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Gallium Zeolites for
Light Paraffin Aromatization

Progress Report

August 15, 1992 - February 15, 1994

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Progress Report

Introduction

Research funding for Ga Zeolites at LSU was initiated on August 15, 1992 under DOE grant # DE-FG05-92ER14291. First year funding was \$109,953 and the second year budget was \$79,999. The focus of the research work is to relate the catalytic properties of Ga Zeolites to the preparation method and to unify the various theories about the active nature of Ga Zeolites for light paraffin aromatization. During this reporting period, thermal analysis of alkylamines has been studied extensively and applied with great success to the problem. New features of alkylamine thermal analysis have been discovered and described. Because of the success of this method for the characterization of cation-containing MFI, some spin-off work on Cu-MFI (which currently has broad interest as an NO decomposition catalyst) has been accomplished.

Research Progress

A vast amount of new research work has been accomplished since the last report, and numerous papers have been or are currently being written about the research work. The most efficient way to detail the research progress is to consider each paper individually.

A. Papers in Print this Reporting Period (copies attached)

"Thermal Analysis of Adsorbed Propanamines for the Characterization of Ga-MFI Zeolites," V. Kanazirev, K.M. Dooley, and G.L. Price, J. Catal. 146, 228 (1994).

Thermal Analysis of alkylamines has often been applied as a method for the characterization of proton-containing zeolites. We initially were interested in using this technique to determine whether or not protons were replaced by Ga cations during various types of catalyst pretreatments. Instead of simply noting a loss in protons as we expected, a new mode of 1-propanamine adsorption and thermal breakdown on Ga cations was discovered and reported in this paper. When Ga is driven to the zeolite via reduction, it has a propensity to condense two 1-propanamine molecules eliminating NH_3 . The NH_3 can be observed desorbing from the catalyst at more than 100°C lower than propene when using a mass spectrometer to monitor the effluent of a TPD experiment. C_6 -nitriles and C_6 -imines are products of the reaction of 1-propanamine over Ga-zeolites.

"Change in the Decomposition Mode of 1-Propanamine due to the Presence of Cations in MFI Zeolite," V. Kanazirev, G.L. Price, and K.M. Dooley, Catal. Lett. 24, 227 (1994).

This paper extends many of the observations concerning thermal analysis of 1-propanamine from Ga to In, thus providing evidence of a generalized technique. It is the first publication which discusses nitrile products of the 1-propanamine thermal analysis process.

B. Accepted for Publication (copies attached)

"Activity of Ga and In Modified MFI Zeolites for Amine Reactions", V. Kanazirev and G.L. Price, accepted to Proc. 10th Int. Zeolite Conference, Garmisch-Partenkirchen, Germany, July 17 (1994).

We have discovered that 1-propanamine undergoes a new mode of condensation and dehydrogenation over Ga and In modified MFI. This paper details the products of this reaction which is largely composed of C₆-nitriles and C₆-imines along with smaller amounts of propionitrile, propene, and other products.

"On the Interaction of 1-Propanamine with Cation-Containing MFI Zeolite", V.I. Kanazirev, G.L. Price, and K.M. Dooley, accepted to J. Catal.

This paper summarizes 1-propanamine thermal analysis and catalytic reaction over H-, Ga-, In-, and Cu-MFI. Surprisingly, under the right conditions, all forms of MFI promote condensation of two 1-propanamine molecules. H-MFI requires a temperature higher than the other forms for the dimerization to take place, and dipropylamine is the primary product over H-MFI. Ga, In, and Cu forms of MFI further promote elimination of one NH₃ molecule from the dimerization adduct followed by dehydrogenation to produce nitriles and imines.

"Formation of Cu-MFI NO Decomposition Catalyst via Reductive Solid State Ion Exchange", G.L. Price and V. Kanazirev, accepted to J. Phys. Chem., January, 1994.

This paper details a method for the preparation of Cu-MFI with a copper loading near 1 Cu/framework Al, which is the highest loading of Cu ever reported. The activity of the catalyst for NO decomposition can be correlated directly with Cu/framework Al ratio.

C. Submitted

"Copper-Containing Zeolite Catalysts", G.L. Price and V. Kanazirev, U.S. Patent Application, Aug. 31, 1993.

The reason for a spin-off study of Cu-MFI can be illustrated by considering the foundations of this patent application. Separate studies of Cu-MFI materials for NO decomposition were being conducted in our laboratories during the same time frame that alkylamine thermal analysis experiments on Ga-MFI were being perfected and interpreted. Our observations on the Ga-MFI led us to believe that zeolitic cations could be distinguished from protons by this method. Cu-MFI materials, which we believed to contain Cu⁺ cations, were readily available materials for a further test of this hypothesis. Eventually, the oligomerization/dehydrogenation of 1-propanamine to C₆-nitriles and imines was discovered and the patent was submitted.

D. In Preparation

"Characterization of Ga-MFI via Thermal Analysis", G.L. Price, V. Kanazirev, and K.M. Dooley.

A series of gallosilicates with the MFI structure have been prepared and studied by hydrogen reduction and 1-propanamine thermal analysis. Non-framework Ga_2O_3 can be detected in all cases, and the hydrogen reduction technique can be used as a measure of both extraframework and framework gallium. The hydrogen reduction characterization technique compares favorably to the elemental analysis and x-ray diffraction determination of unit cell size.

"Propane Conversion on Cu-MFI Zeolite", G.L. Price and V. Kanazirev.

Surprisingly, Cu-MFI converts propane to benzene with a very high selectivity, but unfortunately deactivates at high contact times, probably due to reduction of Cu^+ to Cu^0 . This paper details this reaction and compares the product distributions over this catalyst to H-MFI and Ga-MFI.

"Mechanism of Propane Conversion on Cation-Containing MFI Zeolite", G.L. Price, V. Kanazirev, and K.M. Dooley.

When comparing H-MFI, Ga-MFI, In-MFI, and Cu-MFI in the aromatization of light paraffins, a number of generalizations can be made and new light brought to bear on the reaction mechanism.

"Thermal Analysis of Ga-MFI Catalysts", V. Kanazirev, K.M. Dooley, and G.L. Price.

The technique of thermal analysis of alkylamines on Ga-MFI has been studied extensively and will be reported in this paper. Experiments detailing the effects of temperature programming rates, total pressure, partial pressures, temperature and length of adsorption have been compared and will be reported.

"Characterization of Reduced and Oxidized Ga-Containing MFI Zeolite", K.M. Dooley, T. Guidry, G.L. Price, and V. Kanazirev.

Unlike the reactions of propane and larger paraffins, the aromatization of ethane is very sensitive to the balance between Ga-cations and protons within an MFI zeolite. We have found that this balance can be greatly affected by oxidizing or steaming pretreatments, and also by the presence of H_2O , CH_4 , CO_2 or O_2 in small amounts during the reaction. FTIR and thermal analysis techniques were used to determine their effects on the relative amounts of Ga as intrazeolitic cations of the type Ga^+ or GaO^+ vs. Bronsted sites.

Publications

"Thermal Analysis of Adsorbed Propanamines for the Characterization of Ga-MFI Zeolites," V. Kanazirev, K.M. Dooley, and G.L. Price, J. Catal. 146, 228 (1994).

"Change in the Decomposition Mode of 1-Propanamine due to the Presence of Cations in MFI Zeolite," V. Kanazirev, G.L. Price, and K.M. Dooley, Catal. Lett. 24, 227 (1994).

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