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Change in the decomposition mode of 1-propanamine due to the presence of cations in MFI zeolite

V. Kanazirev [1], G.L. Price and K.M. Dooley

Department of Chemical Engineering, Louisiana State University,
Baton Rouge, LA 70803, USA

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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, NH_3 and propene are simultaneously desorbed above 600 K. 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. NH_3 is released below 600 K, propene and other products are released above 600 K, and a stable residue remains above 800 K. It is suggested that such behavior results from Lewis acid interactions of Ga or In cations with propanamine.

Keywords: Zeolites; 1-propanamine; thermal analysis; gallium zeolites; indium zeolites

1. Introduction

Simple and rather reactive organic molecules such as propanamines have been recently proposed by Gorte and coworkers as a probe for characterization of Brønsted acid sites in zeolite [1–5], aluminophosphate [6,7] and silica–alumina catalysts [8]. Using a microbalance operated with simultaneous mass-spectral analysis under high vacuum, they demonstrated the formation of well-defined adsorption complexes of propanamines with the protons of the catalyst. These stoichiometric adsorption complexes decompose upon temperature programming yielding ammonia and propene via a reaction similar to the Hofmann elimination reaction. The approach advanced by Gorte and his group [1–8] seems to be very useful, especially for catalysts containing only Brønsted acid sites. However, it is well known that solid catalysts, including zeolites, often contain Lewis acid sites along with the protons. In a broad sense, the Lewis acid sites are represented by electron-accepting centers such as zeolite cations and tricoordinated Al atoms of the zeolite framework. Unfortunately, no attempt has been made to investigate

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[1] On leave from the Bulgarian Academy of Sciences, Institute of Organic Chemistry.

separately the impact of the zeolitic cations on the adsorption–desorption features of propanamine. Recently, we have found by thermal analysis experiments [9] that the introduction of Ga into MFI zeolite by impregnation alters significantly the interaction of the catalyst with propanamine.

In the present work, we have chosen a simple model system consisting of H-MFI zeolite mixed with a metal oxide with the aim of elucidating the extent to which the cations of the zeolite are interacting with propanamine. Using a single sample, the model system allows us to study two clearly defined states of acidity. Before reduction with H_2, the mechanical mixture behaves as a Brønsted acid due to the H-MFI component of the catalyst, while during reduction, the zeolitic protons are ion-exchanged with metal cations as has been proven in the case of Ga_2O_3 [10,11] and In_2O_3 [13] as cation sources. Thus, the interaction of propanamine with the metal cations can be separately evaluated.

2. Experimental

The preparation of the mechanically mixed catalyst has been described elsewhere [11]. Source materials were pure β-Ga_2O_3, In_2O_3, and a fully protonated MFI zeolite with SiO_2/Al_2O_3 mole ratio of 40 (Union Carbide). The weight content of Ga_2O_3 and In_2O_3 in the mechanical mixtures was 7.1 and 11% respectively which corresponds to a 1 : 1 ratio of the metal cation to framework aluminum. We designate the non-reduced mechanically mixed catalysts as Ga-MFI and In-MFI and the pure H-form as H-MFI. A Perkin-Elmer TGA-7 microbalance interfaced to an IBM personal computer was used to detect the weight change upon thermal treatment of adsorbed 1-propanamine (1-PA). About 15 mg of catalyst were used in the microbalance experiments with a total flow of 100 cm^3/min He during the thermal analysis experiment. Parallel experiments were performed in a tubular reactor using a mass-spectrometry system [15] to analyze the reactor effluent during the desorption/decomposition of 1-PA. About 50 mg of catalyst were used in this experiment with a He flowrate of 100 cm^3/min. To form the reduced materials, Ga-MFI was treated at 848 K with 25% H_2 in He while In-MFI was treated at 623 K. In the case of the In-modified sample, a lower reduction temperature of 623 K was chosen to avoid the possibility of reduction to In metal as determined in previous work [13,14]. Propanamine adsorption was performed at 323 K for 5 min using a saturator with liquid amine kept at room temperature and 50 cm^3/min He as a carrier gas. The propanamine stream was then further diluted with 50 cm^3/min pure He. The sample was subsequently purged with pure He at 323 K for 10 min and then the thermal analysis of the propanamine was performed by a linear temperature increase from 323 to 848 K at 5 K/min. Typically, each sample was first pretreated in pure He at 848 K, then the propanamine thermal analysis performed. The same sample was subjected to H_2 reduction and finally the propanamine thermal analysis experiment was repeated on the reduced material.

3. Results and discussion

Fig. 1 shows the thermogravimetric TG and DTG curves obtained after 1-PA adsorption on the H-MFI and Ga-MFI samples. The H-MFI and unreduced Ga-MFI samples reveal similar features upon thermal analysis, except that the Ga-MFI TG curve lies slightly below H-MFI. This slight difference results from the differing H-MFI contents of the two materials. In the mechanically mixed catalyst there is only 92.9 wt% H-MFI, the remainder consisting of β-Ga_2O_3, which can be considered an inert diluent. After H_2 reduction, however, the Ga-MFI behaves differently. The amount of weakly adsorbed propanamine which desorbs below 600 K is much less in the case of reduced Ga-MFI, so more adsorbate remains at 600 K. Also, we detect a residue present at the end of the experiment as a stable weight offset above 100 wt%.

The desorption experiments were then repeated using the tubular reactor-MS apparatus. In this work $m/e = 17$ is taken as characteristic of NH_3, $m/e = 41$ for propene, and $m/e = 59$ for 1-PA. However, it must be realized that $m/e = 41$ and $m/e = 17$ are also mass fragments of 1-PA, so as unreacted 1-PA desorbs, there will also be small contributions from $m/e = 41$ and $m/e = 17$ caused by fragmentation. In fig. 2a, for example, it is evident that the small broad peaks at $T < 550$ K for $m/e = 17$ and $m/e = 41$ completely parallel the large peak for $m/e = 59$ and therefore represent mass fragments of 1-PA, while the large peaks at >550 K greatly exceed the $m/e = 59$ baseline and therefore represent actual desorption of propene and NH_3. The mass-spectral data presented in fig. 2 clearly indicate that there is a radical change in the decomposition mode of propanamine for the hydrogen reduced sample. While the unreduced Ga-MFI (included in fig. 2) and H-MFI simultaneously release propene ($m/e = 41$) and ammonia ($m/e = 17$) as products of the decomposition reaction, the reduced sample releases almost all of the ammo-

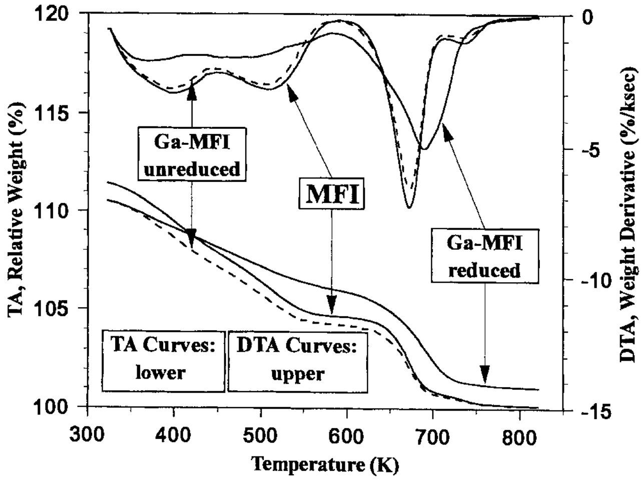

Fig. 1. Thermal analysis curves (lower: TA, upper: DTA) for 1-PA on the indicated catalysts.

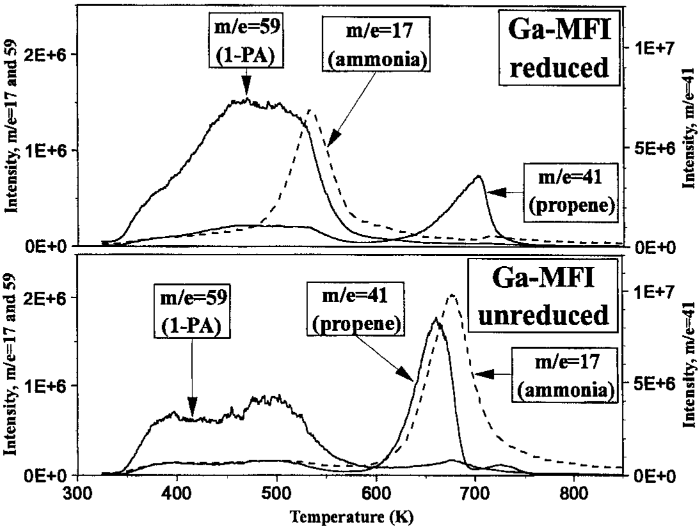

Fig. 2. Mass spectral analysis of the reactor effluent during thermal analysis of 1-PA on Ga-MFI reduced and unreduced catalysts.

nia at an unusually low temperature of 550 K. In addition, the propene band is shifted to a slightly higher temperature compared to the unreduced sample. The exchange of zeolitic protons with Ga ions via the reductive treatment [11,12] causes this change in mode of propanamine decomposition. Virtually no Brønsted acid sites are available in the reduced catalyst, because a high initial Ga_2O_3 loading results in virtually complete replacement of protons by Ga cations. Therefore, the decomposition of the adsorbed propanamine cannot follow the well-known Hofmann elimination route which proceeds through a propanammonium cation that forms at Brønsted sites.

The question arises as to whether or not the propanamine decomposition mode is characteristic only of Ga cationic centers in the zeolite or if other cations are capable of promoting this reaction. The results for reduced In-MFI shown in fig. 3 suggest that these observations are not restricted to gallium cations. The ammonia again appears as the first product of the decomposition reaction, at < 600 K.

At the present stage of our investigation, we can rationalize this phenomenon as the formation of a complex between unsaturated Ga or In cations, acting as Lewis-acid centers, and 1-PA as an electron-donating agent. In contrast to the 1 : 1 stoichiometric complex formed by interaction of propanamine with H^+ [1–8], more than 1 amine molecule per framework Al remains on the catalyst in the temperature range 500–650 K. Moreover, virtually complete evolution of ammonia from the reduced Ga-MFI sample occurs below 600 K, and the adsorbate remaining on the catalyst at 600 K corresponds to about 1.5 propanamine molecules per framework Al. We assume that at least one amine molecule is bonded directly to the cation:

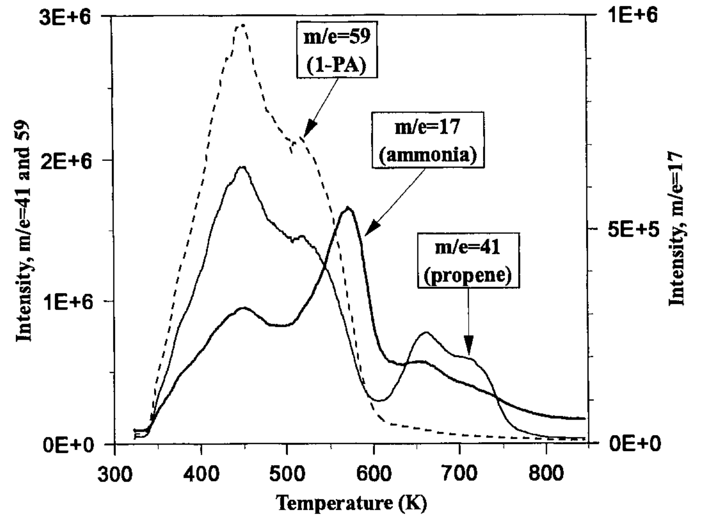

Fig. 3. Mass-spectral analysis of the reactor effluent during thermal analysis of 1-PA on reduced In-MFI catalyst.

$$C_3H_7NH_2 + Me^{n+}Z^{n-} \rightarrow (C_3H_7NH_2Me^{n+})Z^{n-} . \quad (1)$$

But we must also account for the adsorbate still present. Complexes of multiple propanamine molecules with metal salts are well known for more than one century [16] and cation-modified zeolites may act in the same manner when interacting with propanamine. Our data suggest that the thermal analysis process cannot be described as a simple unimolecular decomposition of the complex yielding NH_3 and propene, and thus restoring the initial $Me^{n+}Z^{n-}$ state of the catalyst. More likely a second propanamine molecule also interacts with the cation, and ammonia is the first product leaving the catalyst. A rough estimation based on the integrated intensities of $m/e = 17$ reveals about one half of the nitrogen in the adsorbed propanamine at 473 K is desorbed as ammonia in the first NH_3 peak at about 540 K in fig. 2b. The remaining nitrogen is either part of the stable residue at the end of the experiment (fig. 1) or leaves the catalyst as another N-containing compound. Indeed, if we use the MS to monitor masses characteristic of nitriles ($m/e = 26$ or 54) during the thermal analysis experiment, we detect bands which can be attributed to these species in the conversion of adsorbed propanamine. From fig. 4 it can be seen that in the case of the H-MFI catalyst these masses are for the most part not observed. In contrast, an intense peak with $m/e = 54$ is present during the thermal analysis of 1-PA on the reduced Ga-MFI sample. Propionitrile was confirmed as a major product of the decomposition reaction by GC analysis of samples taken from the reactor effluent during the TPD experiment. Thus the reaction of the adsorbed propanamine on cation modified zeolites such as Ga-MFI includes several steps. Both ammonia and propene are verified as major products, but other N-containing compounds such as nitriles are also present in the reactor effluent,

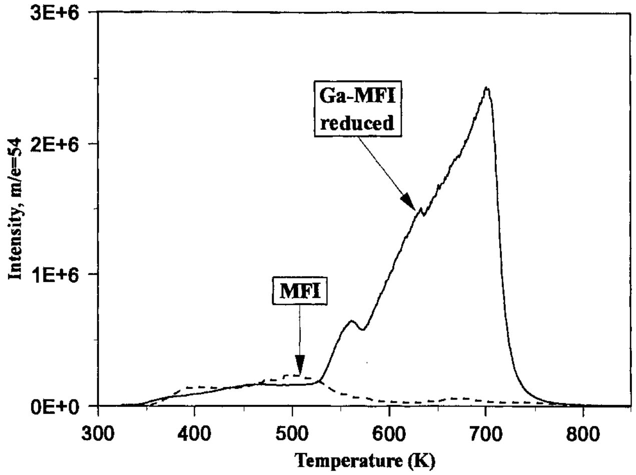

Fig. 4. Comparison of the mass 54 intensity for Ga-MFI and H-MFI thermal analysis of 1-PA.

and this might explain the residue which cannot be desorbed from the catalyst even at 843 K.

Finally, we should note that the decomposition mode of propanamine might be used qualitatively to distinguish between Brønsted centers and Lewis acid sites such as Ga and In cations when both are present in MFI zeolites. Further investigations are still necessary to elucidate the exact mechanism of this new decomposition route of propanamine.

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