Gallium Zeolites for Light Paraffin Aromatization

Final Report

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Geoffrey L. Price and Kerry M. Dooley
Department of Chemical Engineering
Louisiana State University
Baton Rouge, LA 70803

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Research Progress

Research progress for this project is described beginning with a rather simple overview followed by a more detailed listing of the progress in terms of the papers and presentations resulting from this project. The papers are listed below along with a short description of the contents of each paper.

I. Overview of Research Progress

The primary original goal of this project was to investigate the active state of gallium-containing MFI catalysts for light paraffin aromatization, in particular the state of gallium in the active material. Our original hypothesis was that the most active and selective materials were those which contained gallium zeolitic cations, and that previously reported conditions for the activation of gallium-containing catalysts served to create these active centers. We believed that in high silica materials such as MFI, ion-exchange is most effectively accomplished with metals in their 1+ oxidation state, both because of the sparsity of the anionic ion-exchange sites associated with the zeolite, and because the large hydration shells associated with aqueous 3+ cations hinder transport. Metals such as Ga which commonly exist in higher oxidation states need to be reduced to promote ion-exchange and this is the reason that reduction of gallium-containing catalysts for light paraffin aromatization often yields a dramatic enhancement in catalytic activity. We have effectively combined reduction with ion-exchange and we term this combined process "reductive solid-state ion-exchange". Our hypothesis has largely been proven true, and a number of the papers we have published directly address this hypothesis.

As originally proposed, we have studied materials prepared by several different methods, including impregnation of gallium salts on H-MFI, solid-state ion-exchange of Ga_2O_3 with H-MFI, and gallosilicates with the MFI structure. We have found that, in their most active state, all can be shown to consist of Ga zeolitic cations rather than well dispersed gallium species not directly associated with the zeolite. A number of different techniques have helped establish this fact, but our most important observations deal with the determination of H^+ cations which must be replaced by Ga during the activation procedure. Infrared analysis has shown clearly that virtually all H^+ cations are eliminated when Ga-containing H-MFI is reduced at 500-600 °C in H_2 , but further infrared studies focusing on the effects of O_2 and H_2O on the reduced materials have shed new light on the interactions of Ga and protons, and how these interactions can lead to a bifunctional mechanism of light paraffin aromatization. Traces of O_2 or H_2O cause -OH bands characteristic of strong Bronsted sites to reappear in reduced materials, and kinetic measurements show that similar treatments cause a boost in activity of reduced materials.

The investigation of the fate of the protons has also led to exciting discoveries associated with amine thermal desorption from cation-containing MFI, and in fact, these discoveries are best

described as a new avenue of research work. More details are provided below. We have recently extended ion-exchange theories to gallosilicates with the MFI structure, and the Ga/H-MFI ion-exchange has been studied to the point that we can use weight changes associated with the ion-exchange process to determine framework and extraframework gallium content.

Another exciting extension of this project deals with zeolitic cations other than Ga which may also be introduced into H-MFI and other zeolites by reductive solid-state ion-exchange. Indium was an obvious choice because of its close relationship to gallium in the periodic table, but its catalytic properties have not proven to be interesting from a commercialization standpoint. However, it is an interesting cation for comparing with gallium. In particular, $\text{In}_2\text{O}_3/\text{MFI}$ undergoes reductive solid-state ion-exchange more easily than $\text{Ga}_2\text{O}_3/\text{MFI}$, and so the ratio of In^+/H^+ cations in these materials can be higher. Of greater interest has been the application of reductive solid-state ion-exchange to copper on MFI. Theoretically, we can achieve copper loadings of twice the aqueous ion-exchange limit, and these materials have potential application in several NO_x control strategies. Cu-MFI also gives a very good yield of aromatics from propane when initially placed on stream, prior to substantial reduction of copper by the hydrocarbon feedstock. This behavior has led us to speculate that there may be a role for the Cu-MFI catalyst in other hydrocarbon conversion reactions.

One of the most difficult questions we have tackled in this project relates to the wide range of pretreatment conditions which have been reported as being effective for the activation of gallium-containing materials. Our infrared experiments have helped sort out the important aspects of this question. We believe that the purpose of reduction is to disperse the gallium and place it in cation locations in the zeolite, but this reduction process also occurs gradually upon contacting the catalyst at reaction conditions with a light paraffin feedstock. Direct H_2 reduction results in both the conversion of Ga from 3+ to 1+ oxidation state and in the replacement of protons in the zeolite. The replacement of protons can have a negative effect on the overall activity of the catalysts because of their participation in a bifunctional conversion mechanism. However, traces of water or oxygen restore proton acidity in these materials, and activity can therefore be restored. Thus, the Ga/H+ ratio at reaction conditions is the most important parameter affecting overall activity, and various pretreatment conditions which are reported to improve activity are most likely related to influences upon this important parameter. We also have considered the question of what type of reaction mechanism might be operative in the case of materials that have extremely high Ga/H+ ratios and are therefore unlikely to operate as true bifunctional catalysts.

As mentioned previously, a new avenue of research work on the thermal desorption of alkylamines has evolved. Our original venture into this area was intended solely to determine the extent of proton replacement by gallium in these catalysts. Many previous studies on the thermal desorption of light alkylamines have established that the proton content of zeolites may be measured by taking advantage of the formation of a relatively stable alkyl ammonium cation at the proton sites. Weakly bound adsorbate not associated with protons can be selectively desorbed at low temperatures without affecting the alkyl ammonium cations associated with protons, and a measurement of the amount of the strongly bound fraction then provides the number of proton sites. We therefore decided to use this method to determine how many protons were replaced by gallium in our materials, but we

discovered that gallium cations interact with the light alkylamines and catalyze dimerization and dehydrogenation at relatively low temperatures. In effect, we have discovered direct evidence that cations other than protons are in place in the zeolite, and the characteristics of the thermal desorption process are indicators of the cation content of the zeolite. Nitriles and imines are products of the dimerization/dehydrogenation reactions that take place on gallium and these reactions have not been reported previously. We have also been able to show similar effects when protons are replaced by indium and copper.

Some other discoveries also deserve mention. First, we have proven the method of reductive solid-state ion-exchange for zeolites other than MFI, including Beta-zeolite and Mordenite. We have also discovered that the presence of O_2 during the thermal treatment of zeolites which contain organic templating agents causes that formation of a residue which must be burned off by extended thermal treatment in O_2 . Thermal treatment in the absence of O_2 is much cleaner, and this suggests a simpler method for the activation of "as-synthesized" zeolites. Finally, we have discovered a short-lived boost in catalytic activity when methane is added to a light paraffin feedstock over Ga-containing MFI. This discovery is particularly intriguing in relationship to catalytic methane activation and continued research in the cause of this effect is warranted.

II. Publications and Presentations

A. Papers in Print

1. K. Dooley, C. Chang, V. Kanazirev, and G. Price, "Pretreatment Effects on Active State and Aromatization Activity of Ga/ZSM-5 Catalysts", Studies in Surface Science and Catalysis 75, 2415-2418 (1993).

Recent work on Ga-containing ZSM-5 has shown that H_2 -reduced Ga_2O_3 /ZSM-5 mixtures are active and selective for propane aromatization. Extraframework Ga in ZSM-5 enhances rates of olefin and diene dehydrogenation; Ga_2O_3 or steamed gallosilicates aromatize olefins and dienes at 500-600°C. The dispersion and oxidation state of Ga affect the relative rates of dehydrogenation and cracking. The aims of this work were to show that Ga-exchanged materials fall into our theory on Ga reduction and that, although reduction disperses Ga, the form of the catalyst best for aromatics production may not consist of Ga^+ cations.

2. V. Kanazirev, K. Dooley, and G.L. Price, "Thermal Analysis of Adsorbed Propanamine for the Characterization of Ga-MEL Zeolites," Journal of Catalysis 146, 228-236 (1994).

Gallium-containing forms of MFI zeolite have been subjected to adsorption of 1- and 2-propanamine, and the results of subsequent thermal treatment have been analyzed and compared to literature reports for propanamine adsorbed on proton forms of MFI. Zeolitic gallium cations show completely different behavior from zeolitic protons, including a propanamine decomposition mechanism which is different from Hofmann elimination. In this mechanism, NH_3 is desorbed at temperatures as much as 160K below that of H-MFI. Major differences in the decomposition chemistry of the two amines were also

observed when Ga cations were present.

3. V. Kanazirev, G.L. Price, and K. Dooley, "Change in the Decomposition Mode of 1-Propanamine due to the Presence of Cations in MEL Zeolite", Catalysis Letters **24**, 227-233 (1994).

The adsorption and thermal analysis of 1-propanamine has been compared over MFI zeolites which contain H, Ga, and In cations. In the case of H⁺-containing materials, NH₃ and propene are simultaneously desorbed above 600K. This behavior is well known and characteristic of the Hofmann elimination reaction. However, a distinctly different mode of reaction is observed in the case of Ga and In containing materials. NH₃ is released below 600K, propene and other products are released above 600K, and a stable residue remains above 800K. It is suggested that such behavior results from Lewis acid interactions of Ga or In cations with propanamine.

4. V. Kanazirev, G.L. Price, and K. Dooley, "On the Interaction of 1-Propanamine with Cation Containing MFI Zeolite", Journal of Catalysis, **148**, 164-180 (1994).

The interaction of 1-propanamine (1-PA) with H-MFI zeolite and its Ga, In and Cu modifications, prepared by solid-state ion-exchange, has been studied by thermal analysis (TA), high resolution gas chromatography (HRGC), mass spectrometry (MS), and catalytic reactor experiments. Two completely different desorption features have been observed when the H-MFI sample is first equilibrated with 1-PA at 323 and 593K respectively and then heated to 823K. These desorption features have been ascribed to the decomposition of propylammonium and dipropylammonium (DPA) ions adsorbed at the proton sites of the zeolite. Catalytic experiments confirmed dipropylamine as the major product of 1-PA conversion at 593K over an H-MFI catalyst. In contrast, a radical change in the interaction of 1-PA with the zeolite has been observed as a result of the replacement of the protons in MFI with Ga, In or Cu cations. More than one 1-PA molecule can be coordinated to a cation even at relatively high temperatures, facilitating both bimolecular transalkylation and dehydrogenation processes. The desorption features of 1-PA with cation containing MFI differ generally from those of pure H-MFI zeolite. NH₃ product is desorbed at temperatures as much as 160K below that of H-MFI. Nitriles, C₂-C₆ hydrocarbons and some aromatics appear in appreciable amounts in the decomposition products. Gas-phase hydrogen inhibits the dehydrogenation processes and prevents the formation of a residue.

Catalytic experiments in a gradientless batch recirculating reactor have revealed that different dehydrogenation reactions predominate depending on the nature of the zeolitic cation. While a C₆-imine appears as a major product of the reaction of 1-PA over In-MFI, more dehydrogenated N-containing compounds such as propionitrile and a C₆-nitrile predominate over Ga-MFI and Cu-MFI respectively. These differences can be interpreted in terms of the differing Lewis acid strengths and reducibilities of the Ga, In and Cu cations.

5. V. Kanazirev and G.L. Price, "Activity of Ga, In and Cu Modified MFI Zeolites for Amine Reactions", in *Zeolites and Related Microporous Material: State of the Art*, J. Weitkamp, H.G.

Karge, H. Pfeifer and W. Hoelderich (Eds.), Studies in Surface Science and Catalysis, 84, 1935-1942 (1994).

High densities of Ga, In and Cu cations (Me/Al~1) in MFI zeolites have been obtained via thermal treatment of mechanical mixtures of metal oxides with H-MFI resulting in solid-state ion-exchange. Ga and In require an H_2 reducing agent during thermal treatment while Cu requires only an absence of O_2 and undergoes autoreduction during thermal treatment. Using both thermal analysis with MS detection and catalytic testing in a gradientless batch recirculating reactor, the modified catalysts have been shown to be highly reactive towards amines. The desorption features of 1-propanamine with cation containing MFI generally differ from those of pure H-MFI zeolite. Propanenitrile, C_2-C_6 alkenes and aromatics appear in the decomposition products. Catalytic experiments have revealed that Ga, In, and Cu zeolitic cations promote dehydrogenation and condensation reactions of propanamine to different extents. Such behavior probably results from Lewis acid interactions of the zeolite cation with the amine.

6. V. Kanazirev and G.L. Price, "Propane Conversion on Cu-MFI Zeolites", Journal of Molecular Catalysis A:Chemical, 96(2), 145 (1995).

A highly exchanged copper-containing MFI zeolite can be prepared by thermal treatment of CuO/H-MFI mechanical mixtures at 973K in an O_2 free environment. This material effectively catalyzes aromatization reactions of light paraffins and olefins. An unusually high selectivity for benzene is observed during propane conversion. The preparation technique appears to allow replacement of virtually all zeolitic protons with Cu^+ ions. The high temperatures and presence of H-MFI favor the conversion of Cu^{2+} to Cu^+ so the process is termed "reductive solid-state ion-exchange".

7. G.L. Price, V. Kanazirev and D.F. Church, "Formation of Cu-MFI NO Decomposition Catalyst via Reductive Solid State Ion Exchange", Journal of Physical Chemistry, 99, 864 (1995).

High temperature treatment of a mechanical mixture of CuO and H-MFI zeolite in the absence of O_2 produced a Cu ion-exchanged zeolite catalyst with a high activity for the catalytic decomposition of NO to N_2 and O_2 . Cu is probably introduced as Cu^+ cations in zeolitic ion-exchange sites via a solid-state ion-exchange process which includes CuO autoreduction to Cu^+ . ESR, 1-propanamine thermal desorption, and TPR characterization are consistent with this model. This preparation technique has a theoretical exchange limit of 1 Cu/framework Al which is double the limit theoretically imposed on Cu^{2+} exchange. The preferred preparation conditions give rise to a material which approaches this theoretical limit, and there are probably similarities between catalysts prepared by this method and "overexchanged" Cu^{2+} -MFI materials often reported for NO decomposition.

8. G.L. Price and V. Kanazirev, "Copper-Containing Zeolite Catalysts", U.S. Patent #5,583,081 (1996).

Copper-containing MFI zeolite can be prepared by high temperature solid-state ion-exchange of

H-MFI with a Cu(II) oxide or salt under conditions which promote the autoreduction of Cu(II) to Cu(I). Typically, CuO is intimately mixed with H-MFI zeolite at a Cu loading equivalent 1 Cu/framework-Al and the mixture is heated in a O₂ free environment at 973K for 16 hours. Loadings of Cu near 200% of the theoretical Cu(II) aqueous ion-exchange can be achieved.

The copper-containing MFI prepared by this technique is active for the catalytic decomposition of NO to N₂ and O₂ and is also useful for the dehydrodimerization of alkylamines to nitriles and imines.

9. G.L. Price, V. Kanazirev, and K.M. Dooley, "Characterization of [Ga]MFI via Thermal Analysis", *Zeolites* **15**, 725 (1995).

Gallosilicates isostructural with MFI ([Ga]MFI) with different SiO₂/Ga₂O₃ molar ratios were prepared by hydrothermal synthesis and subsequent calcination and conversion to the proton form. Microbalance weight loss determinations both upon H₂ reduction of the calcined [Ga]MFI's and upon reduction of the same materials mechanically mixed with Ga₂O₃, can be used as a simple method for the estimation of both framework and extraframework gallium. This thermogravimetric method is based on the reductive solid-state ion-exchange between any extraframework Ga₂O₃, whether present initially or added, and the protons associated with framework gallium. Thermal analysis (TA) of 1-propanamine (1-PA) was also found to be a sensitive test of the state of gallium in gallosilicates and also indicates that extraframework Ga in [Ga]MFI transfers into cationic positions upon H₂ reduction. Transfer of Ga into cationic positions results in an increase in the amount of 1-PA adsorbed near 600K during TA, compared to the proton form of the gallosilicate. Gallium cations also promote formation of a residue at the end of the TA experiment. There are indications that the extraframework Ga in [Ga]MFI ion-exchanges to a limited degree with protons during the calcination procedure.

10. K.M. Dooley, T. F. Guidry, and G.L. Price, "Control of Intrazeolitic Gallium Cation Content and It's Effects on C₂ Dehydrogenation in Ga-MFI Catalysts", *Journal of Catalysis* **157**, 66-75 (1995).

Ga-doped MFI zeolites are selective C₂ and higher alkane dehydrogenation catalysts. The balance between zeolite proton sites and exchanged Ga-cations, which is known to critically affect the formation of aromatics, is itself greatly affected by the extent of Ga-reduction, steaming, and treatment with oxidizers. Also, although the reaction can be inhibited by H₂ and CH₄, at short times on stream the presence of CH₄ can in some cases enhance the formation of aromatics. The reaction of ethane at low alkane pressures has been used to separate these effects from site deactivation by coking. The kinetics studies were supplemented with site characterization experiments, including thermal analysis of adsorbed 1-propanamine, TPO of the carbonaceous residues, XRD, and FTIR of the catalyst and of adsorbed 1-propanamine. These studies show that at reaction conditions, small quantities of H₂O and/or O₂ can transform intrazeolitic Ga-cation sites back to protons and gallium oxide. This transformation inhibits aromatics formation except for low levels of regenerated Bronsted acid sites; under these conditions, the yield to aromatics can actually be higher. The results are interpreted in terms of the dual-function mechanism for alkane dehydrogenation.

11. G.L. Price, V. Kanazirev, K.M. Dooley, and V.I. Hart, "On the Mechanism of Propane

Dehydrocyclization over Cation-Containing, Proton-Poor MFI Zeolite", Journal of Catalysis, **173**, 17-27 (1998).

The mechanism of propane aromatization over the proton form of MFI and MFI which contains both protons and other cations such as Ga has been studied and reported previously. A bifunctional mechanism has gained favor for catalysts which contain both protons and another cation, but little has been published which focuses on the action of MFI which contains a catalytically active cation such as Ga but is virtually devoid of protons. Ga-, In-, and Cu-containing MFI catalysts have been prepared such that as many of the protons as possible have been replaced, and the catalytic action of these materials for propane aromatization have been compared to purely proton forms of MFI. A propagation mechanism which operates without the action of protons is proposed.

12. V. Kanazirev and G.L. Price, "The Effect of O₂ on the Thermal Activation of Zeolite Beta", Journal of Catalysis **161**, 156-163 (1996).

The process of converting "as-synthesized" zeolites which contain organic templating agents generally begins by calcining the material to remove the organic material. Most often, this initial calcining step is performed in the presence of O₂ which is thought to help burnout residue which forms during the thermal breakdown of the organic template. We have discovered that O₂ promotes the formation of residue from tetraethylammonium ions in zeolite beta (BEA), probably by participating directly in a polymerization process. This discovery has also been extended to tetrapropylammonium ions in MFI and to simple amine adsorbates such as 1-propanamine adsorbed on acid sites in both BEA and MFI. We therefore believe that this is a general rule which may be applied to all amine templates in zeolites.

A more efficient route to organic template removal is to first calcine the material in the absence of O₂ so that the polymerization process which involves O₂ is suppressed. This results in a material which has only a trace of residue which can be removed by heating briefly in O₂ at a moderate temperature. Materials initially calcined in O₂ require either a lengthy treatment at a moderate temperature or a shorter treatment at a higher temperature to completely remove the residue.

13. G.L. Price and V. Kanazirev, "Guest Ordering in Zeolite Hosts", Zeolites **18**, 33-37(1997).

Specific features of the thermal desorption spectra of alkanamines in fully protonated zeolite hosts such as H-MFI and H-BEA can be attributed to short range alkanamine ordering. Each zeolitic proton strongly binds one amine molecule upon formation of an alkyl ammonium ion. A second molecule can attach to an acidic hydrogen of the alkylammonium ion, but steric constraints can eliminate this mode of adsorption, even though the bonding is stronger than hydrogen bonding which exists in solution. More than two amine molecules may participate in the formation of amine chains anchored at a proton site. The length of these chains is determined by the properties of the amine, zeolite structure, zeolite pore volume, and acid site density. Since control of each property is possible, strategies for specific short range interactions may be developed, and long range interactions may be further developed. Long range ordering of guest molecules in host materials such as zeolites are important in creating new materials.

14. K.M. Dooley, G.L. Price, V.I. Kanazirev, and V.I. Hart; "Gallium-Loaded Zeolites for Light Paraffin Aromatization: Evidence for Exchanged Gallium Cation Active Centers", Catalysis Today 31, 305 (1996).

This paper is a review of the various conditions by which "segregated" materials (defined as those which initially exist as a metal-containing phase and zeolite phase) undergo transformation to "unsegregated" materials (defined as a single phase) in the particular case of gallium-containing zeolites. The ramifications on the proton populations and relation to catalytic activity and selectivity is discussed.

B. Presentations

1. K. Dooley (speaker), C. Chang, V. Kanazirev, and G. Price, "Pretreatment Effects on Active State and Aromatization Activity of Ga/ZSM-5 Catalysts", Tenth International Congress on Catalysis, Budapest, Hungary, 1992.
2. V. Kanazirev (speaker) and G.L. Price, "Activity of Ga, In and Cu Modified MFI Zeolites for Amine Reactions", Tenth International Zeolite Conference, Garmisch-Partenkirchen, Germany, July 1994.
3. G.L. Price (speaker) and V. Kanazirev, "n-Propylamine Desorption from Ga-MFI", Proceedings of the AIChE National Meeting, Houston, TX, 1993.
4. G.L. Price (speaker), "Ga Zeolites for Light Paraffin Aromatization", Ninth DOE/BES Heterogeneous Catalysis and Surface Chemistry Meeting, Milwaukee, WI, May 1994.
5. K.M. Dooley (speaker), T.F. Guidry, V.I. Hart, L. Butler, V. Kanazirev, and G.L. Price, "Control of Intrazeolitic Ga and In Cation Content and its Effects on Alkane Dehydrogenations in Pentasils", Southwest Catalysis Society Fall Symposium, Houston, TX, November 1994.
6. K.M. Dooley (speaker), T.F. Guidry, V.I. Hart, L. Butler, V. Kanazirev, and G.L. Price, "Control of Intrazeolite Ga and In Cation Content and its Effects on Alkane Dehydrogenations in Pentasils", 14th North American Catalysis Society Meeting, Snowbird, Utah, June, 1995.
7. G.L. Price (speaker) and V. Kanazirev, "The Effect of Oxygen on the Thermal Activation of Zeolites", Proceedings of the AIChE Annual Meeting, paper #59ag, Miami Beach, FL, November, 1995.
8. G.L. Price (speaker) and V. Kanazirev, "Reductive Solid-State Ion-Exchange of CuO with H-MFI", Proceedings of the AIChE Annual Meeting, paper #82g, Miami Beach, FL, November, 1995.
9. G.L. Price, "Reductive Solid-State Ion-Exchange of Zeolites", Engelhard Corporation,

Beachwood, OH, January, 1996.

10. G.L. Price, "Reductive Solid-State Ion-Exchange of Zeolites", University of Missouri - Rolla, April, 1996.