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Carbon Dioxide Interaction with Ti Y Zeolite

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Introduction: The twin problems of global warming and limited fossil fuel resources have stimulated research into the use of CO_2 to produce fuels and chemical feedstocks [1]. Photochemical CO_2 reduction to methanol is catalyzed by a suspension of colloidal TiO_2 nanoparticles, but the quantum yield is low [2]. Anpo *et al*. reported that this process can be significantly enhanced by the use of titanium oxide species anchored within zeolites [3]. In order to understand the elementary steps of the reactions related to methanol formation from CO_2 and gaseous H_2O in the zeolite, we are exploring the interaction of Ti with the porous framework of the zeolite, and specific interactions of CO_2 with Ti and/or the porous framework.

Methods and Materials: Ti Y zeolite was prepared with 10% aqueous $(NH_4)_2TiO(C_2O_4)_2$ solution with Na Y zeolite, followed by calcination at 350 °C. The structural changes of Ti Y zeolite by dehydration and by the addition of CO_2 were investigated using *in-situ* time-resolved powder x-ray diffraction.

Results and Conclusions: Dehydration of the zeolite was performed *in-situ* by heating the sample in a vacuum. Figure 1 shows a three-dimensional plot of the powder diffraction profiles of dehydrated Ti Y zeolite, collected with a wavelength of 0.8988 Å, during sample heating to 500 °C over a period of 2 hours, followed by a decrease in temperature from 500 to 25 °C for 1 hour. The intensity of the 111 reflection (top panel of Figure 1) increased with time. After dehydration, the sample was exposed to CO_2 gas. Figure 2 shows the *in-situ* powder x-ray diffraction pattern of CO_2 adsorption on the dehydrated Ti Y zeolite. The decrease in the intensity of the 111 refraction (top panel of Figure 2) is due to CO_2 absorption in the supercage. Rietvelt powder profile refinements were performed with the program GSAS. The preliminary analysis of the dehydrated Ti Y zeolite data indicates that the Ti cations occupy SI' in the sodalite cage and SII in the supercage. The Ti-O bond lengths for Ti in SI' and SII are 2.2 and 2.6 Å, respectively. The preliminary analysis of a series of powder diffraction patterns for the dehydrated Ti Y zeolite before, during, and after dosing with CO_2 shows changes in intensity consistent with movement of cations during the CO_2 interaction. A detailed analysis is in progress.

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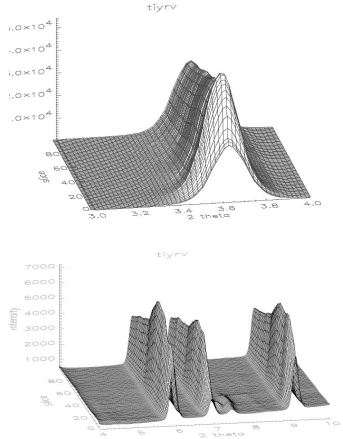

Figure 1. Time-resolved x-ray powder diffraction profiles obtained during the dehydration of Ti Y zeolite from 25 °C to 500 °C over a period of 120 minutes.

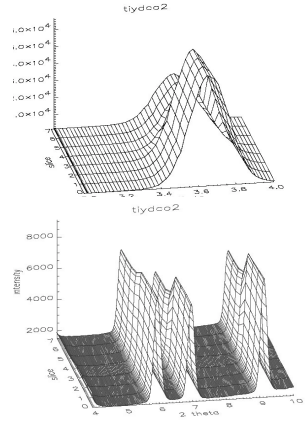

Figure 2. Time-resolved x-ray powder diffraction profiles obtained during dosing of CO_2 on dehydrated Ti Y zeolite.