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Activity of Ga, In and Cu modified MFI zeolites for amine reactions

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High densities of Ga, In and Cu cations ($\text{Me}/\text{Al}=1$) 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 HMFI zeolite. Propanenitrile, $\text{C}_2\text{-C}_6$ 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.

1. INTRODUCTION

Ion exchange of zeolites is roughly limited to a polyvalent cation density of one Me to three zeolitic anionic sites for atoms such as Ga^{3+} and In^{3+} due to the stoichiometry of the ion-exchange process. Recently, we have shown that this restriction can be circumvented by using solid state ion exchange between Me_2O_3 and H-MFI in presence of a reducing agent, such as H_2 [1-2]. A density of 1 Me/Al can be achieved since the oxidation state of the ingoing cation is reduced to 1^+ . In this paper we report that cation modified MFI catalysts prepared by such a process, which we term reductive solid state ion exchange (RSSIE), are highly reactive toward amines.

Alkanamines can react according to different pathways depending upon the catalyst and reaction conditions. Simple unimolecular decomposition of adsorbed alkanamines to an alkene and ammonia (Hofmann elimination) appears to be the sole reaction at low amine coverages over H-forms of zeolites [3-5]. This reaction has been successfully applied by Gorte and coworkers for the determination of the proton acidity. The authors showed the existence of stoichiometric 1/1 proton/amine complexes for propanamines interacting with Bronsted acid centers of H-MFI, isomorphously substituted MFI, and aluminophosphates [4-6]. Early work on H-zeolites has revealed that transalkylation of the alkanamines can also occur at low temperatures and a sufficiently high amine coverage [3]. Transalkylation and dehydrogenation

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of alkanamines proceed even more easily on oxide or metal catalysts [7-9]. Both ZrO_2 and ZnO finely dispersed in Na-ZSM-5 zeolite have been reported to promote the dehydrogenation reaction of alkanamines [10-11]. Studies on metal oxide catalysts have shown that the alkanamine molecules coordinatively bound to strong Lewis-acid centers are dehydrogenated and desorb as a nitrile at higher temperatures [12-13].

In the present investigation we provide evidence that the replacement of the protonic acid sites in MFI zeolite with certain cations radically alters the reaction pathways of propanamines compared to the corresponding H-zeolite.

2. EXPERIMENTAL

UOP MFI zeolite with $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio of 40 was used as the catalyst base material in a fully protonated form which we refer to as H-MFI. The H-MFI zeolite was ball-milled for 3 hours with the pure metal oxide at a loading equivalent of one metal atom per framework aluminum atom. We refer to the 1/1 Me/Al (Me = Ga, In or Cu) materials as Ga-MFI, In-MFI and Cu-MFI. Catalysts were pelletized, crushed and sieved to 0.4-0.8 mm prior to use. The solid state ion-exchange was performed by subjecting the samples first to a thermal treatment in He flow (100 cm^3) at 848K and then to H_2 reduction ($25 \text{ cm}^3/\text{min}$ H_2 and 75 cm^3 He) at 848 for 3h (Ga-MFI) and 623 for 1h (In-MFI). Cu-MFI was not subjected to H_2 reduction but treated in O_2 free He at 973 for 3h [14].

A Perkin-Elmer TGA-7 microbalance interfaced to an IBM personal computer was used to detect the weight change upon thermal treatment, H_2 reduction and thermal analysis (TA) of adsorbed 1-propanamine (1-PA). Parallel experiments were performed in a tubular reactor using a UTI 100C mass-spectrometry system and offline sampling into a GC to analyze the reactor effluent during the desorption/decomposition of 1-PA. Propanamines were also reacted in a gradientless recirculating batch reactor system utilizing 100mg catalyst. The circulation loop of the system was filled with 0.015 bar amine and 1.1 bar He and the reaction was started by diverting the circulating mixture through the reactor equilibrated at 593K. Samples were withdrawn periodically through a gas sampling valve and analyzed by an HP5890 II GC equipped with a 50m PONA capillary column and FID detector. Identification of components was performed by syringe injection of pure standards and by offline sampling into a GC/MS system. A detailed description of the experimental procedures is published elsewhere [15].

3. RESULTS AND DISCUSSION

Microbalance weight loss determination during the isothermal reduction of Ga-MFI and In-MFI revealed, in accordance with the previous TPR measurements [1-2], the occurrence of the following ion-exchange process:

The consumption of zeolite protons in the course of this process has been measured independently by TA of adsorbed 1-PA. The H-MFI and unreduced Ga-MFI samples showed similar features upon thermal analysis consisting of the simultaneous release of propene and ammonia as products of the decomposition reaction [16]. However, a radical change in the

Figure 1. Thermal analysis of adsorbed 1-propanamine on reduced catalysts (DTA - upper curves; TA - lower curves)

Figure 2. Comparison of intensities of selected ions during thermal analysis of 1-propanamine

decomposition mode is observed on reduced Ga-MFI sample. Figure 1 compares the TA curves of adsorbed 1-PA for H-MFI and H_2 reduced Ga-MFI and a material we term 0.5Ga-MFI which was prepared by loading Ga_2O_3 such that $Ga/Al=0.5$. The primary desorption feature in the H-MFI spectrum at 678K is characteristic of 1-PA desorption from Bronsted acid sites, while the Ga-MFI peak at 706K probably reflects the desorption process from Ga-cations acting as Lewis-acid centers. Two high temperature peaks of similar intensity at 681 and 712K are present in the case of the "half exchanged" 0.5Ga-MFI catalyst, strongly suggesting the separate interactions of 1-PA with both protons and Ga-ions of the zeolite. There are also other important differences between the 1-PA desorption features of H-MFI and Ga-MFI respectively. Much more 1-PA is held on the Ga-MFI catalyst, except for a slight capacity difference in the pore filling region below 450K, and a residue appeared as detected by the stable weight offset at 823K. We attribute all these features to the existence of relatively stable complexes between the Ga ions and propanamine molecules [16]. MS data presented in Figure 2 further evidence this phenomenon. Ammonia ($m/e=17$) and propene ($m/e=41$) do not evolve simultaneously during the TA of 1-PA on Ga-MFI. Ammonia desorbs almost completely at a temperature as low as 600K indicating the occurrence of bimolecular transalkylation of 1-PA upon release of NH_3 . Moreover, the

$m/e=41$ peak characteristic of propene is strongly attenuated and dehydrogenation reactions of the adsorbed 1-PA lead to a nitrile product as evidenced by the $m/e=54$ peak in Figure 2. No such peak has been observed for either H-MFI or unreduced Ga-MFI samples. GC analysis of samples taken from the reactor effluent during the TA experiment at temperatures of 670 and 690K for H-MFI and Ga-MFI respectively reveals that the evolving product consists of 92.5% propene and 7.5% C_2-C_6 alkenes with the H-MFI catalyst but 42.3% propanenitrile, 38.5 propene and 19.2% other hydrocarbons for the reduced Ga-MFI sample.

The high reactivity of the cation-exchanged MFI towards propanamine was further confirmed with the In-MFI and Cu-MFI catalysts. The most important feature that Ga, In and Cu zeolitic cations share is the ability to bring together more than one 1-PA molecule at a relatively high temperature. The basic features of the reduced Ga-MFI catalyst which included the evolution of NH_3 at low temperature, separated from propene, release of nitriles and occurrence of a residue at the final temperature of the TA experiment, could also be observed over In-MFI and Cu-MFI catalysts.

The reactivity of both H-MFI and cation-containing materials prepared by solid state ion exchange for amine conversion was investigated in more detail using a batch recirculating

Figure 3. Conversion of 1-propanamine on H-MFI

but is only about one tenth the DPA yield at identical reaction times. The formation of such alkylidenalkanamines has been previously reported during the catalytic conversion of alkanamines on alumina and has been ascribed to the specific action of Lewis-acid centers of the alumina catalyst [7-8]. Only a small amount of propanenitrile, another C_6 nitrile and some heavier N-containing compounds could be further identified among the reaction products at higher contact times. Figure 3 also indicates that hydrocarbon formation is slow compared to the transalkylation reaction which yields DPA. Propene appears as the first hydrocarbon product followed by hexenes which are probably formed through dimerization routes. C_6 hydrocarbons become the dominant product at contact times of 82.5 ks or larger.

The catalytic data for Ga-MFI depicted in Figure 4 provide convincing evidence of a new mode of 1-PA interaction with cation exchanged MFI zeolites. Analogous to the H-MFI

reactor. The product distribution for the conversion of 1-PA on H-MFI at 593K is shown as a function of time in Figure 3. Transalkylation of 1-PA leading to the formation of dipropanamine (DPA) as the primary reaction route over H-MFI results. The DPA yield goes through a maximum due to formation of hydrocarbons and heavier products at long contact times. The C_6 imine (N-propylidenpropanamine) yield parallels that of DPA

Figure 4. Conversion of 1-propanamine on Ga-MFI

conversion proceeds, propanenitrile eventually becomes the major product and the amount of the C₆ nitrile identified as the 2-methylpentanenitrile [16] increases steadily along with the production of hydrocarbons.

The product distribution as a function of time for the batch conversion of 1-PA on the reduced In-MFI is shown in Figure 5.

Figure 5. Conversion of 1-propanamine on In-MFI

consistent with observation of a large weight offset at the final temperature of the 1-PA thermal analysis experiment.

The importance of the dehydrogenation reaction over In-MFI was additionally studied with dipropanamine. Figure 6 shows that both dehydrogenation and transalkylation of DPA

sample, the formation of DPA is the primary process occurring at low contact times. Ga-MFI differs from H-MFI in that the production of DPA occurs faster, a C₆ imine is produced in larger quantities, and the C₆ imine appears to be an primary product of 1-PA conversion. The most pronounced difference between H-MFI and Ga-MFI lies in the promotion of specific dehydrogenation reactions by Ga-MFI. Figure 4 shows that as the 1-PA

reduced In-MFI is shown in Figure 5. The initial conversion of 1-PA is directed to DPA and C₆ imine as the primary products. Less propanenitrile and slightly more C₆ nitrile and hydrocarbons are produced compared to Ga-MFI. A comparison of the product yields for all three catalysts reveals that a large fraction of the 1-PA remains on the catalyst in the case of In-MFI which points to the occurrence of side reactions which yields a residue. This is

Figure 6. Conversion of dipropanamine on In-MFI

rearrangement of the C₆ imine intermediate but that the 1-PA directly participates in the mechanistic pathways leading to nitriles. In addition, less tripropanamine (TPA) is produced (mole ratio 1-PA/TPA of about 3 at 5ks) than expected from the stoichiometry of the transalkylation reaction. If the transalkylation reaction proceeds mainly on In ions located on the exterior of the MFI crystal, a 1-PA/TPA mole ratio close to 1 is expected.

Figure 7. Conversion of 1-propanamine on Cu-MFI

content continues to increase at high contact time and reaches 83% of the product at 254 ks. No saturated hydrocarbons, except traces of ethane, and no aromatics are present while the following hydrocarbon distribution is attained at the conclusion of the catalytic experiment:

are facile reactions accounting for the majority of the reaction products. An equilibrium is easily attained and side reactions such as hydrocarbon formation proceed along with minor changes in the yield of other alkanamines and C₆ imine products. Interestingly, the formation of nitriles is strongly suppressed suggesting that the mechanism of nitrile formation does not involve consecutive dehydrogenation and

Figure 7 depicts 1-PA conversion data for Cu-MFI zeolite. In contrast to all other catalysts under investigation, the 1-PA conversion on Cu-MFI leads largely to nitriles and hexenes during the initial stages of the reaction. The C₆ nitrile is a primary reaction product with a concentration of about twice that of both propanenitrile and hexenes. Only small amounts of DPA and C₆ imine and no methane are present among the products. The hydrocarbon

ethene 24.8%; propene 11.8%; butenes 6.6%; pentenes 17%; hexenes 39.8%. The role of Cu ions for the catalytic chemistry observed was further investigated by a separate experiment utilizing the same Cu-MFI catalyst which has been further subjected to H_2 reduction at 673K. Since H_2 would reduce the Cu ions to metallic copper and regeneration of the Bronsted acid sites is expected, radical changes in the product distribution of 1-PA conversion is anticipated. Indeed, the selectivity pattern in this experiment resembled that of the H-MFI catalyst; DPA reappeared as the major reaction product and a low yield of nitriles was registered even at high contact times.

The present study shows that the introduction of Ga, In and Cu ions into the MFI zeolite via reductive solid state ion exchange (RSSIE) promotes specific and sometimes unexpected catalytic transformation of alkanamines. Classic organic chemistry provides a number of analogies between the action of metal ions toward amines in solution and the interaction of amines with zeolite cations. Besides accepting protons from Bronsted acids, amines can also add to Lewis acids by sharing the free electron pair. The ability to coordinate metal ions is another well known characteristic of amino groups. Cu^{2+}/Y is an example of metal ion containing zeolite which is known to multiply coordinate amines in well defined complexes. However, it is difficult to determine the exact mechanism of 1-PA transformation on cation containing MFI because the different reaction pathways contributing to a very complicated reaction network. The formation of 2-methylpentanenitrile from 1-PA for example has, in our knowledge, never been reported and further investigations are still necessary to elucidate the mechanism of this interesting reaction.

We believe that the RSSIE approach based on H_2 reduction (Ga, In) [1-2] or autoreduction (Cu) [14] extends the scope of the classic solid state ion exchange (SSIE) reviewed by Karge and Beyer recently [17]. The ingoing element experiences a reduction in oxidation state from n^+ to 1^+ in the course of the ion exchange which enables every anionic site of the zeolite to be compensated by a single cation. This effect cannot be achieved by the common ion exchange methods since an M^{n+} cation accounts for the charge balance of n zeolitic anionic sites. Notice that the Ga, In, and Cu systems reported here are rather unique in the sense that they represent Me^{1+} systems that are virtually devoid of protons but, unlike the alkali metal zeolites (e.g., Na-MFI), have significant catalytic activity. Interestingly, Karge et al. have reported [18] that the complete replacement of the protons with La^{3+} in a Y zeolite does not lead in an active catalyst for cracking and transalkylation of hydrocarbons unless contacted with small amounts of water which results in the formation of proton sites. The authors concluded that the "bare" La^{3+} cations are not active sites for these reaction. In contrast, the catalytic pattern observed in this study can be attributed to the specific cation -amine interaction without participation of protons.

Finally, we are aware that very little is known about the properties of the Me^+ zeolite cations as Lewis-acid centers. Certainly the designation of these cation as Lewis-acid is only a rough simplification since the actual interactions including coordination and electron transfer with both zeolite framework and adsorbate may be more complicated than one can assume.

4. CONCLUSIONS

High densities of Ga, In and Cu cations ($Me/Al=1$) in MFI zeolites can be achieved by reductive solid state ion exchange (RSSIE) using H-MFI mechanically mixed with the respective metal oxide. The modified catalysts have pronounced activity in propanamine

transformation. Strong cation-amine interactions combined with the absence of proton acidity in the zeolite lead to a reaction network comprising dehydrogenation, transalkylation and condensation processes of the amine reagent. The potential of the cation containing zeolites to perform specific and sometimes unexpected transformations with amines may be exploited in the steadily growing field of organic synthesis on zeolite catalysts.

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