Enhanced Activity of Nanocrystalline Zeolites for Selective Catalytic Reduction of NOx

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OBJECTIVES

Nanocrystalline zeolites with discrete crystal sizes of less than 100 nm have different properties relative to zeolites with larger crystal sizes. Nanocrystalline zeolites have improved mass transfer properties and very large internal and external surface areas that can be exploited for many different applications. For example, nanocrystalline NaY with a crystal size of 23 nm has been synthesized in our lab with approximately 30% of the total surface area attributed to the external surface. Thus, the external surface of nanocrystalline zeolites can be utilized as an additional reactive or sorptive surface for catalytic applications. The additional external surface active sites and the improved mass transfer properties of nanocrystalline zeolites offer significant advantages for selective catalytic reduction (SCR) catalysis in coal-fired power plants relative to current zeolite based SCR catalysts. The proposed studies will build on the preliminary results on nanocrystalline NaY and will broaden the scope to study other promising zeolite based SCR catalysts, such as transition metal (iron, vanadium and copper) exchanged nanozeolites and alkaline earth (barium) exchanged nanozeolites.

The technical objectives of the proposed project are:

1. To synthesize and characterize nanocrystalline zeolites (ZSM-5 and NaY) with discrete crystal sizes of 100 nm or less and external surface areas of greater than 100 m^2/g. The nanocrystalline zeolites will be extensively characterized by scanning electron microscopy (SEM), powder x-ray diffraction, and BET adsorption isotherms.
2. To prepare bifunctional nanocrystalline zeolite catalysts using standard ion-exchange procedures. Copper, vanadium, barium and iron-exchanged zeolites will be prepared. The bifunctional zeolites will be extensively characterized by a suite of spectroscopic techniques.
3. To investigate the reactivity of the nanocrystalline zeolites prepared in Technical Objectives 1 and 2 for the SCR of NOx with ammonia. Initial studies will be conducted using FTIR spectroscopy and solid state NMR spectroscopy to evaluate whether the nanocrystalline zeolites exhibit unique reactive sites for SCR-NOx.
4. Promising candidates for Phase II development will be identified in catalyst testing using a flow reactor under realistic operating conditions for SCR-NOx reactions.

ACCOMPLISHMENTS TO DATE

In the first quarter of the grant period, approximately 2 g of nanocrystalline NaY was prepared using the method of recycling the synthesis solution. Four batches of nanocrystalline NaY were subsequently obtained from the same synthesis solution and were combined for catalytic studies. The average crystal size of the nanocrystalline NaY was 16 nm. The average external surface area was 252 m^2/g and the average total specific surface area was 511 m^2/g. Additional batches of nanocrystalline NaY were prepared for ion-exchange with copper, vanadium, barium and iron.

The nanocrystalline NaY is unstable to aqueous phase ion-exchange. A loss of crystallinity was observed in the X-ray diffraction data and a decrease in the specific surface area was observed in nitrogen adsorption experiments after prolonged exposure of nanocrystalline NaY to water.

FUTURE WORK

Future work will focus on vapor phase exchange methods for the preparation of copper, vanadium, barium and iron-exchanged nanocrystalline NaY. The advantage of these methods is that the sample will have limited exposure to water during the exchange process. Once the ion-exchanged nanocrystalline NaY has been prepared, FTIR and solid state NMR studies of the reactivity of these materials for the SCR of NOx with ammonia will be conducted. The unique reactivity of the nanocrystalline NaY will be assessed and the different ion-exchanged nanocrystalline NaY will be compared to the sodium form. In the final phase of the project, the most promising materials will be evaluated under more realistic operating conditions SCR-NOx reactions.