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## Structural Characterization of Titanium- and Molybdenum-Based Zeolites

E. Fujita (BNL) and J. Hanson (BNL)

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**Introduction:** Molybdenum carbide has recently been identified as a potential catalyst for methane reforming and hydrodesulfurization [1]. We are exploring the preparation of molybdenum carbide and oxide nanoclusters in the confined cages of zeolites, since the well-defined nano-environment of zeolites may provide templates for the size and shape selective preparation of nanoclusters. Photochemical CO<sub>2</sub> reduction to methanol is catalyzed by titanium oxide species anchored within zeolites [2]. Therefore we are also studying the interaction of Ti with the porous framework of the zeolite, and specific interactions of CO<sub>2</sub> with Ti and/or the porous framework.

**Methods and Materials:** Mo-based zeolites were prepared by addition of gaseous Mo(CO)<sub>6</sub> to the dehydrated NaY zeolite (sample 1). The white material changes to gray upon heating to 350 °C (sample 2). The IR spectrum of the gray material indicates no CO stretching frequencies. White Mo-based zeolite (sample 3) was also prepared by impregnation of Mo(CO)<sub>6</sub> into dehydrated NaY in dry hexanes followed by calcinations at 400 °C with O<sub>2</sub> flow. This material indicates lower Mo content than samples 1 and 2. XANES data on these materials and other standard complexes were measured.

**Results:** XANES results for Mo-based zeolites and other Mo model complexes are shown in Figures 1 and 2. Although the formal oxidation state of Mo(CO)<sub>6</sub> is Mo(0), the L<sub>III</sub> edge of Mo(CO)<sub>6</sub> is surprisingly shifted to higher energy compared to those of Mo<sub>2</sub>C and MoS<sub>2</sub>, probably due to strong back-donation through the formation of a molybdenum-to-carbon  $\pi$  bond. The L<sub>III</sub>-edge of sample 1 and 3 is similar to that of MoO<sub>3</sub>. However, the edge of the gray Mo-based zeolite, sample 2, is shifted to lower energy and is similar to that of MoS<sub>2</sub>. This air-stable material may contain MoO<sub>2</sub>. Further characterization is in progress.

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### References:

[1]. J. G. Chen, "Carbide and Nitride Overlayers on Early Transition Metal Surfaces: Preparation, Characterization, and Reactivities" *Chem. Rev.*, **96**, 1477-1498 (1996).

[2]. M. Anpo, H. Yamashita, Y. Ichihashi, Y. Fujii, and M. Honda, "Photocatalytic Reduction of CO<sub>2</sub> with H<sub>2</sub>O on Titanium Oxides Anchored within Micropores of Zeolites: Effects of the Structure of the Active Sites and the Addition of Pt", *J. Phys. Chem. B* **101**, 2632-2636 (1997)

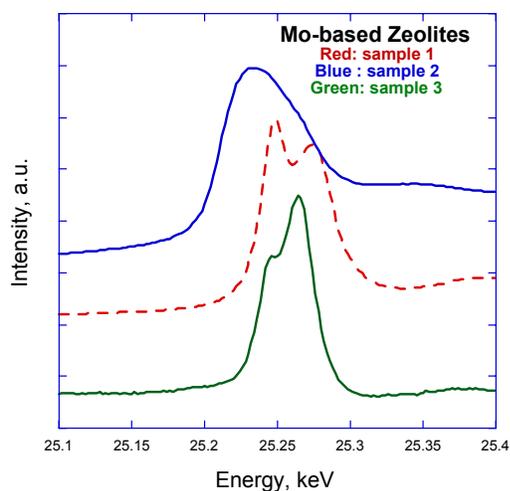


Figure 1 MoL<sub>III</sub>-edge XANES of Mo Y zeolite sample 1 (red), sample 2 (blue), and sample 3 (calcined MoY, green)

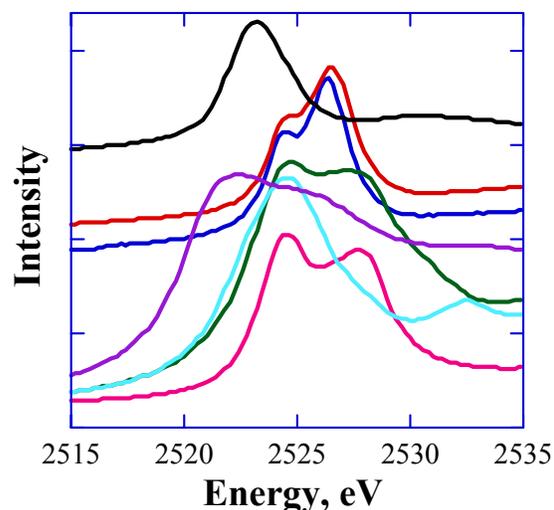


Figure 2 MoL<sub>III</sub>-edge XANES of Mo Y zeolite and other Mo complexes. Calcined Mo Y zeolite, i.e. sample 3 (red), uncalcined MoY (blue). MoS<sub>2</sub> (black), Mo<sub>2</sub>C (purple), Mo(CO)<sub>6</sub> (light blue) MoO<sub>2</sub>(acac)<sub>2</sub> (pink) and MoO<sub>3</sub> (green)