Development of Nanocrystalline Zeolite Materials as Environmental Catalysts

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Abstract

This project involves the development of nanometer-sized zeolites and zeolite nanostructures as environmental catalysts. Zeolites, which are widely used in applications in separations and catalysis, are aluminosilicate molecular sieves with pores of molecular dimensions. Recently, there has been a great deal of interest in the synthesis of nanocrystalline zeolites (zeolites with crystal sizes of 100 nm or less) and their unique properties relative to conventional micron-sized zeolite crystals. Nanocrystalline zeolites possess very large internal and external surface areas that can be exploited for many different applications. For example, nanocrystalline silicalite with a crystal size of 20 nm has an external surface area of ~175 m^2/g (approximately 30 percent of the total surface area on the external surface). For comparison, the external surface area of a 1 micron silicalite crystal is approximately 2 m^2/g which accounts for less than 1 percent of the total surface area. A key feature of nanocrystalline zeolites is that the external surface can be utilized as a reactive or sorbtive surface resulting in materials with a wide variety of physical and chemical characteristics. In principal, bifunctional zeolite materials can be designed in which the external and internal surfaces have different functions.

Nanocrystalline ZSM-5, silicalite (purely siliceous form of ZSM-5), and Y zeolites have been synthesized in our lab with discrete crystal sizes as small as 15 nm. Hollow zeolite structures have also been prepared using zeolite nanocrystals as seeds and mesoporous silica as a template and silica source for zeolite growth. First, mesoporous silica is coated with nanocrystalline zeolite seeds. Then, the coated mesoporous silica is subjected to a hydrothermal treatment in an autoclave. During the hydrothermal treatment, the zeolite crystals grow larger using the mesoporous silica as the silicon source for crystal growth. Hollow zeolite structures with controlled porosity have many potential applications in diverse areas including drug delivery, chemical storage, chemical sensors, and catalysis.

Applications of nanocrystalline zeolites in environmental protection will be discussed. In particular, the increased adsorption capacity of nanocrystalline zeolites for volatile organic compounds such as toluene has been demonstrated. In addition, unique reactivity of nanocrystalline NaY for the selective catalytic reduction of NO_2 with reductants such as propylene or urea has been investigated with FTIR spectroscopy. In the absence of oxygen and water, selective catalytic reduction of NO_2 with propylene at low temperatures (473 K) resulted in the complete reduction of NO_2 to N_2 and O_2. Nanocrystalline NaY zeolite exhibits enhanced $deNO_x$ at low temperature (T = 473 K) compared to commercial NaY zeolite, as shown by an FT-IR study on the selective catalytic reduction of NO_2 with urea. Silanol groups and extraframework aluminum species on the external surface of nanocrystalline NaY were found to be responsible for the higher SCR reaction rate and decreased formation of undesired products relative to commercial NaY zeolite. Isotopic labeling coupled with infrared analysis indicates that N-N bond formation involves both a N-atom originating from NO_2 and a N-atom originating from urea. Nanocrystalline alkali zeolites can be visualized as new catalytic materials that have NO_x storage capacity in the internal pores and high reactivity on the external surface. This is the first clear example in the literature demonstrating that the increased external surface area (up to ~40 percent of the total surface area) of nanocrystalline zeolites can be utilized as a reactive surface with unique active sites for catalysis.