NANOPOROUS MATERIALS

Researchers are developing novel zeolite-based materials with 1-D nanopores for automotive applications.

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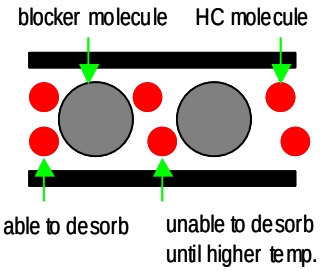
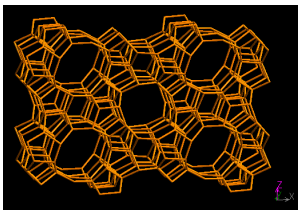
Objective: Social concerns about the environment and stricter federal and state regulations make low-emission vehicles increasingly desirable. At present, catalytic converters used with conventional gasoline engines do not capture hydrocarbon (HC) pollutants before reaching operational temperatures – the situation known as the "cold-start" problem – while catalytic converters used with diesel engines do not oxidize nitrogen oxides (NO_x), a major cause of acid rain. The Snurr group is addressing the cold-start problem by developing an "HC trap" that will capture the HC's in the first several minutes of driving and release them when the catalytic converter reaches its optimal temperature. The HC trap is based upon a special class of zeolites with non-intersecting, 1-D pores that are so small that molecules cannot pass by one another. When these conditions exist, the lighter HC components in the middle of the pore are unable to desorb if there are more strongly adsorbing heavier molecules near the end of the pore. Thus, even a small fraction of strongly adsorbing "blocker" molecules could effectively trap a sizeable amount of HC's. The Snurr group is also collaborating with the team led by Dr. Broadbelt in conducting theoretical modeling of zeolites in an effort to improve their performance as NO_x reduction catalysts.



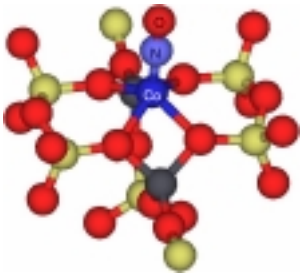
A sketch of a 1-D pore of a zeolite that acts as a "hydrocarbon trap," which is designed to reduce pollution of conventional gasoline engines.

Approach: Temperature-programmed desorption (TPD) is used to investigate HC trapping. For the NO_x catalysts, quantum mechanical calculations are performed using the density functional theory (DFT) formalism to determine the minimum energy geometries of the active sites and their electronic and catalytic properties.



ZSM-5 zeolite

Results: The Snurr group has investigated several zeolites of various morphologies as HC traps using mixtures of propane and toluene as a model system. In EUO, a zeolite with 1-D pores, propane is trapped within the pores by toluene and desorbs to the gas phase only after toluene begins to desorb, which happens at a temperature 35 °C higher than that recorded in the absence of toluene. Similarly, in mordenite, another zeolite with 1-D pores, propane desorbs in the presence of toluene at an intermediate temperature that is 100 °C higher than that observed in the absence of toluene. This HC trapping is not observed in ZSM-5, a zeolite with 3-D pores. Thus, the feasibility of the HC trap has been successfully demonstrated. In a separate study, the researchers led by Dr. Snurr and Dr. Broadbelt have modeled cobalt-exchanged ferrierite, a promising catalyst for NO_x reduction. Two of the three cobalt extraframework sites proposed in the literature have been investigated with DFT calculations. The electronic structure, geometry, and IR spectra of eight cobalt clusters have been calculated and compared to experiment. Exchanged cobalt cations are shown to be most stable in the high-spin electronic configuration. The calculations also demonstrate the important role of zeolite aluminum location in extraframework cobalt siting. Only one of the eight clusters is able to reproduce all of the experimental characteristics of the predominant cobalt species. With the knowledge of both the extraframework site and the relative aluminum arrangement in that site, current calculations are evaluating the catalytic activity of cobalt as a function of its local zeolite environment.



Quantum mechanical calculations of cobalt active site in ferrierite.

Publications: Czaplewski KF, Reitz TL, Kim Y-J, Snurr RQ *Mircroporous and Mesoporous Materials* **2002**, 56:55; McMillan SA, Broadbelt LJ, Snurr RQ *J.Phys. Chem. B* **2002**, 106:10864.