Catalysis Letters Vol. 92, Nos. 3–4, February 2004 (© 2004)

Discrimination of MgO ions by means of an improved *in situ* photoluminescence cell and of propyne as probe molecule

Marie-Laurence Bailly[a], Guylène Costentin[b,*], Jean Marc Krafft[a], and Michel Che[a,b].

[a]*Laboratoire de Réactivité de Surface and Institut Universitaire de France, UMR 7609 - CNRS, Université Pierre et Marie Curie,*
4, place Jussieu, 75252 Paris Cédex 05, France
[b]*Institut Universitaire de France*

Received 5 August 2003; accepted 28 October 2003

Technical improvement of the photoluminescence cell and its coupling to a dynamic vacuum system allow to avoid quenching phenomena. These results in emission spectra of MgO, which are better-resolved and more stable in time, leading to a better characterization of the very reactive oxide ions, i.e., those in low coordination. Apart from a more precise assignment of the spectra, new developments are proposed to evaluate the relative distribution of ions of low coordination. Discrimination of the oxide ions with different coordination numbers is also possible by studying *in situ* their interaction with propyne as a probe molecule.

KEY WORDS: photoluminescence; oxide ions; basicity; coordination; alkaline earth; quenching; dynamic vacuum; *in situ* probe molecule; propyne.

1. Introduction

Photoluminescence is one of the very few techniques that is sensitive to the coordination of oxide ions [1–9]. In the case of alkaline earth oxides, the coordination number of the surface oxide ions greatly influences their electron-donor properties [10], and is expected to also influence their basic properties. Photoluminescence exhibits many practical advantages to study the surface of catalysts since it is a nondestructive and very sensitive technique that can be used for powders.

However, the bands are often quite broad due to the convolution of several contributions, making their assignment difficult. Some technical problems result in irreproducibility of the bands and have been reported by several authors. For example, Idriss *et al.* have underlined the importance of the position of the photoluminescence cell in the beam to obtain reproducible intensities [11]. Attention has also been paid to the conditions of pretreatment of the sample that can modify its morphology. Thus, Coluccia *et al.* considered that heating a MgO sample under static vacuum to 1273 K with a ramp of 1 $\mathrm{K\,min^{-1}}$ ensured reproducible results [10].

Moreover, one of the main and important characteristics of the photoluminescent process concerns possible energy transfer [12–14]. Thus, particular attention should be paid to check if the nature of the excited photoluminescent site is the same as that of the emitting one. Energy can also be transferred to a nearby gas-phase molecule and this results in the extinction of the emission of the original excited site or molecule—this is described as a quenching phenomenon. For example, O_2 is well known to participate in quenching signals of surfaces of several photoluminescent systems [14–18]. Thus, it becomes very important in the photoluminescence studies to drastically reduce the quenching phenomena.

The goal of this work has been to design a special photoluminescence cell in order to overcome quenching phenomena as much as possible and to obtain reproducible spectra. We then investigated *in situ* the reactivity of the surface oxide ions with propyne used as the probe molecule.

2. Experimental

2.1. Materials

The studied sample was a MgO sample of $200\mathrm{m^2g^{-1}}$, hereafter referred to as precipitation-MgO. Its precursor $Mg(OH)_2$ was precipitated from a $Mg(NO_3)_2$ solution by ammonium hydroxide [19] and transformed into precipitation-MgO by heating under vacuum at 1273 K for 1 h. The complete transformation into a periclase structure was checked by XRD.

The effect of the interaction of propyne with MgO surfaces on the photoluminescence signals was studied at room temperature. Propyne was previously purified by the freeze-pump-thaw technique. Successive doses of propyne were introduced at room temperature until the equilibrium pressure reached 1 torr (1torr = 133.32Pa). After 15 min of contact, the sample was outgassed at

---

[*] To whom correspondence should be addressed.
E-mail: costenti@ccr.jussieu.fr

1011-372X/04/0200–0101/0 © 2004 Plenum Publishing Corporation

room temperature. The sample was then progressively heated to 1273 K under vacuum and maintained at this temperature until a 10^{-6} torr pressure is reached.

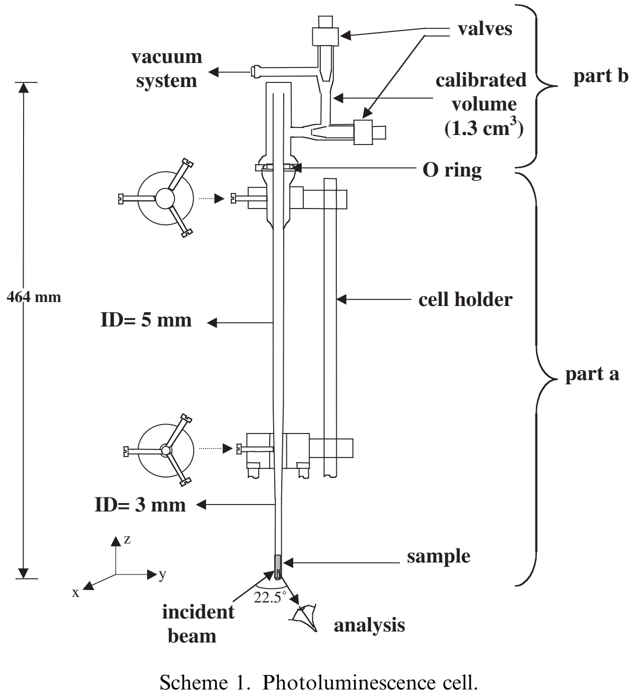
2.2. *Photoluminescence measurements*

The spectrofluorophotometer was a Spex Fluorolog II, from Jobin-Yvon, equipped with a 450-W Xe lamp as an excitation source with a resolution of 0.3 nm, and with color filters to eliminate scattered light. The excitation or emission wavelengths were selected using a double monochromator. Owing to the energy range of the source, only excitation wavelengths above 220 nm were available. The excitation and emission band passes were 5 and 1.9 nm respectively for all spectra reported here.

The photoluminescence spectra of the precipitation-MgO sample were recorded at room temperature. All the presented emission spectra were collected with an excitation wavelength of 230 or 270 nm.

2.3. *Photoluminescence cell*

The photoluminescence cell is represented in scheme 1. The bottom part, referred to as part (a), contains the sample (10 mm high), and is made of suprasil quartz tube (Heraeus product, QS quality) in order to avoid signals of impurities and fluorescence that are often present in conventional silica tubing. The incident beam and photoluminescence signal are in the *xy* horizontal plane, as shown in scheme 1. The vertical (*z*) and lateral (*x*,*y*) positions of the cell in the analysis chamber (not shown) are controlled by means of six screws in the upper and bottom parts of the cell holder, whose cross sections are shown in scheme 1. It makes the position of the cell easy to control and reproduce from one sample to the other.



Scheme 1. Photoluminescence cell.

In order to limit quenching phenomena as far as possible by gas-phase molecules, the following points have been considered:

- To improve the evacuation of gases and to avoid the turbulence of the powder sample upon pumping, the internal section of the photoluminescence cell has been increased continuously from 3 (bottom) to 5 mm (top) (scheme 1, part (a)).
- A tailor-made junction connecting the photoluminescence cell to the vacuum system (scheme 1, part (b)) allows *in situ* treatments under dynamic vacuum. This junction involves (i) quite a large lid whose function is to trap the powder that could have moved up upon pumping and, via pollution of the o-ring, lead to leaks and even to damage of the vacuum system itself, (ii) two valves to contact the cell to the vacuum system, (iii) a small calibrated volume (1.3 cm^3), defined once the two valves are closed and allows to introduce a controlled amount of gas in the cell, and finally, (iv) a link to the vacuum system. Consequently, thermal pretreatment and adsorption–desorption experiments as well as spectra recording can be performed *in situ* and under dynamic vacuum conditions (final pressure of 10^{-6} torr with a turbomolecular pump).

3. Results

The effect of dynamic vacuum conditions on the intensity and the shape of the bands are investigated, and the collected data are compared with a typical spectrum, reported by Coluccia *et al.* for MgO powder [14], which is representative of results published in the literature for this oxide.

3.1. *Improved stability of photoluminescence spectra versus time*

Two series of photoluminescence spectra, shown in figure 1, corresponding to dynamic (series (a)) and static vacuum (series (b)), are monitored for an excitation at 230 nm on the precipitation-MgO sample, as a function of time. In dynamic vacuum conditions, the cell is constantly connected to the pump, whereas in static vacuum conditions, the cell is isolated from the pumping system before recording spectra. The first spectrum of each series (spectra (a) and (b), at t = 10 min) are quite comparable in shape, but spectrum (a) recorded under dynamic vacuum is more intense than spectrum (b) recorded under static vacuum. Moreover, the subsequent spectra of series (b) recorded under static conditions drastically decrease in

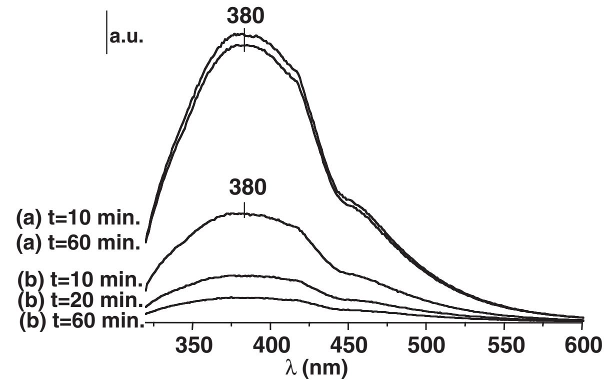


Figure 1. Emission spectra monitored at 230 nm of precipitation-MgO sample as a function of time. Spectra collected (a) under dynamic vacuum, (b) under static vacuum.

intensity with time, with a quite complete loss of the signal after 60 min. At this step, the initial pressure of 10^{-6} torr had increased to 5×10^{-3} torr, showing that the decrease in intensity was related to the quenching phenomena by gas-phase molecules. Indeed, photoluminescence signal is very sensitive to oxygen traces [14–18]. By contrast, the spectra of series (a), recorded under dynamic vacuum, indicate the stability of the spectra both in shape and intensity after 60 min; the final pressure at this step is still 10^{-6} torr. This shows the extreme sensitivity of photoluminescence spectra to experimental conditions.

3.2. Improved resolution of photoluminescence spectra

Figures 2 (a) and (b) show the emission spectra of MgO samples monitored at 270 nm reported by Coluccia *et al.* [14] and by us (dynamic vacuum) respectively. The shape of the two emission spectra are different: spectrum (a) exhibits a broad band with a maximum emission at around 390 nm, whereas two maxima are detected in spectrum (b), at 395 and 460 nm. In fact, the latter contribution is ill defined in spectrum (a). This comparison indicates that recording the spectrum under dynamic vacuum results in better resolution of the spectra. From the excitation spectra (also shown in figure 2(b)) monitored at these two maxima of emission, it can be deduced that these emissions are associated with excitations at 230 and 270 nm respectively, which can be assigned to oxide ions $O^{2-}{}_{4C}$ (four-coordinated, 4C, oxide ions at edges) and $O^{2-}{}_{3C}$ (three-coordinated, 3C, oxide ions at corners) respectively, from the literature [6,9,20].

3.3. Effect of propyne, used as a probe molecule, on the photoluminescence spectrum

The effect of propyne used as a probe molecule on the photoluminescence spectra is shown in figure 3. Starting from a clean surface, i.e., sample outgassed at 1273 K, the introduction of increments of propyne and subsequent evacuation at room temperature leads to a progressive decrease of the signal intensity (figure 3(a)). After saturation of the sample for 15 min with an equilibrium pressure of 1 torr of propyne followed by evacuation at room temperature, a drastic decrease of the signal intensity is observed. Moreover, the shape of the signal is also modified, with a shift of the maximum of the emission band toward high energy (380 to 355 nm). The evacuation at increasing temperature results in a progressive recovering of the signal (figure 3(b)). Apart from the progressive increase of the intensity, the maximum of the emission signals shifts from 323 K nm and the contribution at 460 nm relative to $O^{2-}{}_{3C}$ is recovered from 423 K.

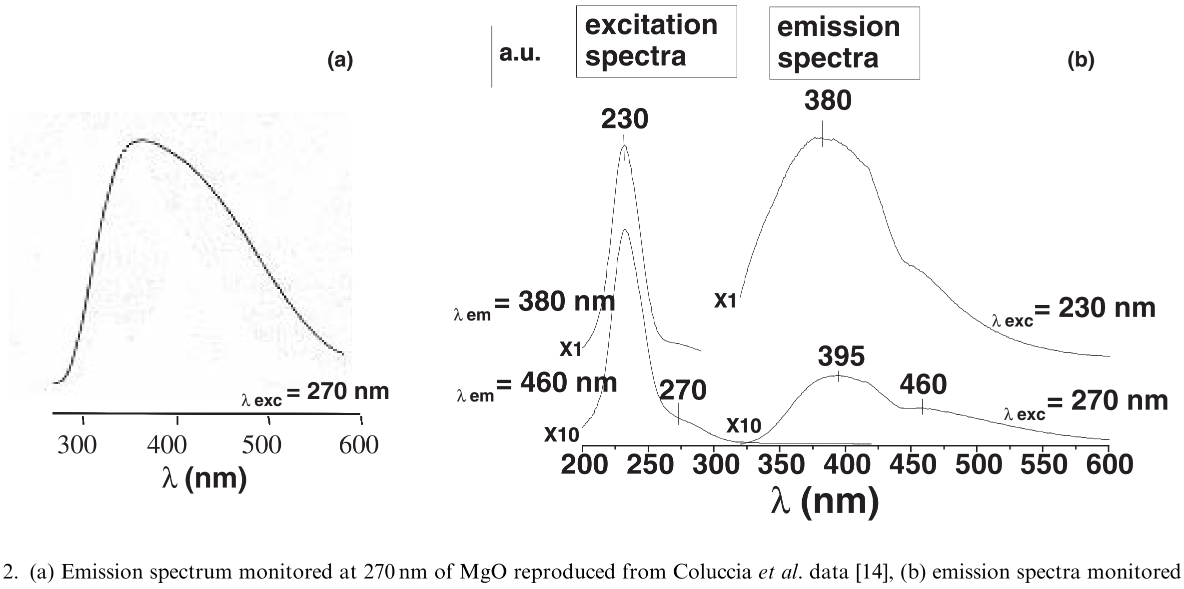


Figure 2. (a) Emission spectrum monitored at 270 nm of MgO reproduced from Coluccia *et al.* data [14], (b) emission spectra monitored at 230 and 270 nm of the precipitation-MgO sample and corresponding excitation spectra collected under dynamic vacuum.

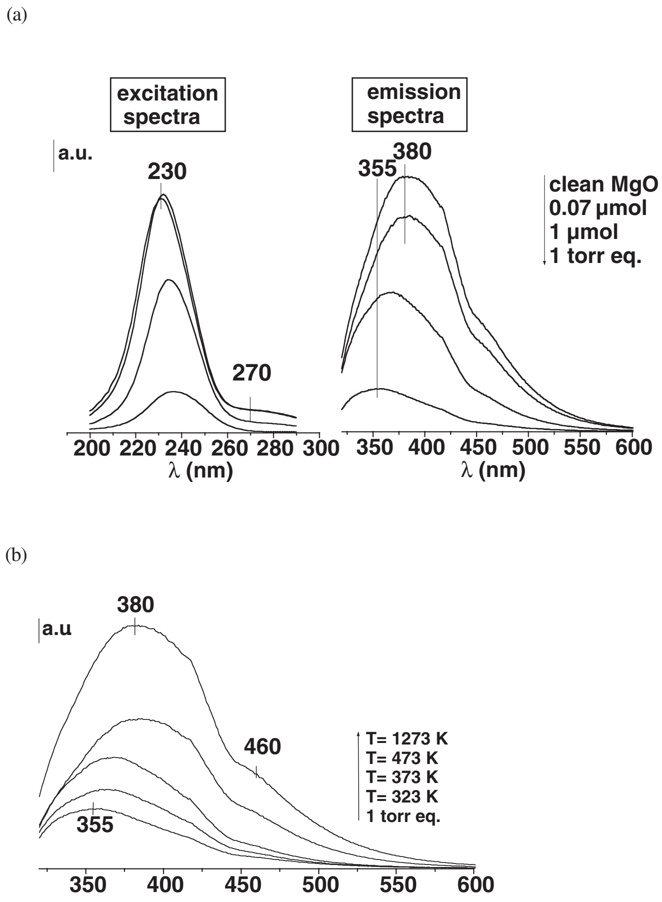


Figure 3. Emission spectra monitored at 230 nm of precipitation-MgO sample (a) before and after introduction of increments of propyne and corresponding excitation spectra, (b) after adsorption of one Torr and equilibrium of propyne and subsequent evacuation at increasing temperature.

4. Discussion

The improved operating conditions result in a better resolution as well as in a much improved stability of the spectrum versus time, making possible the comparison of intensities of bands of different spectra.

4.1. Assignments of the photoluminescence spectra

Previous literature results were mainly based on the photoluminescence response of the spectra monitored at excitation values determined from UV–vis absorption [6,20]. $O^{2-}{}_{4C}$ and $O^{2-}{}_{3C}$ ions were proposed to be excited at 230 and 270 nm respectively. Owing to the broadness of the emission spectra, discrimination of the emission energies was a difficult problem. From the improved resolution conditions, it is shown that $O^{2-}{}_{4C}$ and $O^{2-}{}_{3C}$ ions are excited at 230 and 270 nm respectively and emit at 380 and 460 nm respectively. From the variation of the Madelung potential with the coordination number of O^{2-} ions [20], the $O^{2-}{}_{5C}$ contribution is expected to occur at higher energy (around 350 nm), now confirmed by the shoulder around 350 nm on the emission spectrum monitored at 230 nm (figure 2(b)). Theoretical calculations by Shluger *et al.* [9] are consistent with these data.

4.2. *Pseudo quantitative analysis of the concentrations of $O^{2-}{}_{LC}$ ions (LC = low coordination)*

Until now, the evaluation of the concentrations of $O^{2-}{}_{4C}$ and $O^{2-}{}_{3C}$ was deduced from comparison of the relative intensity of the 390-nm band on two emission spectra monitored at 230 and 270 nm respectively. Apart from the expected modification of intensity versus time in static vacuum conditions, the photoluminescent yield of $O^{2-}{}_{3C}$ was overestimated, because the emission energy considered (390 nm) was not the same as that of the emitting $O^{2-}{}_{3C}$ (460 nm). Thus, owing to the improved stability of the signal intensity versus time, we can now propose a pseudo-quantitative procedure to evaluate the contributions of several species at maximum photoluminescent yield for each of them. The evaluation should be based on excitation rather than emission spectra, due to their better resolution [2]. From the excitation spectra monitored at 380 and 460 nm respectively, the deconvolution of the contributions at 230 and 270 nm on both spectra can be performed. The ratio of the areas of the resulting peaks excited at 270 and 230 nm, monitored at 460 nm and 380 nm respectively, represents the relative concentrations of $O^{2-}{}_{3C}$ to $O^{2-}{}_{4C}$ ions. In the case of the precipitation-MgO sample, the $O^{2-}{}_{3C}/O^{2-}{}_{4C}$ ratio has been found to be 0.06.

This pseudoquantitative approach allows following the evolution of this ratio as a function of the pretreatment temperature of the sample. Moreover, the effect of MgO-preparation methods on the distribution of oxide ions in low coordination can be evaluated by this procedure, complementary to TEM and BET characterizations [21], and the results obtained are consistent with catalysis data for MgO samples prepared with different methods [22].

4.3. *Discrimination of surface oxide ions using propyne, as probe molecule*

Having improved the stability of the bands as a function of time, we have investigated, by *in situ* photoluminescence, the reactivity of O^{2-} surface ions.

In fact, the energy transfer resulting in quenching of the spectrum proceeds via two mechanisms: (i) dynamic quenching by collision with gas-phase molecules or weak interaction with adsorbed species and (ii) quenching via the formation of complexes adsorbed on the emitting site [2,17,23–25]. Recently, Shelimov *et al.* have determined the fraction of adsorbed molecules on the basis of Langmuir-type adsorption isotherm, and, from complementary kinetic data of the photocatalytic reduction of NO by CO on Mo/SiO_2, have proposed specific interaction of both gases with different surface sites [25].

In the case of interaction of the surface with a single gas, a simple evacuation of the gas phase at room temperature before recording the spectra avoids both the quenching from collision with gas phase molecules and that related to weakly adsorbed species. The higher intensity of the spectra collected under dynamic vacuum (figures 2(c), 3) underlines how sensitive the spectrum intensity is to these collisions and weak interactions with the surface. More precisely, the fact that the 460-nm contribution is particularly affected by quenching and is consistent with the expected higher reactivity of $O^{2-}{}_{3C}$ to air contaminants such as CO_2 or water. High vacuum (10^{-6} torr)maintained stable by dynamic conditions is required to probe and quantify such ions of low coordination on the MgO surface.

Thus, the modifications in intensity and/or shape of the spectra reported on figure 3(a) versus increasing amounts of propyne, unambiguously result from the interaction of the MgO surface with chemisorbed species, considering that the physisorbed species are removed by evacuation at room temperature. If the whole spectrum decreases in intensity, the observed shift toward high energy indicates that the three oxide ($O^{2-}{}_{3C}$, $O^{2-}{}_{4C}$ and $O^{2-}{}_{5C}$) contributions described earlier are not affected in the same way. In fact, the decrease in intensity of the emission at 460 and 380 nm as well as that of their respective contributions at 270 and 230 nm in the corresponding excitation spectra indicates that propyne is adsorbed on $O^{2-}{}_{3C}$ and $O^{2-}{}_{4C}$. By contrast, the shift of the maximum of the emission band from 380 to 355 nm shows that the $O^{2-}{}_{5C}$ ions do not interact with propyne, which thus appears to be a selective probe of $O^{2-}{}_{3C}$ and $O^{2-}{}_{4C}$ ions. The exact nature of the adsorbate (molecular or dissociative form) will be discussed in a forthcoming paper, in correlation with FTIR characterization [26–29]. This phenomenon is reversible since the signal is totally recovered by heating under vacuum to 1273 K (figure 3(b)). From the shift of the maximum of the emission from 355 to 380 nm, it can be observed that the $O^{2-}{}_{4C}$ ions begin to be recovered from 323 K, whereas the contributions at 460 nm, related to $O^{2-}{}_{3C}$ ions, are recovered at 423 K: the lower the coordinence of the oxide ions, the stronger is its interaction with propyne.

5. Conclusion

Photoluminescence is a useful technique to characterize the surface of powder samples, which is sensitive to the coordination number of oxide ions. To limit quenching phenomena of photoluminescence by gas-phase molecules, experiments have been carried out under dynamic vacuum using a special cell; this results in a better resolution of the emission spectra and in an optimization of the photoluminescent yield of the more reactive surface species, namely oxide ions of low coordination.

Moreover, *in situ* adsorption of propyne on MgO followed by evacuation at room temperature of the gas in excess and physisorbed species shows that this probe molecule can discriminate the oxide ions of low coordination. Indeed, this molecule selectively adsorbs on $O^{2-}{}_{3C}$ and $O^{2-}{}_{4C}$ ions, whereas it does not interact with $O^{2-}{}_{5C}$ ions. It is expected that the deprotonation ability of various oxide surfaces toward protonated probe molecules, and thus their basic properties, can be followed in relation to the distribution of surface-oxide ions of low coordination.

References

[1] M. Che and A.J. Tench, Adv. Catal. 31 (1982) 77.
[2] M. Anpo and M. Che, Adv. Catal. 44 (1999) 119.
[3] Y. Kubokawa and M. Anpo, in *Adsorption and Catalysis on Oxide Surfaces*, M. Che and G.C. Bond (eds), (Elsevier, Amsterdam, 1985) p. 127.
[4] A.J. Tench and R.L. Nelson, Trans. Faraday Soc. 63 (1967) 2254.
[5] M. Anpo, M. Sunamoto and M. Che, J. Phys. Chem. 93 (1989) 1187.
[6] S. Coluccia, A.J. Tench and R.L. Segall, J. Chem. Soc., Faraday Trans. I 75 (1979) 1769.
[7] M. Anpo, M. Sunamoto, T. Doi and I. Matsuura, Chem. Lett. 4 (1998) 7014.
[8] W.W. Duley, Phil. Mag. B49 (1984) 159.
[9] A.L. Shluger, P.V. Sushko and L.N. Kantorovich, Phys. Rev. B59 (1999) 2417.
[10] S. Coluccia, A. Barton and A.J. Tench, J. Chem. Soc., Faraday Trans. I 77 (1981) 2203.
[11] H. Idriss and M.A. Barteau, J. Phys. Chem. 96 (1992) 3382.
[12] N.J. Turro, *Molecular Photochemistry* (Benjamin, New York, 1967).
[13] N.J. Turro, *Modern Molecular Photochemistry* (Benjamin/Cummings, Menlo Park, CA, 1978).
[14] S. Coluccia, A.M. Deane and A.J. Tench, J. Chem. Soc. Faraday Trans. I 74 (1978) 2913.
[15] M. Anpo and Y. Kubokawa, J. Phys. Chem. 88 (1984) 5556.
[16] M. Anpo, M. Kondo, S. Coluccia, C. Louis and M. Che, J. Am. Chem. Soc. 111 (1989) 8791.
[17] M. Anpo, Y. Yamada, Y. Kubokawa, S. Coluccia, A. Zecchina and M. Che, J. Chem. Soc., Faraday Trans. I 84 (1988) 751.
[18] A. Zecchina and F.S. Stone, J. Chem. Soc. Faraday Trans. I 72 (1976) 2364.
[19] V.R. Choudhary and M.Y. Pandit, Appl. Catal. 71 (1991) 265.
[20] E. Garrone, A. Zecchina and F.S. Stone, Phil. Mag. B42 (1980) 683.
[21] M.L. Bailly, G. Costentin, H. Lauron-Pernot, J.M. Krafft and M. Che, in preparation
[22] M.L. Bailly, G. Costentin, H. Lauron-Pernot, J.M. Krafft and M. Che, in preparation
[23] M. Anpo, I. Tanahashi and Y. Kubokawa, J. Phys. Chem. 84 (1980) 3440.
[24] M. Anpo, I. Tanahashi and Y. Kubokawa, J. Phys. Chem. 86 (1986) 1.
[25] B. Shelimov, V. Dellarocca, G. Martra, S. Coluccia and M. Che, Catal. Lett. 87 (2003) 73.
[26] M.L. Bailly, G. Costentin, H. Lauron-Pernot, J.M. Krafft, P. Bazin, J. Saussey and M. Che, in preparation
[27] H. Knözinger and S. Huber, J. Chem. Soc., Faraday Trans. I 94 (1998) 2047.
[28] J.C. Lavalley, Catal. Today 27 (1996) 377.
[29] C. Binet, A. Jadi, J. Lamotte and J.C. Lavalley, J. Chem. Soc., Faraday Trans. I 92 (1996) 123.