



## Effects of the zeolite particle size on the charge separated states



M. Hureau<sup>a,\*</sup>, A. Moissette<sup>a</sup>, L. Tzanis<sup>b</sup>, T.J. Daou<sup>b,\*\*</sup>

<sup>a</sup> Université de Lille, LASIR, UMR 8516 CNRS, Sciences et Technologies, Bâtiment C5, 59655 Villeneuve d'Ascq Cedex, France

<sup>b</sup> Université de Strasbourg, Université de Haute Alsace, Axe Matériaux à Porosité Contrôlée (MPC), Institut de Science des Matériaux de Mulhouse (IS2M), UMR CNRS 7361, ENSCMu, 3 Bis Rue Alfred Werner, 68093 Mulhouse Cedex, France

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### ABSTRACT

Electron transfers occurring after sorption and photoexcitation of *p*-terphenyl molecules in the porous void of two MFI type zeolites were investigated. The influence of the morphology and particle size, i.e.; nanosheets and conventional coffin-shaped micron sized crystals (big crystals) on these phenomena were emphasized. The irradiation of PTP occluded in big crystals induces the formation of a radical cation which evolves to an electron-hole pair through the capture of another electron of zeolite. In contrast, if photoexcitation of PTP incorporated in nanosheets induces also radical cation, it is interesting to note that the electron-hole pair formation is not favored in such environment. The absence of charge compartmentalization within nanosheets is put forward to explain the inhibition of electron transfer to create the charge transfer complex. Indeed, the small thickness of nanosheets prevents electron hopping over long distance after ionization and consequently, as the electron is trapped nearby the radical cation, direct recombination is favored.

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### 1. Introduction

The ability of porous materials such as zeolites to stabilize charge separated states for long periods after guest molecule ionization is now well established and is an intrinsic property of the inner surface of the pore space [1–9]. Besides the type of the molecule, the effect of some parameters (Al content in the framework, pore dimension, charge balancing cation, ...) has been clearly highlighted on the ionization efficiency and on the slowing down of the process of recombination after charge separation [10–14]. These phenomena can be influenced by reducing the zeolite particle size or by creating hierarchical zeolites (generation of mesoporosity) due to shorter diffusion path length (DPL).

Many approaches have been reported to promote the diffusion properties of zeolite, by introducing mesopores into zeolites by using post-synthetic demetallation of zeolite framework, hard-templating strategy (zeolite crystallization within confined space), soft-templating strategy (mesopore generation via supra-molecular self-assembly) and the creation of nanosheet or nano-sponge zeolitic materials using bifunctional surfactants including a

directing agent function for the formation of zeolite, linked by an alkyl spacer, and an hydrophobic alkyl chain inhibiting a further growth of the material [15–44].

Conventional synthesis of MFI-type zeolites generally leads to the formation of crystals whose size are of the order of several microns and which is characterized by a porous network formed by the interconnection of straight quasi circular channels (5.4 Å × 5.6 Å) with sinusoidal elliptical channels (5.1 Å × 5.4 Å). This structure is of particular interest for several environmental applications such as the removal and/or remediation of anions in water and VOCs in air [45–51]. ZSM-5 and Silicalite-1 are two zeolites with MFI structure that differ on the silicon to aluminum molar ratio of the microporous framework. The latter is a pure silica form whereas zeolite ZSM-5 is an aluminosilicate with Si/Al molar ratios that can vary between 10 and 500. In ZSM-5 zeolite the electroneutrality of the framework is counterbalanced by the presence of extra-framework cations, which constitute specific adsorption sites.

Herein, we report the influence of the morphology and particle size, i.e.; nanosheets and conventional coffin-shaped big crystals, on the electron transfers occurring in the porous void of Na<sup>+</sup>-containing MFI-type zeolites after photoexcitation of *p*-terphenyl molecule adsorbed in their porosity.

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [matthieu.hureau@univ-lille1.fr](mailto:matthieu.hureau@univ-lille1.fr) (M. Hureau), [jean.daou@uha.fr](mailto:jean.daou@uha.fr) (T.J. Daou).

## 2. Experimental

### 2.1. Synthesis of MFI-type zeolites

**Table 1** resumes the molar composition of formulation gels and the hydrothermal conditions used to synthesize MFI-type conventional big crystals and nanosheets zeolites.

**Synthesis of MFI-type zeolite nanosheets:** The nanosheet sample was synthesized using  $C_{22}H_{45}N^+(CH_3)_2-C_6H_{12}N^+(CH_3)_2-C_6H_{13}Br_2$  as specific surfactant (Scheme 1) according to references. [15,31] Typically sodium hydroxide (99% Riedel de H Haën) was dissolved in distilled water in a 45 ml Teflon-lined stainless steel autoclave.  $C_{22}H_{45}N^+(CH_3)_2-C_6H_{12}N^+(CH_3)_2-C_6H_{13}Br_2$  and sulfuric acid (Aldrich) were then added, under stirring. After homogenization, tetrahydroxylane (TEOS Aldrich 98%) and aluminum sulfate were added, drop wise to set the molar composition of the gel to:  $0.3Na_2O:0.18H_2SO_4:0.01Al_2O_3:1SiO_2:0.1C_{22}H_{45}N^+(CH_3)_2-C_6H_{12}N^+(CH_3)_2-C_6H_{13}Br_2:40H_2O$ . The gel was stirred at 1000 rpm during 30 min at 60 °C, prior to be placed in tumbling oven at 150 °C for 4 days under tumbling conditions at 60 rpm. After crystallization, the zeolite product was filtered, washed with distilled water and dried at 100 °C. The surfactant was finally removed by calcination in a muffle furnace at 550 °C during 8 h.

**Synthesis of MFI-type zeolite conventional big crystals:** For comparison, conventional MFI zeolite large crystals with a coffin-shape morphology (denoted as big crystals) were synthesized in the same condition described above for MFI-type nanosheets by adding 2.03 g of a tetrapropylammonium hydroxide (TPAOH) aqueous solution (20 wt %, Fluka) instead of the appropriate amount of gemini-type quaternary ammonium surfactant. The gel composition was therefore  $0.3Na_2O:0.18H_2SO_4:0.01Al_2O_3:1SiO_2:0.2TPAOH:40H_2O$  [44].

Both ZSM-5 zeolite samples were  $Na^+$ -ion-exchanged ( $H^+$  to  $Na^+$  cation exchange) with a 1 M NaCl aqueous solution heated at 50 °C during 5 h. Typically, 1 g of zeolite ZSM-5 is soaked in 25 mL of this NaCl solution. The ion exchange process was repeated three times for both samples.

### 2.2. Physicochemical properties

The crystallinity and purity of the synthesized materials were checked by powder X-ray diffraction (XRD) on a PANalytical MPD X'Pert Pro diffractometer operating with Cu  $K\alpha$  radiation ( $\lambda = 0.15418$  nm) and equipped with an X'Celerator real-time multiple strip detector (active length =  $2.122^\circ 2\theta$ ). The powder pattern was collected at room temperature in the range  $3 < 2\theta < 50^\circ$  with a  $2\theta$  angle step of  $0.017^\circ$  and a time step of 220 s. Small angle powder X-ray diffraction patterns in the  $0.5$ – $10^\circ$  region were recorded on a glass plate with a  $0.02^\circ$  step size (step time = 1 s) and a variable slit mode. The morphology, homogeneity and particle sizes of the synthesized samples were investigated with a scanning electron microscope (SEM) (Philips XL30 FEG) and by transmission electron microscopy (TEM) using a Philips model CM200, under an acceleration voltage of 200 kV, with a point-to-point resolution of 0.3 nm.

The Si/Al molar ratio and the sodium content of the synthesized samples were estimated by X-Ray Fluorescence (XRF) spectrometry (Philips, Magic X).

A Micromeritics 2420 ASAP was used for nitrogen sorption measurements. Prior to each experiment, 50 mg of the calcined zeolitic samples were outgassed to a residual pressure of less than 0.8 Pa at 300 °C for 15 h. Nitrogen sorption measurements were performed at  $-196$  °C. Specific surface areas were determined from the Brunauer-Emmet-Teller (BET) equation in the  $p/p^0$  range between 0.05 and 0.25. The total pore volume was determined from the nitrogen adsorbed volume at  $p/p^0 = 0.99$  and the  $t$ -plot method was used to distinguish micropores from mesopores. The mesopore size distributions were deduced from the adsorption branch of the isotherm using the Density Functional Theory (DFT) model [52,53].

### 2.3. Sorption procedure

Both zeolite samples were heated up to 450 °C under Ar. Then, the dehydrated zeolites were cooled to room temperature under dry argon. Weighed amounts of *p*-terphenyl (PTP,  $C_{18}H_{14}$ , Sigma-Aldrich 99.5%) corresponding to 0.5 PTP/Unit Cell were introduced into the cell under dry argon and the powder mixture was shaken. The powders were transferred under dry argon in a quartz glass Suprasil cell for spectral experiments. The powder mixtures were stocked in the dark at room temperature until complete sorption.

### 2.4. Diffuse reflectance UV–visible absorption (DRUVv)

The progressive incorporation of PTP was monitored as a function of time by conventional diffuse reflectance UV–visible absorption spectroscopy. The UV–vis–NIR absorption spectra of the samples were recorded between 200 and 1800 nm using a Cary 6000 spectrometer. The instrument was equipped with an integrating sphere to study the powdered zeolite samples through diffuse reflectance; the corresponding bare zeolite was used as the reference. The DRUVv spectra were plotted as the Kubelka-Munk function.

$$F(R) = (1 - R)^2 / 2R = K/Sc \quad (1)$$

where  $R$  represents the ratio of the diffuse reflectance of the loaded zeolite to that of the dehydrated neat zeolite,  $K$  designates an absorption coefficient proportional to the concentration  $C$  of the chromophore and  $Sc$  the scattering coefficient of the powder. Spectral sets  $F(\lambda, t)$  were recorded as function of  $\lambda$  (wavelength) at several  $t$  (time) during the course of the PTP sorption and after photoionization.

### 2.5. Kinetic calculations

The charge recombination kinetic was analyzed through the  $C(t)$  decay. Mono or two exponentials do not reproduce accurately the decays. The concentration decays  $C(t)$  were accurately fitted using the Albery function that takes into account the heterogeneity of the

**Table 1**  
Molar composition of synthesis gels and hydrothermal conditions for the preparation of MFI conventional big crystals and nanosheet zeolites.

	Gel composition in molar ratio								T (°C)	Time (days)
	Na <sub>2</sub> O	H <sub>2</sub> SO <sub>4</sub>	TPAOH	$C_{22}H_{45}N^+(CH_3)_2-C_6H_{12}N^+(CH_3)_2-C_6H_{13}Br_2^a$	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	(Et) <sub>2</sub> O	H <sub>2</sub> O		
MFI big crystals	0.3	0.18	0.2	0	0.01	1	4	40	150	4
MFI nanosheets	0.3	0.18	0	0.1	0.01	1	4	40	150	4

<sup>a</sup> See Scheme 1.

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