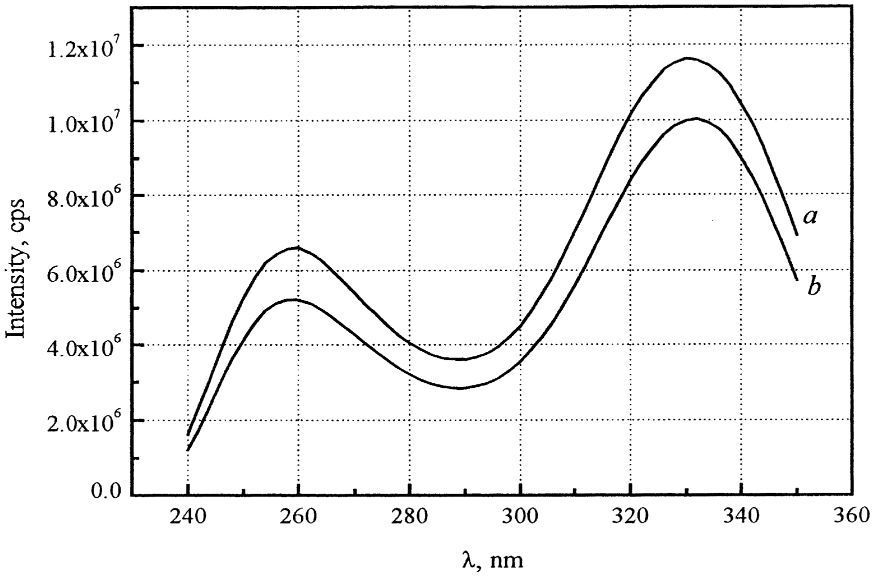

Figure 1. Photoluminescence excitation spectra of 2.5 wt% Mo/SiO$_2$ under vacuum at λ(emission) of (a) 400 and (b) 470 nm.

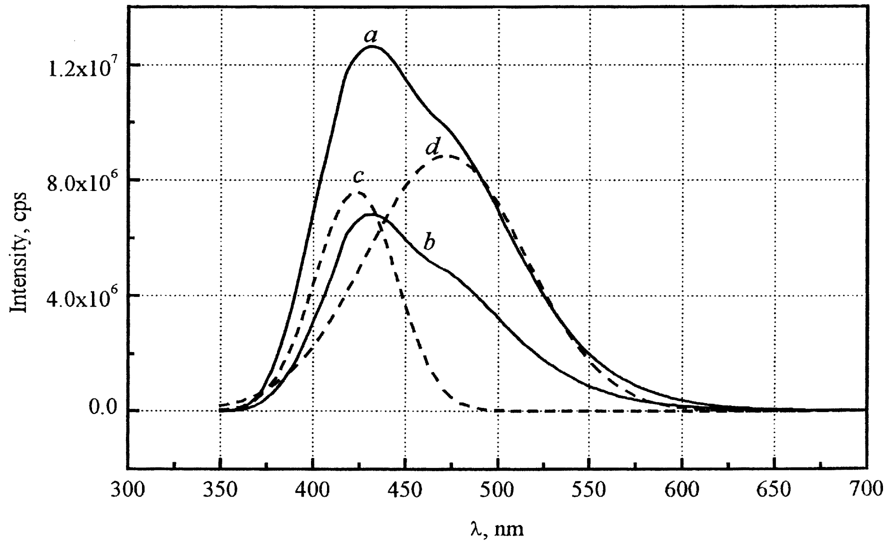

Figure 2. Photoluminescence emission spectra of 2.5 wt% Mo/SiO_2 under vacuum at λ(excitation) of (a) 330 and (b) 260 nm; (c) and (d) are deconvolutions of (a) into two Gaussian lines.

assigned to only one type of surface molybdenum species (probably to an octahedral oxo-complex of Mo^{6+}) which has two absorption transitions from the ground to excited states.

The photoluminescence excitation and emission spectra of the 0.23 wt% Mo/SiO_2 sample (figure 3) are very similar to those shown in figures 1 and 2 for 2.5 wt% Mo/SiO_2. The only difference is that the second maximum in the emission spectrum of 0.23 wt% Mo/SiO_2 at λ(excitation) = 265 nm is more distinct and shifted to 477 nm (figure 3, curve (b)). In the experiments described below, the excitation wavelength was set at 330 nm, and the photoluminescence intensity was measured at 430 nm.

3.2. *Effect of gases on the photoluminescence spectra*

Admission of NO, O_2, CO, and N_2O onto Mo/SiO_2 samples results in a marked decrease in the photoluminescence intensity (quenching effect), but has only a minor effect on the line shape of the emission spectrum (figure 4). The amplitude of the maximum emission was therefore taken in this work as a measure of the photoluminescence intensity *I*.

The quenching effect of O_2 and N_2O is found to be completely reversible, i.e., the initial photoluminescence intensity can be restored by brief evacuation of the sample at room temperature. In the case of CO and NO, the quenching effect is only partially reversible as

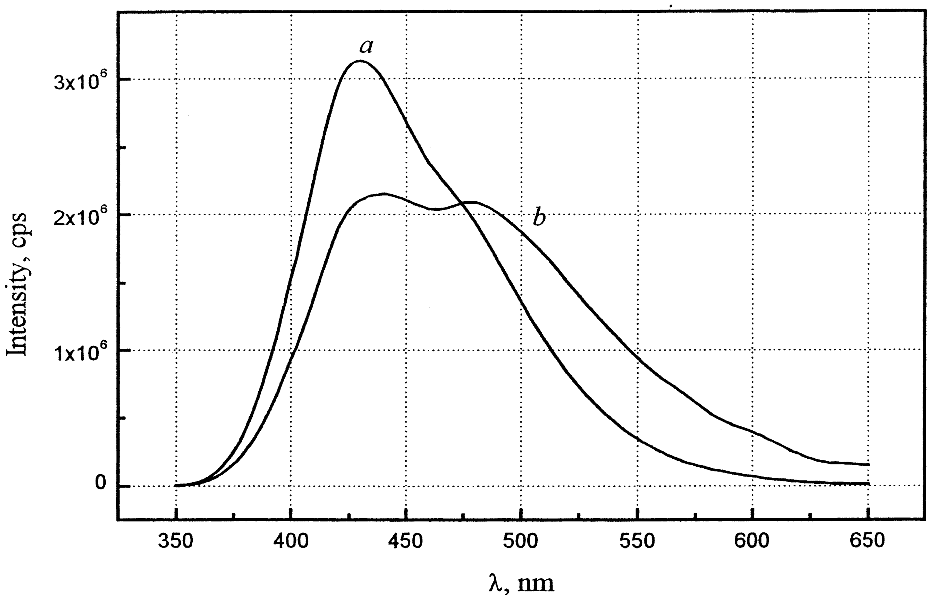

Figure 3. Photoluminescence emission spectra of 0.23 wt% Mo/SiO_2 under vacuum at λ(excitation) of (a) 330 and (b) 265 nm.

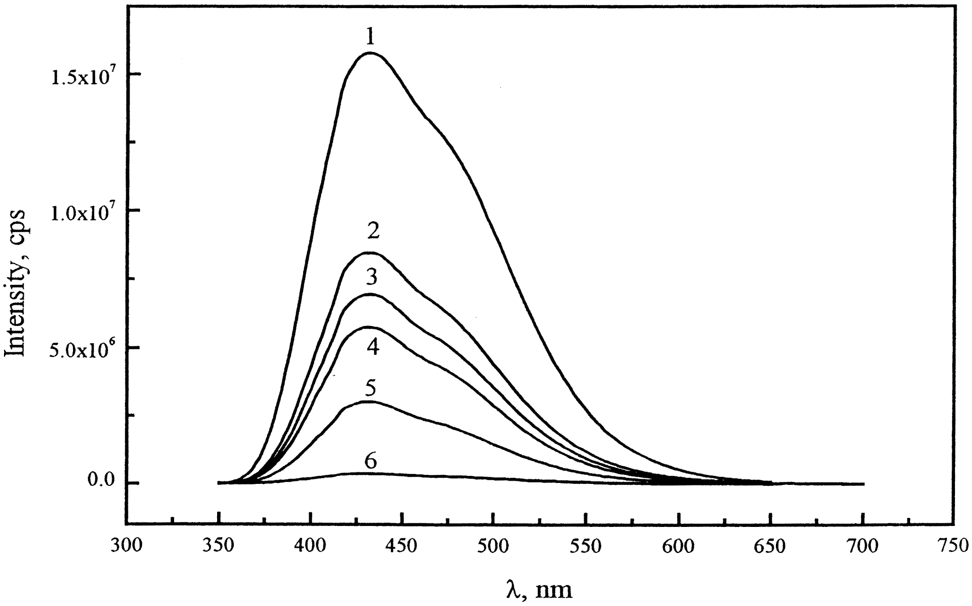

Figure 4. Effect of oxygen on the photoluminescence intensity of 2.5 wt% Mo/SiO_2 sample: (1) under vacuum; and at oxygen pressure of (2) 1.4×10^{-3}, (3) 8.4×10^{-3}, (4) 1.5×10^{-2}, (5) 6.1×10^{-2}, and (6) 1.22 torr.

illustrated by figure 5. Even after prolonged evacuation at room temperature, the photoluminescence intensity attains only 70–80% of its initial level. This indicates that some CO and NO molecules are more strongly adsorbed on the surface. The initial intensity can be fully restored, however, by heating the sample in oxygen and then under vacuum at 500 °C.

Plots of relative photoluminescence intensity I_0/I (I_0 is the initial intensity under vacuum) versus pressure of the quenching gas are shown in figure 6. Figure 7 demonstrates that the dependence of the relative intensity on oxygen pressure is very similar for the samples with different molybdenum loadings.

Two features are remarkable and worth noting. First, the strong quenching effect of NO, O_2, and CO should be emphasized: the photoluminescence intensity at higher pressures is smaller by nearly two orders of magnitude than the initial intensity under vacuum. Hence, virtually all emission sites of Mo/SiO_2 are quenchable by these gases. This is in contrast to what has been reported earlier [4,7] for impregnated Mo/SiO_2 catalysts: the quenching by oxygen and other gases was not complete

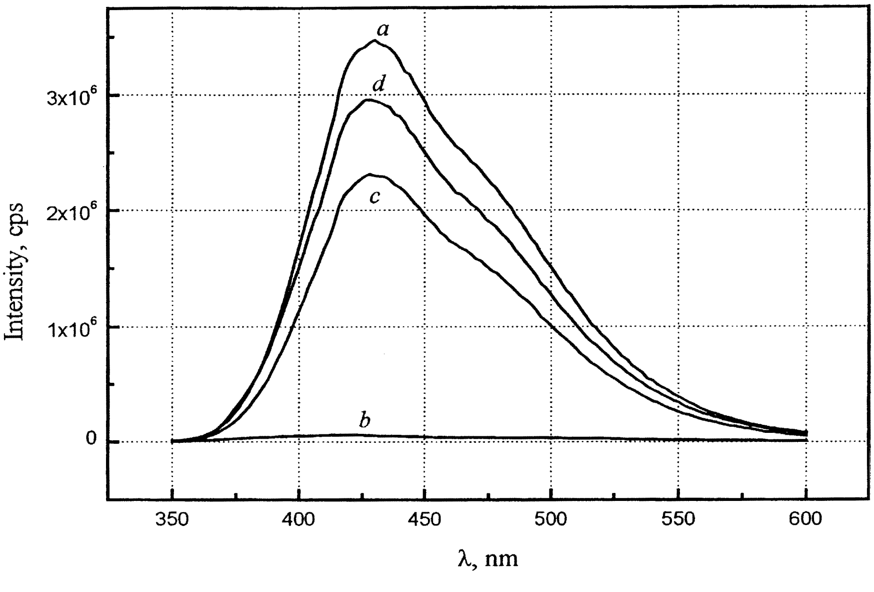

Figure 5. Photoluminescence emission spectra of 0.23 wt% Mo/SiO_2: (a) under vacuum; (b) after admission of CO (5 torr); after subsequent evacuation at 20 °C for (c) 12 and (d) 30 min.

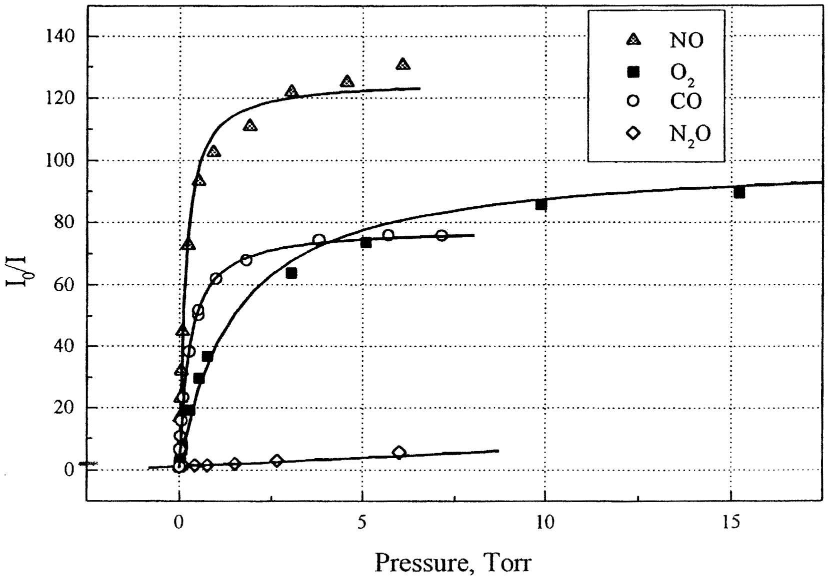

Figure 6. Relative photoluminescence intensity of Mo/SiO_2 vs. pressure of quenching gases. The experimental data are shown by symbols, the solid curves are the best fits to equation (1). Molybdenum content in the samples is 0.23 wt% (NO, O_2, CO) or 2.5 wt% (N_2O).

and about 20% of the phosphorescence remained unquenched in the presence of excess oxygen. Note that the quenching effect of N_2O is very weak. Perhaps the strong quenching effect of NO and O_2 is due to the paramagnetism of these molecules. CO and N_2O are diamagnetic, but CO is chemically active and readily interacts with the excited state $(\sim Mo^{5+}–O^-)^*$ to yield CO_2 (see below).

The second remarkable feature is the nonlinear character of the plots shown in figures 6 and 7 (except that for N_2O). Two principal mechanisms of photoluminescence quenching in the presence of quencher molecules in the gas phase are possible [7,8]: (1) dynamic collisional quenching by molecules from the gas phase; or (2) quenching via the formation of weak complexes between the excited light-emitting sites and adsorbed quencher molecules. In case (1), the Stern–Volmer equation, which predicts a linear dependence of the relative photoluminescence intensity I_0/I on the quenching gas pressure, should be operative. The nonlinear character of the plots in figures 6 and 7 prompted us to assume that only adsorbed molecules can quench efficiently enough the excited light-emitting surface states.

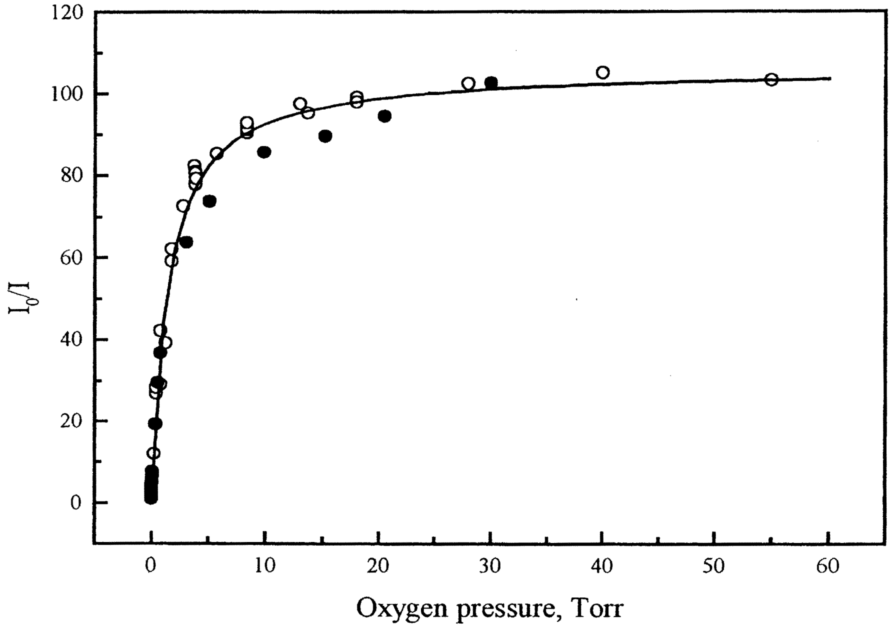

Figure 7. Effect of oxygen on the relative photoluminescence intensity I_0/I of 0.23 wt% (●) and 2.5 wt% (○) Mo/SiO_2. The solid curve is the best fit to equation (1).

4. Discussion

4.1. Quantitative analysis of the quenching mechanism of photoluminescence

The following processes can be proposed under UV irradiation of Mo/SiO_2 in the presence of a quencher:

$$\sim\mathrm{Mo}^{6+}{=}\mathrm{O}^{2-} + h\nu \xrightarrow{\alpha I_{\mathrm{UV}}} (\sim\mathrm{Mo}^{5+}\text{–}\mathrm{O}^{-})^{*} \qquad \text{(excitation)}$$

$$(\sim\mathrm{Mo}^{5+}\text{–}\mathrm{O}^{-})^{*} \xrightarrow{k_{\mathrm{Ph}}} \sim\mathrm{Mo}^{6+}{=}\mathrm{O}^{2-} + h\nu' \qquad \text{(photoluminescence)}$$

$$(\sim\mathrm{Mo}^{5+}\text{–}\mathrm{O}^{-})^{*} \xrightarrow{k_{\mathrm{T}}} \sim\mathrm{Mo}^{6+}{=}\mathrm{O}^{2-} + h\omega \qquad \text{(thermal radiationless decay)}$$

$$(\sim\mathrm{Mo}^{5+}\text{–}\mathrm{O}^{-})^{*} + \mathrm{Q}_{\mathrm{ads}} \xrightarrow{k_{\mathrm{Q}}} \sim\mathrm{Mo}^{6+}{=}\mathrm{O}^{2-} + \mathrm{Q}^{*} \qquad \text{(quenching)}$$

where $\sim Mo^{6+}{=}O^{2-}$ denotes a molybdenyl bond of the surface Mo^{6+} ion, I_{UV} is the intensity of the UV light, α is a proportionality coefficient, and $(\sim Mo^{5+}\text{–}O^{-})^{*}$ is a charge transfer excited triplet state; k_{Ph} and k_T are the rate constants for deactivation of $(\sim Mo^{5+}\text{–}O^{-})^{*}$ via emission of a photon ($h\nu'$) or phonon ($h\omega$), respectively, and k_Q is the quenching rate constant by adsorbed quencher molecule Q_{ads}.

The following equation for the photoluminescence intensity I emerges from the above reaction scheme under the assumption that $(\sim Mo^{5+}\text{–}O^{-})^{*}$ is at steady state, i.e., $d[\sim Mo^{5+}-O^{-}]^{*}/dt = 0$:

$$I_0 = k_{\mathrm{Ph}}[\sim\mathrm{Mo}^{5+}-\mathrm{O}]^{*}_{\mathrm{ss}} = \frac{\alpha I_{\mathrm{UV}}[\sim\mathrm{Mo}^{6+}{=}\mathrm{O}^{2-}]k_{\mathrm{Ph}}}{k_{\mathrm{D}} + k_{\mathrm{Q}}\Theta}$$

where $k_D = k_{Ph} + k_T$, Θ is the fraction of quenchable surface sites occupied by adsorbed molecules, and the subscript ss refers to the steady state.

The photoluminescence intensity under vacuum I_0 is expressed as

$$I_0 = \frac{\alpha I_{\mathrm{UV}}[\sim\mathrm{Mo}^{6+}{=}\mathrm{O}^{2-}]k_{\mathrm{Ph}}}{k_{\mathrm{D}}}$$

and the relative photoluminescence intensity is

$$\frac{I_0}{I} = 1 + \frac{k_{\mathrm{Q}}\Theta}{k_{\mathrm{D}}}.$$

The Θ value can be found from the classical equation for the Langmuir-type adsorption isotherm

$$\Theta = \frac{bP}{1 + bP}$$

where P is the pressure of a quenching gas.

Finally, we obtain the following equation for the relative photoluminescence intensity:

$$\frac{I_0}{I} = 1 + \frac{k_{\mathrm{Q}}bP}{k_{\mathrm{D}}(1 + bP)}. \qquad (1)$$

Table 1
Fitting parameters k_Q/k_D and b for equation (1) and absolute quenching rate constants

Quenching gas	k_Q/k_D	b (torr^{-1})	$k_Q \times 10^{-6}$ (s^{-1}) [a]	k_Qb/k_D (torr^{-1})
NO	126 ± 25 [b]	6.8 ± 0.9 [b]	1.9	857
O_2	102 ± 3 [c]	0.6 ± 0.05 [c]	1.5	61
CO	67 ± 10 [c]	4.2 ± 0.4 [c]	1.0	281
N_2O	–	–	–	0.74

[a] Calculated with $k_D = 1.5 \times 10^4\ s^{-1}$ [7].
[b] Average from fitting of three data sets.
[c] Average from fitting of two data sets.

The solid curves for O_2, CO, and NO shown in figures 6 and 7 were calculated by equation (1) using a computer best fit procedure while varying parameters k_Q/k_D and b (table 1). A good agreement between the experimental points and the calculated I_0/I values is evident from figures 6 and 7.

4.2. Relation of the photoluminescence data to the mechanism of photocatalytic NO reduction by CO

As follows from table 1, the k_Q/k_D ratio and consequently the quenching rate constant k_Q decrease in the order $NO > O_2 > CO$. The stronger quenching effect of NO as compared with that of CO is in agreement with our data on the kinetics of the photocatalytic reduction of NO by CO on Mo/SiO_2 [2,3]. The ratio $k_Q(NO)/k_Q(CO) = 2.8$ was derived by Lisachenko *et al.* [3] by comparing the rates of NO and CO consumption upon UV irradiation of Mo/SiO_2 in a CO–NO mixture and in pure CO. This value is in qualitative agreement with $k_Q(NO)/k_Q(CO) = 126 : 67 = 1.9$ from the photoluminescence data (table 1). The absolute k_Q values are also listed in the table. They were calculated from k_Q/k_D taking $k_D = 1.5 \times 10^4\ s^{-1}$ ($\tau = 68\ \mu s$ at 298 K) which was reported by Anpo *et al.* [7] for impregnated molybdenum oxide catalyst (0.1 wt% Mo).

In the low-pressure range, i.e., when $bP \ll 1$, equation (1) reduces to the well-known Stern–Volmer equation:

$$I_0/I = 1 + k_{\mathrm{Q}}bP/k_{\mathrm{D}}.$$

Hence, at low pressures the relative photoluminescence intensity becomes a linear function of a quenching gas pressure.

The quenching effect of gases at a given pressure is determined by the product k_Qb/k_D which decreases in the order $NO > CO > O_2 \gg N_2O$ (table 1). The quenching effect of N_2O is negligibly small as compared with that for the other gases studied. In the low-pressure range (at $P < 2$ torr), CO is a stronger quencher than oxygen. Similar results were also reported by Iwasawa and Ogasawara [4]: at room temperature the photoluminescence of silica–molybdena catalysts prepared by conventional impregnation method or by grafting

$Mo(\pi\text{-}C_3H_5)_4$ to OH groups of the silica surface was more strongly quenched by CO than by oxygen at the same pressure of the quenching gas.

It should be noted, however, that the quenching efficiency of O_2 and CO at room temperature markedly differs from that reported by Anpo *et al.* [7] for the photoluminescence of Mo/SiO_2 measured at 77 K. In the latter case, oxygen adsorbed on the surface was found to be an approximately 18 times more efficient quencher than CO. Most likely, the difference in the quenching efficiency at 77 and 300 K is due to different quenching mechanisms for NO and O_2 on the one hand, and that for CO on the other hand. The interaction of carbon monoxide with $(\sim Mo^{5+}\text{–}O^-)^*$ results in the reduction of molybdenum ions and yields reaction products [12] as follows:

$$(\sim Mo^{5+}\text{–}O^-)^* + CO \longrightarrow \sim Mo^{4+} + CO_2.$$

This process can be considered as "chemical" quenching. In contrast, no reaction products were found upon UV irradiation of Mo/SiO_2 in the presence of paramagnetic NO and O_2 molecules. In this case there is "physical" quenching. The "physical" quenching by O_2 is little affected by the temperature, whereas the "chemical" quenching by CO is strongly inhibited at low temperatures. The rate of the photoinduced reduction of Mo/SiO_2 by carbon monoxide at 77 K is negligibly small as compared with that at 300 K.

5. Conclusion

The relative intensities of photoluminescence of Mo^{6+}/SiO_2 photocatalysts were measured at room temperature under vacuum and in the presence of NO, O_2, CO, and N_2O in the pressure range ~0.001–50 torr. To the best of our knowledge, such a wide range is investigated for the first time. It is found that the quenching of photoluminescence intensity by these gases can be quantitatively well described in the entire pressure range studied in the framework of a simple kinetic scheme assuming that only adsorbed molecules can quench efficiently enough the light-emitting excited state of Mo/SiO_2. It is found that a Langmuir-type adsorption isotherm can be applied for calculating the fraction of adsorbed quencher molecules. An expression that correctly describes the relationship between photoluminescence intensity I_0/I and gas pressure in the entire region has been derived. At low pressures, this expression reduces to the Stern–Volmer equation which predicts a linear dependence of I_0/I on the pressure. The quenching efficiency of paramagnetic NO and O_2 molecules and reactive CO molecules was found to be high. It decreases in the order $NO > O_2 > CO$, whereas N_2O only weakly affects the photoluminescence intensity.

It should be also emphasized that this photoluminescence study has provided additional proofs of some substantial steps in the earlier proposed mechanism of the photocatalytic NO reduction by carbon monoxide on Mo/SiO_2 [1,2]. In particular, the correct description of the NO photoreduction kinetics was attained by Subbotina *et al.* [2] under the assumptions that, first, the deactivation rate constant k_D is much smaller than the quenching rate constant k_Q and, second, that the NO molecule can efficiently quench the $(\sim Mo^{5+}\text{–}O^-)^*$ excited state without chemical interaction ("physical" quenching) in contrast to "chemical" quenching by CO molecules to yield Mo^{4+} and CO_2. The photoluminescence data obtained demonstrate the correctness of these assumptions. Moreover, reasonably good quantitative agreement for the $k_Q(NO)/k_R(CO)$ ratio (within 20%) was obtained from the kinetic and photoluminescence studies.

Acknowledgment

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