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Communications

Effect of Water on the Control of Methylene Blue within CsY Zeolite; Photoacoustic Spectroscopic Method

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We report in this communication that within Cs-exchanged Y zeolites (CsY) the monomer-dimer equilibrium of methylene blue (MB) can be controlled by hydration-dehydration process. The possible structure of MB dimer has been proposed as a sandwich of monomers by Förster¹ and called H-type dimer.² Zeolite-hosted dyes are prospective materials for uses as dye pigments³ or as optical data storage systems.^{4,5} The possibility of persistent spectral hole burning for a system of supercage of zeolite Y and encapsulated MB was demonstrated by R. Hoppe *et al.*⁵ Therefore we are interested in the role of water on the control of monomer-dimer ratio within Y zeolites. Since the free volume of supercage of zeolite Y⁶ is about 830 Å,³ the inclusion of dimeric form of MB by dimerization of adsorbed monomeric MB could be proceeded within hydrated Y zeolite. It was reported that MB has the inherent tendency to dimerize in aqueous solution and the equilibrium constant of dimerization was about 4×10^4 .⁷

We have taken advantage of photoacoustic spectroscopy (PAS) to investigate the adsorption of MB in CsY. According to Rosencwaig-Gersho theory⁸ for the photoacoustic effect, the acoustic signal in optically opaque and thermally thick solids such as dye adsorbed zeolites is proportional to the optical absorption coefficient of the solid sample with respect to wavelength and varies as (the chopping frequency)^{-3/2}. The PAS technique made it possible to detect quantitatively the monomer-dimer equilibrium of adsorbed dyes in the zeolitic space. The schematic diagram of a home-made photoacoustic spectrometer is shown in Figure 1-(a). The light source is a 1000W high pressure Xe-lamp (Oriel, 66022) controlled by the power supply (Oriel, 68820). The slit width

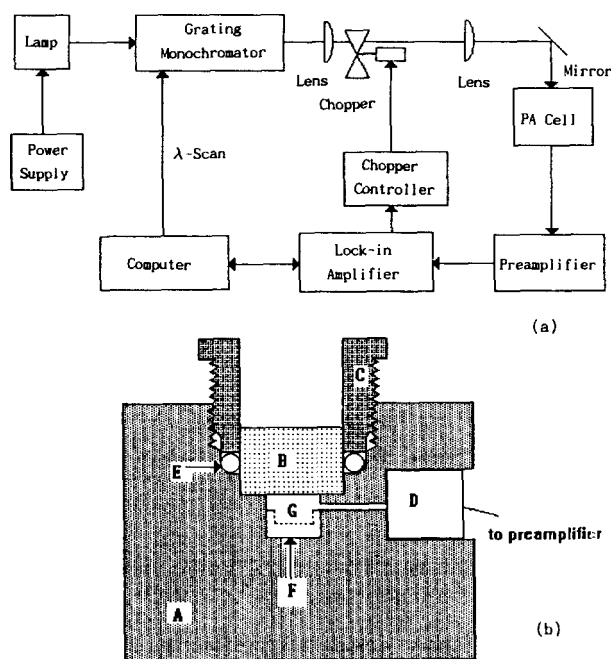


Figure 1. The schematic diagram of (a) photoacoustic spectrometer and (b) photoacoustic cell; A, cell body; B, quartz window; C, sealing nut; D, microphone; E, O-ring; F, sample holder; and G, cell space.

of the grating monochromator (Oriel, 77250) was 1.25 nm. The monochromatic light was modulated to 30 Hz by the chopper (Stanford Research, SR540) and focussed into the cell through the lenses and mirror. The microphone in the cell monitored the modulated pressure change resulted from photoacoustic phenomena. The microphone signal was detected with a preamplifier (Stanford Research, SR550) and a lock-in amplifier (Stanford Research, SR530). The range of amplified signal was $\sim 100 \mu\text{V}$. Figure 1-(b) illustrates the cell that consists of three parts: quartz window, sample chamber, and microphone. Spectra of MB-included CsNaY samples were recorded from 350 nm to 800 nm and normalized by that of carbon black at the same modulation frequency.

Zeolite NaY with the Si/Al ratio of 2.8 was ion-exchanged

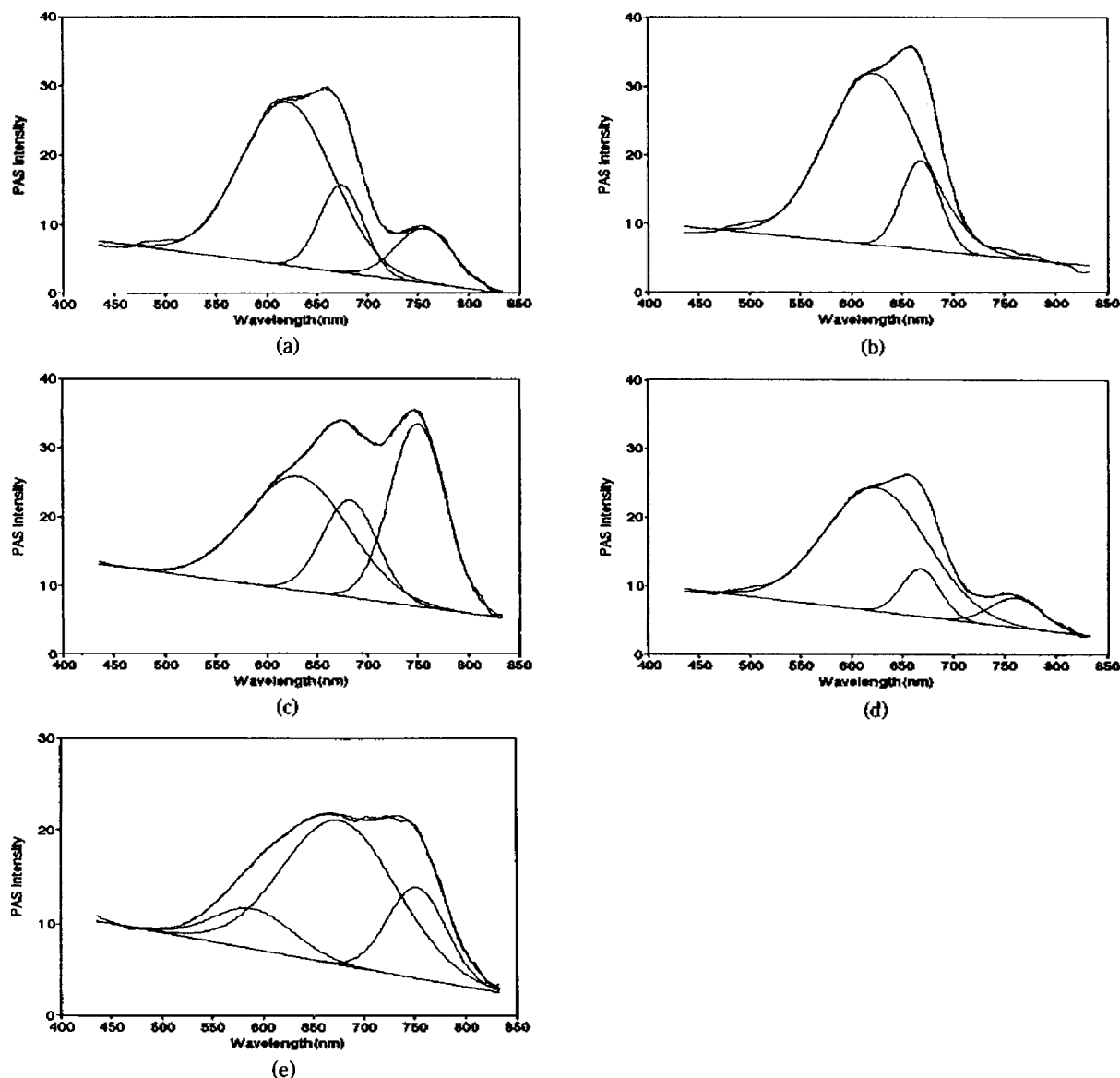
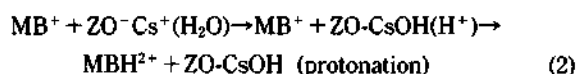
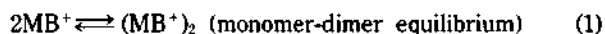


Figure 2. Photoacoustic spectra and fitted curves by deconvolution bands of (a) as-prepared MB-included CsY zeolite (MB-CsY), (b) fully hydrated MB-CsY, (c) dehydrated MB-CsY, (d) rehydrated MB-CsY, and (e) methanol saturated MB-CsY.

to Cs^+ . Because the Cs^+ ion has relatively weak electric field among alkali metals, we expected that the water molecule in hydrated shell of Cs^+ is easily removed during dehydration. NaY was stirred in 0.5 N-CsCl solution for 4 days to prepare CsY. The exchanged zeolite was filtered, washed with distilled water and dried at 100°C . The 34% cationic site was occupied by Cs^+ ion. 0.1 g of CsY was diluted in 30 mL of water for 3 hours by stirring at room temperature. $\text{MB } 10^{-6}$ M solution of 120 mL was added to the above solution. After adsorbing MB for 12 hours, MB-adsorbed Y was filtered and dried at 60°C for 12 hours. Dye content of 1.2×10^{-6} mol per gram sample is found by the photometric evaluation of the amount in solution.

Figure 2-(a) shows the photoacoustic spectrum (PAS) of as-prepared CsY and the fitted curve by the Gaussian deconvolution. The MB-included CsY exhibits a dimer absorption maximum around 620 nm, a monomer, around 660 nm, and

a protonated MB (MBH^{2+}), around 760 nm. The band area ratio of $(\text{MB}^+)_2/\text{MB}^+$ calculated by deconvolved bands is about 3.9. Though MB has the inherent tendency to dimerize in aqueous media, dimer/monomer area ratio is less than 10 because the supercharge of hydrated Y zeolite has narrow channels just inclusion of the dimer. The appearance of MBH^{2+} is attributed to the proton which is formed by water dissociation resulted from the electrostatic field of alkali metal cation such as Cs^+ or Na^+ .



MB-loaded CsY was fully hydrated by exposure in the atmosphere for 30 days. MBH^{2+} band in PA spectrum completely disappeared due to shielding of the proton by an

hydration shell increasing the dimer/monomer ratio to 4.8, as shown in Figure 2-(b). The decreased band area of monomeric forms is nearly the same as the half of the increased one of dimer. This result indicates that the PAS method can be applied to the quantitative investigation of the monomer-dimer equilibrium within zeolite.

The PA spectrum shown in Figure 2-(c) was obtained in N₂ atmosphere after partially dehydration in vacuum oven of 10⁻³ mmHg at 50 °C for 6 hours. The enhanced MBH²⁺ band could be attributed to the protons generated by the dissociation of water molecules resulted from the dehydration of CsY. The slightly increased monomer and the decreased dimer band (dimer/monomer=2.2) confirm the unique role of water having the high dielectric constant on dimerization of dye.²⁹ Most of the dissociated dimers were converted to the protonated monomer form as shown in the deconvolution bands (figure 2-(c)).

Figure 2-(d) illustrates the reversible dimerization of monomeric forms resulted from rehydration process. During the saturation of methanol less polar than water within the dehydrated sample (Figure 2-(e)), however, the dimerization did not proceed and the dimer band blue-shifted.

We obtained the following conclusions from the above results. (a) The dehydration process within CsY zeolite leads to the water dissociation. (b) While the shielding proton in hydrated sample could not contribute to the protonation of MB⁺, the unshielded one in dehydrated sample reacted easily with MB⁺ to form the MBH²⁺. (c) The dimerization and protonation of methylene blue within CsY zeolite are reversibly proceeded by the hydration-dehydration.

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Facile Reduction of Carboxylic Acids to Aldehydes by Lithium Gallium Hydride

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A number of methods for the direct transformation of carboxylic acids into aldehydes by using lithium in methylamine,¹ diisobutylaluminum hydride,² thexylborane,³ thexylhaloborane,⁴ bis(4-methylpiperazinyl)aluminum hydride,⁵ the Grignard reagent catalyzed by dichloro-bis(π -cyclopentadienyl)titanium or N,N-dimethylchloromethyliminium chloride,⁶ and lithium tri-*tert*-butoxyaluminum hydride,⁷ and 9-borabicyclo[3.3.1]nonane(9-BBN) species⁸ have been reported.

In the course of exploring the reducing properties of lithium gallium hydride, we observed that benzoic and caproic acids consumed one hydride rapidly for reduction, but the further reduction proceeded very slowly. These results suggested the possibility of aldehyde synthesis from carboxylic acid using this reagent.

The reduction of carboxylic acids were carried out by the addition of 0.5 equiv lithium gallium hydride in diethyl ether at 0 °C and room temperature. As shown in Table 1, aliphatic acids, such as acetic, hexanoic, and cyclohexanecarboxylic acids provided the corresponding alcohol in 73-75% yield at 0 °C and 62-68% yield at room temperature. An α,β -unsaturated aliphatic acid, crotonic acid was converted into the corresponding unsaturated aldehyde in a 70% yield at 0 °C and a 65% yield at room temperature. However, acrylic acid was converted into the corresponding unsaturated aldehyde in a 50% yield at 0 °C and a 48% yield at room temperature. The low yield of acrylic acid comparing with other carboxylic acids was presumably due to the attack of hydride on the double bond of the compound. Aromatic carboxylic acids, such as benzoic, 2-methylbenzoic and α -naphthoic acids,

Table 1. Yields of Aldehydes in the Reduction of Representative Carboxylic Acids with LiGaH₄ in Diethyl Ether^a

Acid	Time (h)	Yield of Aldehyde ^b (%)	
		0 °C	Room Temperature
hexanoic	12	73	68
cyclohexanecarboxylic	12	73	65
crotonic	12	70	65
acetic	12	75 ^c	62 ^c
acrylic	12	50	48
benzoic	6	67	53
2-methylbenzoic	6	65	52
cinnamic	6	48	40
α -naphthoic	6	60	48

^a Reacted with 2 equiv reagent in hydride for carboxylic acid.

^b Yields were estimated by GLC. ^c Yields were estimated by 2,4-dinitrophenylhydrazine.