

Analysis of Solid Catalysts Surfaces Using Laser-Induced Luminescence Diagnosis

C. Lalo,^{1,2} J. Deson,¹ A. Gédéon,¹ and J. Fraissard¹

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Two applications of laser-induced luminescence spectroscopy for characterizing species at low concentrations in Y zeolites are reported. In reduced copper-exchanged NaY zeolites, time-resolved laser-induced phosphorescence of Cu⁺ ions allows the determination of the density of different Cu⁺ sites, while in acidic Y zeolites, adsorption sites of an aromatic base, quinoline, are identified by laser-induced fluorescence.

KEY WORDS: Solid catalyst surfaces; laser-induced luminescence; Y zeolites; copper ions; acid sites; quinoline.

INTRODUCTION

Y zeolites are organized media and possess a homogeneous internal structure with a well-defined sequence of cages. Their three-dimensional framework consists of TO₄ (T = Si, Al) tetrahedra linked by shared oxygen atoms. The anionic nature of the framework is generally caused by the substitution of Al for Si within the TO₄ tetrahedra and is locally neutralized by the presence of exchangeable cations within the interstices of the structure. Cavities of three types are known to exist in Y zeolites, the largest being the supercages, with an internal diameter of 1.3 nm.

The efficiency of Cu-loaded Y zeolites for the decomposition of nitrogen oxides depends on the coordination and the density of Cu⁺ ions, while the efficiency of HY zeolites as heavy oil cracking catalysts depends on the acidic surface sites which are accessible to the hydrocarbon molecules and located in the supercages.

Analysis of Y zeolite surfaces using laser-induced luminescence diagnosis allows the characterization of

species at a low density level. From the linear dependence of the intensity of the luminescence upon the concentration of the species, relative densities in the sample can be measured. Moreover, time-resolved spectroscopy allows the characterization of independent emitting centres.

In pretreated samples of Cu-exchanged Y zeolites,⁽¹⁾ laser-induced phosphorescence of Cu⁺ ions allows the detection of *in situ* Cu⁺ sites, while in acidic Y zeolites, laser-induced fluorescence spectroscopy of an aromatic base, quinoline, is used for recognition of adsorption sites.⁽²⁾

EXPERIMENTAL

Sample Preparation and Characteristics

Cu-Exchanged Y Zeolites

The initial NaY zeolite used was LZY-52 from UOP (Si/Al = 2.4). The chemical composition of the copper-exchanged zeolites corresponds to a Cu²⁺-for-Na⁺ exchange level (λ) of 35 or 58%. The prepared samples were introduced directly in a quartz optical cell and

¹ Laboratoire de Chimie des Surfaces UPMC-CNRS, URA 1428, 4 place Jussieu, 75252 Paris Cedex 05, France.

² To whom correspondence should be addressed. e-mail: lalo@ccr.jussieu.fr. Fax: 33-01 44 27 55 36.

evacuated at ambient temperature for 5 h (10^{-4} Pa). The zeolites were then heated slowly to the desired temperature T_d (623 K), held at this temperature for time t (12 or 34 h), and then brought slowly back to 298 K. The dehydrated samples (D) are denoted $\text{Cu}\lambda\text{Y-Td}(D/t)$. Some of them were reduced in hydrogen (10^3 Pa) for 30 min or 1 h at constant temperature ($T_r = 623$ or 723 K). The reduced samples (R) are denoted $\text{Cu}\lambda\text{Y-T}_r(R/t)$.

Acidic Y Zeolites

Three types of Y zeolites have been studied, NaY, HY, and dealuminated HY. NaY zeolite (LZY52) was supplied by Union Carbide Co. HY zeolite was UOP NH_4Y zeolite, denoted Y64. D-HY zeolite was prepared⁽³⁾ from NH_4Y . It was partially dealuminated by steaming and subsequently washed twice with $\text{Na}_2\text{H}_2\text{EDTA}$; its crystallinity is near 90%.

In these samples, adsorption sites are silanol groups SiOH (NaY), Brønsted acidic bridging SiO(H)Al groups (HY), and in the last, both Brønsted sites and electron-acceptor Lewis centers, which may be coordinatively unsaturated aluminium ions.

The three samples were activated under "shallow bed conditions": a powder layer less than 5 mm thick and dehydration under dynamic vacuum before and during heating for 14 h at $12 \text{ K}\cdot\text{h}^{-1}$ to 725 K at less than 10^{-2} Pa. Quinoline vapor was adsorbed at 300 K. The amount of quinoline in each sample was determined by volumetry and gravimetry. The samples prepared contain 0.1 and 1 mg of quinoline per g of zeolite.

Experimental Technique

In a quartz optical cell under vacuum (10^{-4} Pa) zeolites samples were photoexcited at 240 nm using a frequency-doubled dye laser, and the fluorescence was recorded from 300 to 650 nm. The apparatus was described previously.⁽¹⁾ The laser emitted 0.3 mJ at 240 nm, the pulse width being about 30 ns. The size of the beam was adjusted by a dispersing lens and a diaphragm so as to obtain maximum coverage of the sample.

Luminescence was detected perpendicularly to the laser beam through a quartz collecting lens by a photomultiplier (Hamamatsu R212UH) at the exit slit of a monochromator and stored in a gated integrator. The noise of the signal is due to the high sensitivity of the system and to the irregularities of the energy of each laser pulse. The signal decay at selected wavelengths was recorded with a digital storage oscilloscope (Tektronics 2432) and transferred to a microcomputer (PC compatible), the limit of the detection system being 1

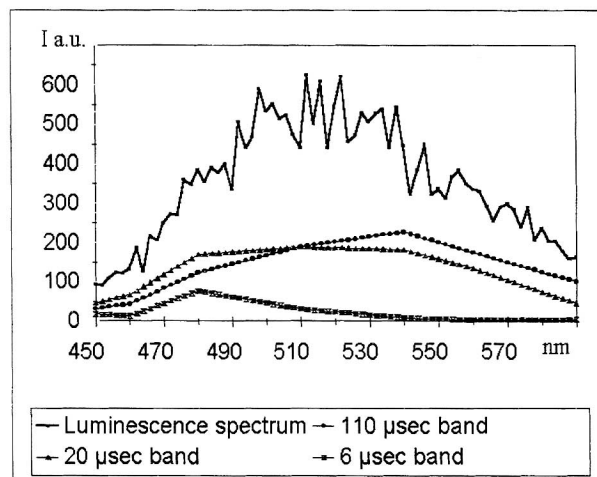


Fig. 1. Decomposition of the laser-induced luminescence spectrum for samples reduced in hydrogen $\text{Cu}35\text{Y-723}(R/30 \text{ min})$.

μs . Computer processing of the measurements consisted of a deconvolution of the multiexponential signal decay.

RESULTS

Laser-Induced Phosphorescence of Cu^+ Ions in Reduced Copper-Exchanged Y Zeolites

The absorption of UV light by Cu^+ ions occurs as a singlet-singlet transition, $3d^{10} \rightarrow 3d^94s$; energy is then transferred nonradiatively to the lowest-lying triplet state and phosphorescence is observed.^(4,5)

The laser-induced photoluminescence spectrum of vacuum dehydrated samples or samples reduced in hydrogen shows a broad-band emission from 450 to 600 nm, peaking at 490 nm (Fig. 1). By following the luminescence at selected wavelengths, a triexponential decay was observed showing the contributions of three components with lifetimes of 6 ± 2 , 20 ± 5 , and $110 \pm 10 \mu\text{s}$, and the luminescence spectra can be decomposed into several bands specific for each component. From the linear dependence of the intensity of each luminescence band upon the concentration of the species in the sample, different trends for the variation of the concentration with the sample pretreatment are found: the influence of the sample Cu content, the reduction time, and the temperature have been studied. Two of the emitting centers, with lifetimes of 20 and 110 μs , correspond to Cu^+ ions with different locations in the superlattice as has been shown⁽⁶⁾ by $^{129}\text{Xe-NMR}$. The effect

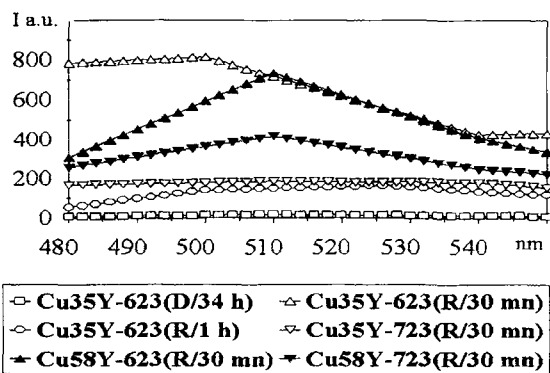


Fig. 2. Effect of pretreatment on the laser-induced luminescence spectra of the 20- μ s component.

of the pretreatment on one of these two components is shown in Fig. 2.

It appears that significant concentrations of Cu^+ sites can be detected in samples heated at a high temperature under vacuum for a long time, showing that the Cu^{2+} ion is, to some extent, autoreduced to cuprous ion during dehydration and that prolonged reduction in hydrogen diminishes the concentration of Cu^+ ions which can undergo further reduction to Cu^0 .

Laser-Induced Fluorescence of Quinoline Adsorbed on Acidic Y Zeolites

Quinoline is well-known to exhibit only phosphorescence in nonpolar media.^(7,8) In polar media, the fluorescence is attributed to an inversion of the relative disposition of energy levels of n, π^* and π, π^* character. Moreover, this N-heterocyclic base offers interesting luminescence spectra when it interacts with an acid: fluorescence spectra of quinolinium ion and of charge-transfer complexes have been observed.⁽⁸⁻¹¹⁾

Under photoexcitation at 240 nm, laser-induced luminescence spectra of quinoline adsorbed on the three samples reveal interactions between the adsorbate and the surface sites. Unstructured broad bands with lifetimes of less than 1 μ s are observed. This short lifetime indicates that it is fluorescence. Emitting centers were identified from the emission origin and maxima of the bands.

On NaY, a broad band peaking at 380 nm with an emission origin near 320 nm is characteristic of the formation of a hydrogen-bonded quinoline complex between quinoline and nonacid silanol groups [Fig. 3 (1)]. However, the spectrum is more extended near 450 nm than the fluorescence of this complex observed in solvents.⁽⁹⁾

On HY samples, the luminescence is the most intense. The less loaded specimens exhibit two bands,

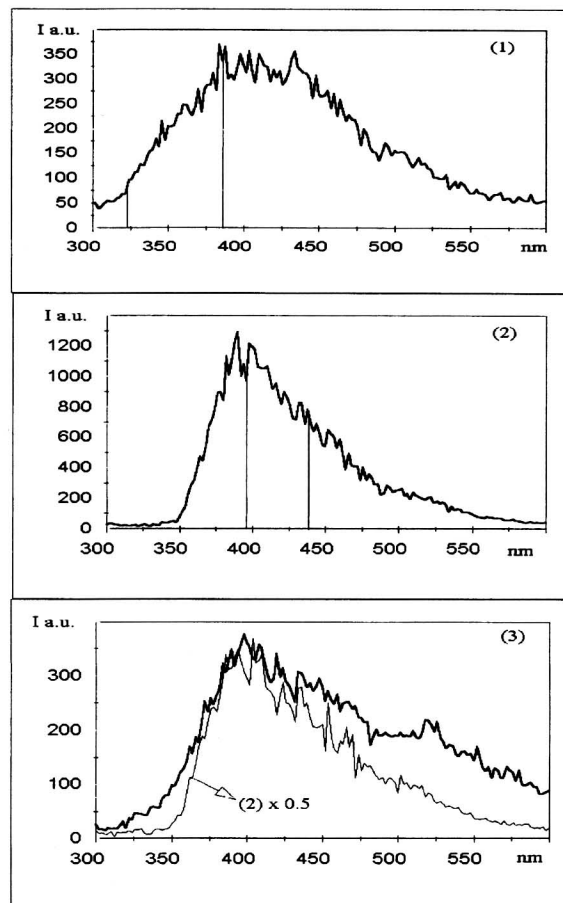


Fig. 3. Laser-induced fluorescence spectrum of quinoline adsorbed (1) on NaY (0.1 mg quinoline/g adsorbent), (2) on HY (1 mg/g), and (3) on dealuminated D-HY (0.1 mg/g).

peaking at 400 and 450 nm. The band peaking at 400 nm with an emission origin at 360 nm, which becomes the more intense for more loaded samples, corresponds to the spectrum of the protonated form of quinoline: the protonation of quinoline on Brønsted sites is characterized by the fluorescence of quinolinium ion [Fig. 3 (2)].

Some intrinsic structural defects such as oxygen vacancies are also electron-acceptor centers. Tentatively we attribute the band peaking near 450 nm to the fluorescence of quinoline adsorbed on these sites. Since aromatic compounds tends to absorb first at electron-acceptor sites until they are saturated and then interact with surface hydroxyl groups,⁽¹²⁾ in future work, attempts will be made to determine the concentration of Brønsted sites in HY specimens from the variation of the relative intensity of the two bands at 400 and 450 nm with the concentration of quinoline.

On dealuminated-HY zeolite, the luminescence is significantly more extended toward longer wavelengths [Fig. 3 (3)]: the complexation with electron-acceptor Lewis sites is characterized by the fluorescence of a charge-transfer complex which is strongly red-shifted compared to the cation. An attempt was made to observe saturation of these sites by increasing the concentration of adsorbate. However, D-HY samples consist in part of an amorphous phase, and surface irregularities such as dislocations are also polarizing sites for the electronic system of adsorbates and lead to the fluorescence of aggregates, which can apparently mask that of compounds distributed within cavities.

Consequently, it appears that quantitative determination of the concentration of acidic sites in the cavities should be possible only for highly crystalline HY zeolites, assuming that the fluorescent probe is uniformly distributed within zeolites.

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