

## Formation of Uniform Mesopores in ZSM-5 Zeolite through Treatment in Alkaline Solution

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Treatment of ZSM-5 in alkaline solution dramatically changes morphology of the ZSM-5, leading to the formation of mesopores whose size is almost uniform without destruction of microporous structure.

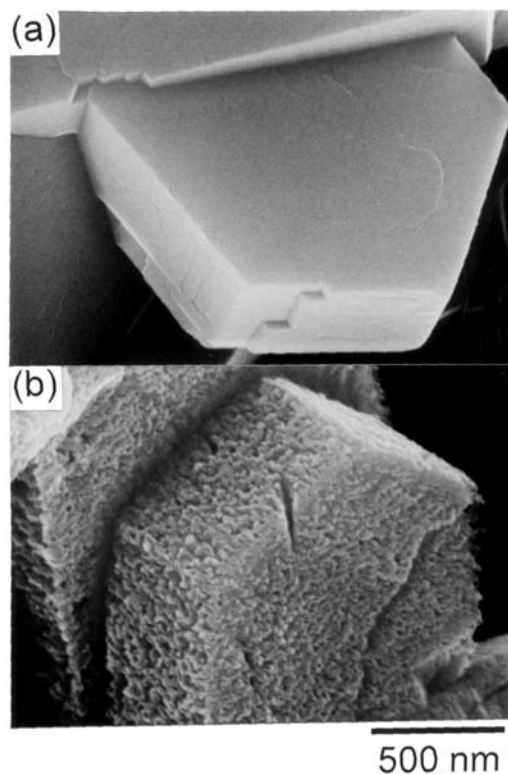
Zeolites have been encountering a growing interest because of its wide variety of applications for catalysts in industry. For this reason there are currently massive efforts in trying to synthesize new kinds of zeolite and zeolite-like materials.<sup>1</sup>

Acid treatment of zeolites is a well-known method to change  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of zeolite framework, thus to change the properties connected with the ratio. For instance, an improved stability can be observed in a dealuminated ultra-stable Y zeolite. On the contrary, less information has been reported concerning alkali treatment of zeolite.<sup>2-4</sup> In contrast to acid treatment which preferentially removes framework Al atoms, alkali treatment was found to extract framework Si atoms selectively.<sup>2</sup> Previous studies on the alkali treatment of ZSM-5 and silicalite using sodium carbonate<sup>3</sup> and sodium hydroxide<sup>4</sup> aqueous solutions at high concentrations, showed by means of XRD that Si removal occurs without changes in crystallinity of zeolites. In this communication, we will show that alkali treatment of zeolite using sodium hydroxide solution as an alkaline medium under relatively mild conditions leads to a creation of uniform-sized mesopores without deterioration of crystallinity.

$\text{NH}_4$ -type ZSM-5 zeolite with  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of 39.4 (HSZ-840NHA, lot. # NTZS-4) was supplied by Tosoh Corp. This is designated as "as-received" in this report. ZSM-5 crystals have uniform shape and particle size with planer surfaces, as shown in Figure 1(a). Alkali treatment of ZSM-5 zeolite was performed with 0.2 M NaOH aqueous solution. A flask made of polyethylene was used to treat ZSM-5. First, 300 mL of the NaOH solution in the flask was heated to 353 K with a reflux condenser in a water bath, and then 10 g of as-received zeolite was added there while stirring. After 300 min, the slurry was cooled down immediately in an ice bath and filtered. The filtered cake was dried in an air oven at 383 K overnight. After drying, alkali-treated ZSM-5 was rinsed with distilled water at 353 K for 2 h to eliminate silicate materials which could be precipitated during the alkali treatment.

FE-SEM was used for observing the morphology of the alkali-treated ZSM-5. The specific surface area, micro- and mesopore volumes of as-received and alkali-treated ZSM-5 were determined by use of  $\text{N}_2$  adsorption at 77 K. The total surface area was calculated according to the BET isothermal equation, and the micropore volume was evaluated by the t-plot method<sup>5</sup>. Mesopore volume was determined by the Dollimore-Heal method.<sup>6</sup>

Morphological changes of ZSM-5 zeolite during alkali treatment were quite dramatic. As clearly shown in Figure

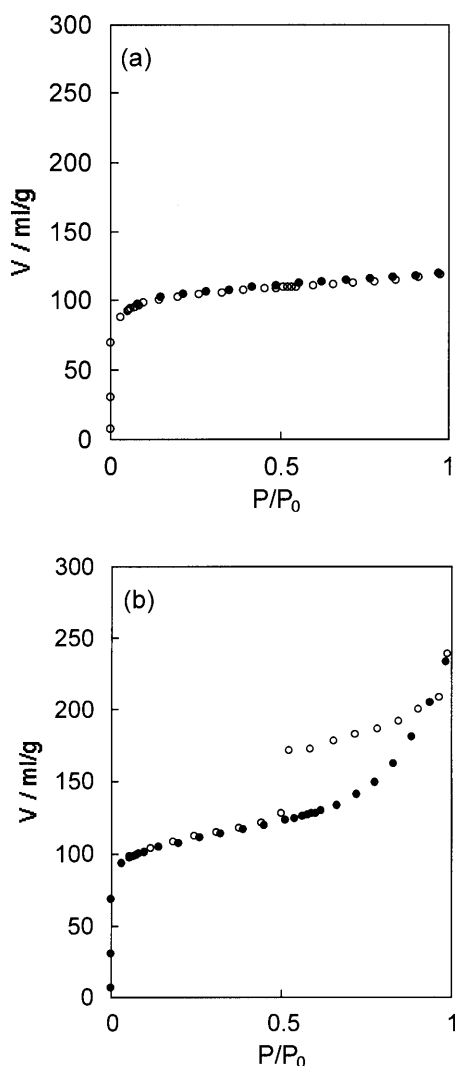


**Figure 1.** SEM images for (a) as-received and (b) alkali-treated ZSM-5.

1(b), some grooves and voids appeared on the surface of ZSM-5 particles by the alkali treatment.

The as-received and alkali-treated ZSM-5 zeolites showed some differences in the porous structure evaluated by the  $\text{N}_2$  adsorption method. Figure 2 illustrates the adsorption isotherms of  $\text{N}_2$  observed on (a) as-received and (b) alkali-treated ZSM-5. In the case of alkali-treated ZSM-5, a hysteresis loop was clearly observed during the desorption measurement, strongly suggesting the formation of mesopores on ZSM-5. Compared with the materials having mesopores such as M41S,<sup>7</sup> a sharper increase in isotherm was observed at around  $P/P_0 = 0.5$ , where the size of mesopore is ca. 4 nm. The BET surface areas (316 and 320  $\text{m}^2/\text{g}$  for as-received and alkali-treated ZSM-5, respectively) were unchanged and a little change was observed in the micropore volumes (0.171 and 0.133  $\text{cm}^3/\text{g}$ , respectively) by the alkali treatment, while mesopore volumes (0.072 and 0.279  $\text{cm}^3/\text{g}$ , respectively) were quite different. The differential of the mesopore volumes corresponds to 6.15 mmol-Si per gram of zeolite, whereas the as-received ZSM-5 has 15.6 mmol-Si/g. This means that a large portion of the zeolite, ca. 40%, has been dissolved during alkali treatment.

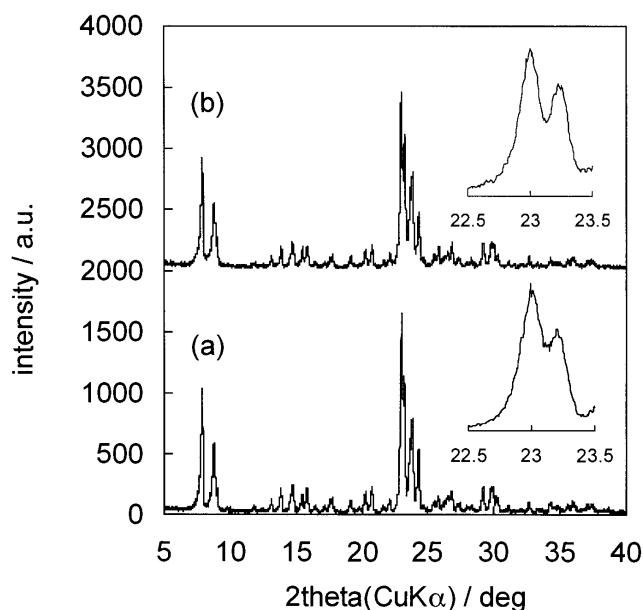
Although ZSM-5 did not hold its original morphology after the alkali treatment, the XRD patterns show that the alkali-



**Figure 2.**  $N_2$  adsorption isotherms at 77 K for (a) as-received and (b) alkali-treated ZSM-5.

treated ZSM-5 maintains its crystallinity, as shown in Figure 3. The diffraction peaks assigned to MFI topology did not change at all in their intensities and lattice parameters after the alkali treatment. Besides, the diffraction peaks at around  $2\theta = 23^\circ$  appeared to be split more clearly by the alkali treatment.

Judging from the results obtained in this study, it can be concluded as follows: ZSM-5 zeolite becomes to show mesoporosity by treatment with an alkaline solution without deterioration of the microporous structure. The mesopores, which are produced by the alkali treatment technique, has a similar and/or more uniform pore size to mesoporous materials such as M41S.



**Figure 3.** XRD patterns for (a) as-received and (b) alkali-treated ZSM-5.

The previous efforts to synthesize mesoporous materials have not successfully brought forth a catalyst having strong acidity and stability such as zeolites. In contrast, alkali treatment of zeolite could be a promising method to create a uniform meso-structured material with zeolitic acidity.

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