

Propane conversion on Cu-MFI zeolites

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Received 15 June 1994; accepted 3 November 1994

Abstract

A highly exchanged copper-containing MFI zeolite can be prepared by thermal treatment of CuO/H-MFI mechanical mixtures at 973 K in an O₂ 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 Cu²⁺ to Cu⁺ so the process is termed 'reductive solid-state ion-exchange'. The participation of Cu⁺ cations in the aromatization mechanism is discussed.

1. Introduction

The conversion of short chain alkanes such as propane to aromatic hydrocarbons is an interesting example of catalytic chemistry which has recently attracted the attention of numerous researchers. MFI zeolite modified by Ga or Zn via techniques such as ion-exchange, impregnation, or mechanical mixing, are the most frequently studied catalysts for this process [1–7]. In addition, the production of aromatic hydrocarbons from light alkanes using Ga-containing MFI has been commercialized [8].

Mechanistic studies on the Ga-MFI system have provided evidence of a synergistic effect of the Brønsted acid centers of the zeolite and dispersed gallium species in the aromatization reaction [9–13]. In our previous work on Ga₂O₃/H-MFI mechanically mixed catalysts

[5,10,14,15], we have shown that when treated with H₂ at 700–900 K or a light hydrocarbon feedstock, Ga₂O₃ directly interacts with the acidic zeolite and Ga⁺ replaces protons resulting in the formation of cationic gallium species. Hence, the catalyst cannot be considered as a simple mixture of an dehydrogenating component (Ga₂O₃) and an acidic counterpart (H-MFI). Moreover, there exists a question of whether or not the cationic gallium or zinc species catalyze specific reaction steps other than the dehydrogenation of the propane reagent. In a recent publication, Ono et al. [16] showed the occurrence of solid-state ion-exchange between ZnO and H-MFI zeolite and suggested the crucial role of Zn²⁺ cations for isobutane activation, not only with respect to enhanced dehydrogenation, but also for C–C bond cleavage. In contrast, the complete replacement of the zeolitic protons by cationic indium via solid-state ion-exchange has been found to completely suppress n-pentane conversion [17]. Kwak and Sachtler [12] reached a similar conclusion while

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studying propane aromatization on $\text{GaCl}_3/\text{H-MFI}$ catalysts prepared by chemical vapor deposition of GaCl_3 into the pores of H-MFI. The complete replacement of H^+ with gallium resulted in a catalyst with no activity for propane aromatization.

Early research efforts recognized that alkali metal exchanged MFI zeolites were ineffective as propane aromatization catalysts even after Ga or Zn addition. Alkali-containing MFI zeolites, however, slowly catalyze the formation of aromatics from propene with a selectivity for benzene production which is higher than the selectivity of Ga-containing H-MFI [18]. Acid–base pairs of the alkali metal cation and the neighboring basic oxygen anions were suggested as the active site for this olefin aromatization reaction. Ono and coworkers [6,19] have also concluded that Zn or Ga cations are the active sites for the aromatization of alkenes when weakly acidic borosilicates were used as the base zeolite.

In this paper, we show that Cu-modified MFI zeolite is highly active and selective for the dehydrocyclodimerization reaction of propane. Our discovery of this catalytic reaction stems from the observation that aromatics were major products of the thermal analysis of adsorbed 1-propanamine on Cu-MFI zeolites prepared by reductive solid-state ion-exchange (RSSIE) [20,21].

2. Experimental

2.1. Catalyst preparation

H-MFI zeolite (fully protonated) with an overall elemental $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 26 was obtained from PQ (CBV-3020, Lot ZH-35). The H^+ content of the sample was determined by 1-propanamine thermal desorption [20] and the value of $746 \mu\text{mol H}^+/\text{g}$ dry zeolite was estimated which corresponds to $43 \text{ SiO}_2/\text{framework-Al}_2\text{O}_3$ assuming $\text{H}^+/\text{framework-Al}=1$. The H-MFI zeolite was mechanically mixed with CuO powder (Aldrich 99% reagent grade) at a ratio of $\text{Cu}/\text{H}^+ = 1$ (5.7 wt% CuO on a dry zeolite basis). Mechanical mixing was performed in a ball-mill

with 65 stainless steel balls which was rotated at 1.4 Hz for 6 h. The powdered product was then pelletized, crushed and sieved to 35–60 mesh particles. This sample we designate as CuO/H-MFI. Cu was driven into the zeolite via solid-state ion-exchange which was accomplished by thermal treatment in a controlled environment tubular calcining furnace [20]. To avoid deep bed steaming, about 20 g CuO/H-MFI was spread flat on a quartz tray at $<0.2 \text{ g}/\text{cm}^2$ and purged with $200 \text{ cm}^3/\text{min}$ Ar which was passed through a trap of copper shavings thermostated at 773 K to remove trace O_2 . Thermal conditions were: ambient to 393 K in 0.2 h, hold 393 K for 1.5 h, 393 to 973 K in 3 h, hold 973 K for 16 h, then cool to ambient. We refer to the thermally treated material as Cu-MFI. The sample was stored without special precautions to avoid contact with air, so samples were heated in pure He or evacuated at 848 K for 0.5 h just before use in adsorption or catalytic experiments.

2.2. Thermal analysis of 1-propanamine

Thermal analysis (TA) of 1-propanamine (1-PA) with product detection by mass spectrometry (MS) was performed with 17–20 mg sample placed in a coaxial quartz tubular reactor as described previously [20,22]. The sample was purged with $100 \text{ cm}^3/\text{min}$ He flow while the temperature was increased from 298 to 848 K at $10/\text{K min}$ with a final hold of 15 min, followed by rapid cooling to 323 K just prior to amine adsorption. The sample was then briefly evacuated and 0.2 bar 1-PA was allowed to adsorb for 10 min. The catalyst was then evacuated for 10 min and He flow was restored to purge the reactor. TA of 1-PA was carried out via temperature programming from 323 to 823 K at $5 \text{ K}/\text{min}$. The reactor effluent was analyzed continuously using a UTI 100C mass spectrometer operated in EI mode at 70 eV. Off-line samples from the reactor effluent were also injected in an HP 5890 II GC described below in the catalytic reactor system section.

2.3. Determination of bulk CuO_x by temperature programmed reduction

Temperature programmed reduction (TPR) experiments to detect bulk CuO_x in the zeolite samples were carried out in a Perkin Elmer TGA-7 microbalance equipped with gas and adsorbate supply system as described elsewhere [20]. The sample (10–15 mg) was first dried in He (100 cm^3/min) by heating from ambient to 848 K at 20 K/min then cooled quickly to 323 K. After a short equilibration in a flow of 25 cm^3/min H_2 and 75 cm^3/min He at 323 K, the temperature was raised to 848 K at 20 K/min and a weight decline corresponding to reduction of CuO_x to Cu metal was detected. Pure samples of CuO and Cu_2O (Aldrich) were used as standards to compare with TPR features of the copper-containing samples.

2.4. Catalytic reactor experiments

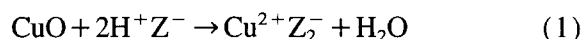
Catalytic reactor experiments were performed in a gradientless recirculating batch reactor system described elsewhere [23]. Typically, 25 mg of catalyst was placed in a quartz reactor surrounded by an electrically heated furnace with temperature control. The circulation loop consisted basically of a magnetically operated piston pump, check valve arrangement, mixing volume, and reactor which could be evacuated. In a typical experiment, the catalyst was first evacuated (1 Pa) and then heated under vacuum at 423, 573 and 823 K for 0.5 h at each temperature. Then about 114 kPa He was admitted to the reactor section and the reactor was isolated and brought to the reaction temperature of 748 K. The circulation loop was filled with about 14 kPa propane and 100 kPa helium and the reaction was then started by diverting the circulating mixture through the reactor. Samples were withdrawn periodically through a traced line to the evacuated loop on a gas sampling valve of an HP 5890 II GC equipped with a 50 m PONA capillary column, FID detector and cryogenic operation. Matheson instrument grade propane was additionally purified by freeze–evacuate–thaw cycles and 0.01 wt% propene and 0.04 wt%

isobutane were determined to be the only impurities in the final propane reagent. Propene gas (Matheson) contained about 0.015 wt% propane and was utilized without further purification.

3. Results and discussion

3.1. Evidence of reductive solid-state ion-exchange of Cu into H-MFI

The pioneering work of Kucherov and Slinkin [24] resulted in a novel solid-state ion-exchange process that occurs according to:



where Z^- is an anionic zeolite site

Subsequent investigations by Karge et al. [25] revealed that the rather difficult deaggregation of CuO limits this process to the consumption of only about 25% of the hydroxyl groups of H-MFI during thermal treatment in vacuum at 770 K for up to 21 h. By applying considerably higher temperatures up to 1000 K and an O_2 free environment, we have reached much higher loadings of Cu on MFI [20,21]. We term this process reductive solid-state ion-exchange (RSSIE) since the auto-reduction of CuO is thought to be a crucial step in the process mechanism which we represent in a simplified manner by:

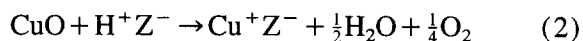


Fig. 1 illustrates the reduction of bulk CuO and Cu_2O by TPR which we have applied as a technique for the determination of bulk CuO_x in our copper-containing catalysts. DTA peaks specific for H_2 reduction of CuO and Cu_2O can be clearly seen in Fig. 1 and the observed weight loss in both TA curves strictly obey reduction to metallic copper:

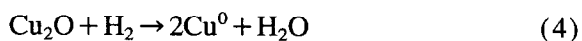


Fig. 2 compares the TA and DTA curves for pure H-MFI, CuO/H-MFI and Cu-MFI. As expected,

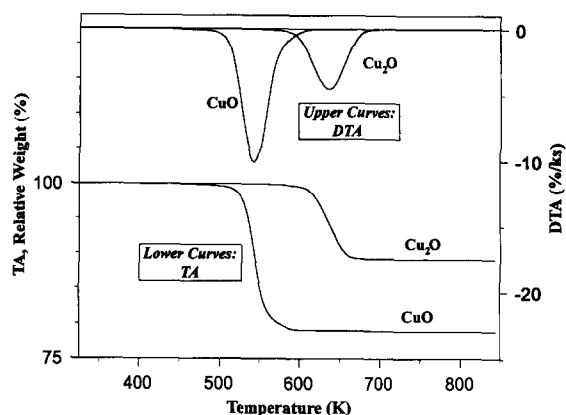
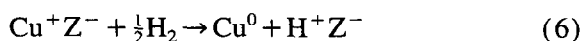
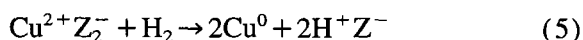


Fig. 1. Thermal analysis of bulk CuO and Cu₂O standards in 25% H₂/75% He reagent gas.

no specific weight loss due to reduction was observed with the H-MFI sample, while CuO/H-MFI and Cu-MFI show only the presence of bulk CuO (no Cu₂O) but in substantially different amounts. For the CuO/H-MFI sample (which was heated briefly to 848 K), 86% of the initial CuO was present. But for Cu-MFI (heated to 973 K for 16 h), only 13% of the original CuO remained. This is a clear evidence that the high temperature treatment stimulates the solid-state ion-exchange. The CuO exchanged in the CuO/H-MFI sample corresponds to the exchange of 28% of the proton sites in H-MFI if the Cu²⁺ mechanism (Eq. 1) is operative. This value is similar to the 25% consumption of protonized hydroxyls reported by Karge et al. [25] for CuO/H-MFI mixtures which were heated at somewhat lower temperatures but for a longer duration. The same calculation for the Cu-MFI sample, however, gives a value of 174% for Cu²⁺ exchange which is far above the stoichiometric limit imposed by Eq. 1. Since reduction of Cu zeolitic cations is expected to be given by:



and Eqs. 5 and 6 are expected to yield virtually no weight change, the reductive solid-state mechanism (Eq. 2) is the only one which can explain the observed weight changes in the TPR experi-

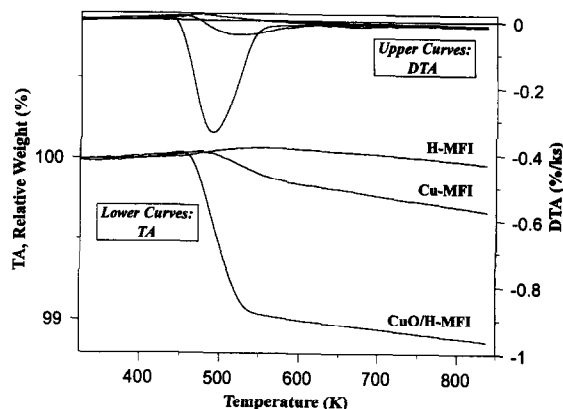


Fig. 2. Determination of bulk CuO_x by thermal analysis in a 25% H₂/75% He reagent gas.

ment and such high conversion levels of CuO in the Cu-MFI sample.

Eq. 2 suggests that the presence of O₂ in the gas phase will shift the reaction equilibrium to the left and suppress Cu⁺ ion exchange. This was observed previously and reported [20]. Also, Eq. 2 probably accounts for the phenomenon of 'over-exchange' observed with copper-containing MFI prepared by wet ion-exchange. When studying copper-containing MFI loaded to 150% of the Cu²⁺ ion exchange capacity, Sarkany et al. [26] detected three different Cu species and estimated that the sample contained 25% CuO, 35% [Cu–O–Cu]²⁺ and 40% Cu²⁺. In Sarkany's work, calcination was accomplished in O₂ and we postulate that if vacuum or inert gas at a high temperature was used instead, a material similar to Cu-MFI reported here would result.

These results provide evidence that deaggregation of CuO occurs during thermal treatment in O₂ free environment and that Cu⁺ ions stabilized in the MFI may be the final product of this ion-exchange process.

3.2. Interaction of 1-propanamine with Cu-containing MFI

The RSSIE process represented by Eq. 2 requires consumption of zeolitic H⁺ sites. Gorte and coworkers have developed a convenient method for the determination of H⁺ in zeolites

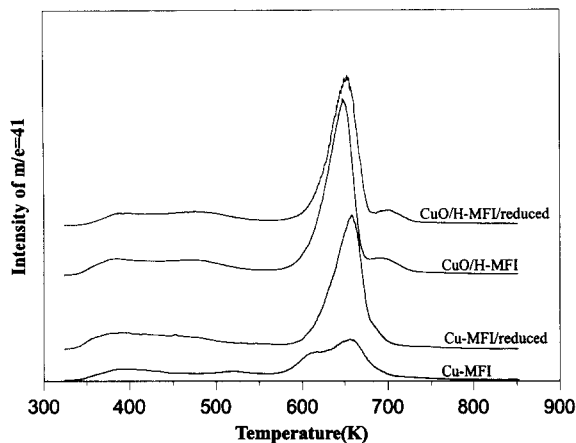


Fig. 3. Comparison of the thermal analysis of 1-propanamine in a He reagent gas over Cu-containing catalysts. Mass spectrometer response at $m/e = 41$.

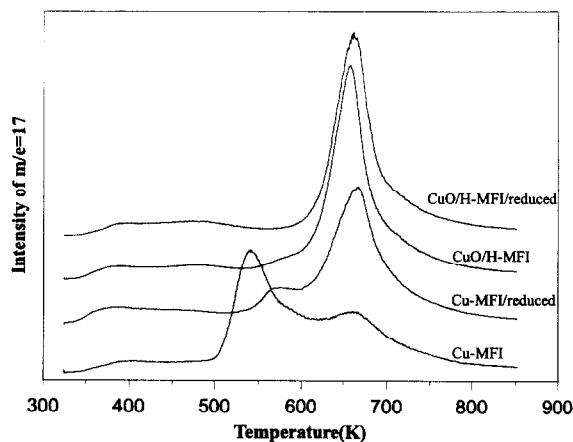


Fig. 4. Comparison of the thermal analysis of 1-propanamine in a He reagent gas over Cu-containing catalysts. Mass spectrometer response at $m/e = 17$.

using alkylamines as probe molecules [27]. We have also applied this technique to Cu-MFI and CuO/H-MFI. We have also investigated Cu-MFI and CuO/H-MFI reduced in hydrogen (termed Cu-MFI/reduced and CuO/H-MFI/reduced, respectively) because we expect fundamental changes in proton content via Eqs. 5 or 6 for these materials.

Figs. 3 and 4 show characteristic masses of propene ($m/e = 41$) and ammonia ($m/e = 17$), respectively, during the TA of 1-PA over Cu-MFI, Cu-MFI/reduced, CuO/H-MFI, and CuO/H-MFI/reduced. The simultaneous evolution of

propene and ammonia is typical of the decomposition of propanammonium cations formed by the interaction of 1-PA with zeolitic proton sites [27]. Both CuO/H-MFI and CuO/H-MFI/reduced yield propene and ammonia simultaneously which is virtually identical to the features of the pure H-MFI sample (not shown in the Figs. 3 and 4). A completely different behavior, however, is observed for Cu-MFI. There is a strong attenuation of the $m/e = 41$ peak at 670 K characteristic of protons along with the appearance of a low temperature $m/e = 17$ peak. Cu-MFI is apparently devoid of H^+ sites as required by Eq. 2 and the observed behavior is characteristic of an interaction between 1-PA and Cu zeolitic cations. These features are almost completely reversible via the reduction of Cu-MFI as seen for Cu-MFI/reduced in Figs. 3 and 4. The reversibility is consistent with proton restoration upon reduction given by Eq. 6.

During the 1-PA TA experiments, we simultaneously monitored 25 mass fragments, some of which were characteristic of aromatic hydrocarbons. Fig. 5 presents TA data for $m/e = 91$ (characteristic of toluene) and both Cu-MFI and Cu-MFI/reduced showed a higher activity for producing aromatics from adsorbed 1-PA than the other catalysts. Cu-MFI yielded the most aromatics and after H_2 reduction, the propensity to form aromatics is still high but significantly lower as

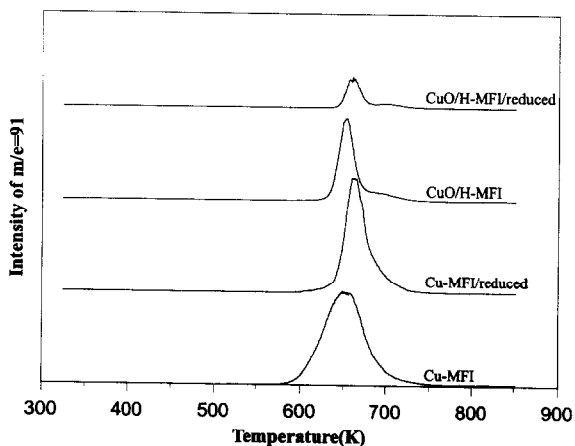


Fig. 5. Comparison of the thermal analysis of 1-propanamine in a He reagent gas over Cu-containing catalysts. Mass spectrometer response at $m/e = 91$.

Table 1
Qualitative distribution of selected products during TA of 1-PA

Sample	H-MFI	Cu-MFI	Cu-MFI/reduced	CuO/H-MFI	CuO/H-MFI/reduced
Total area of the characteristic peaks (arbitrary units)	2792	1918	2210	2593	2176
Distribution (%):					
$m/e = 17$ (ammonia)	21.9	27.3	20.6	20.3	22.2
$m/e = 41$ (propene)	77.5	34.2	66.6	73.8	75.1
$m/e = 54$ (nitriles)	0.2	19.7	1.7	0.7	0.5
$m/e = 91$ (aromatics)	0.4	18.8	11.1	5.2	2.2

noted for Cu-MFI/reduced. Table 1 presents a qualitative comparison of the product distribution for the four products of immediate interest from all catalysts under investigation and is based upon the mass spectral peak areas in the 500–800 K region during 1-PA thermal analysis. These data

provide interest in further comparisons of the aromatization activity of these Cu-containing catalysts. The effect of Cu zeolitic cations on catalysis of 1-PA is also apparent from the evolution of nitriles represented via $m/e = 54$ in Table 1. This catalytic property of Cu-MFI is suppressed when H₂ reduction precedes the 1-PA adsorption as can be seen for Cu-MFI/reduced in Table 1.

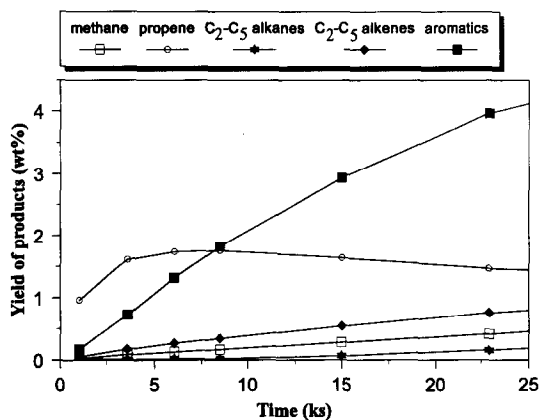


Fig. 6. Catalytic reaction of propane over Cu-MFI at 748 K.

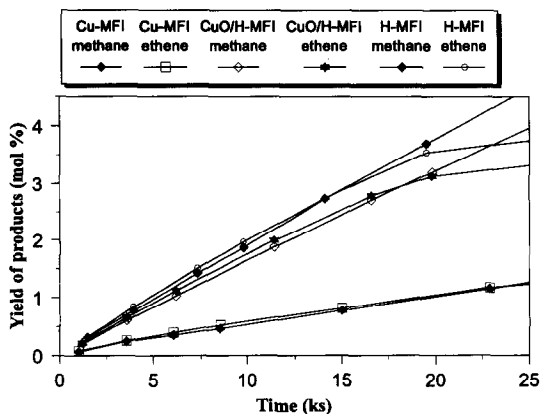


Fig. 7. Comparison of methane and ethene yields from the propane reaction at 748 K over Cu-MFI, CuO/H-MFI, and H-MFI.

3.3. Catalytic activity of Cu-MFI

3.3.1. Propane conversion

Cu-MFI possesses a high activity for propane conversion as shown in Fig. 6. Propane dehydrogenates rapidly to propene which appears to be an initial product of propane conversion. Rapid cyclization of propene accounts for the formation of aromatic hydrocarbons (which consist primarily of benzene) while the formation of other alkanes and alkenes proceeds much more slowly. The results for H-MFI, Cu-MFI and CuO/H-MFI cat-

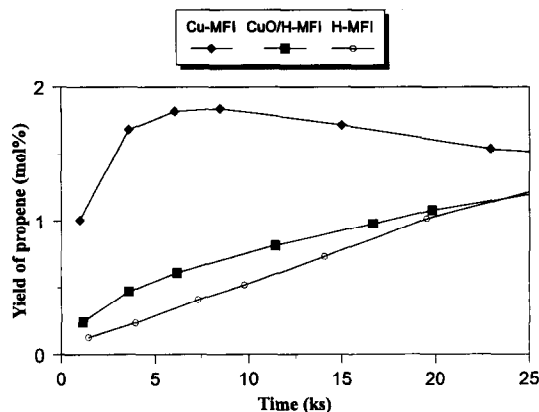


Fig. 8. Comparison of propene yields from the propane reaction at 748 K over Cu-MFI, CuO/H-MFI, and H-MFI.

Table 2
Reaction of propane at 748 K

Catalyst	H-MFI	CuO/H-MFI	Cu-MFI
Reaction time (ks)	19.5	19.8	15.0
Conversion (wt%)	5.43	5.17	5.47
Distribution of products (wt%)			
methane	25.65	23.22	5.16
ethene	43.02	40.50	9.49
ethane	4.53	3.48	0.99
propene	18.60	20.64	29.93
butenes	3.22	3.41	0.48
butanes	3.09	3.11	0.28
C ₄ ⁺	0.54	0.94	–
Aromatics	1.35	4.69	53.69
Distribution of aromatics (%)			
benzene	43.6	51.2	75.5
toluene	56.4	46.7	18.0
C ₈ aromatics	–	2.1	6.0
C ₉ aromatics	–	–	0.5

alysts which are compared in Figs. 7–8 provide a more detailed insight into the catalytic features of Cu-MFI. The methane–ethene yields in Fig. 7 show that methane/ethene = 1 for all three catalysts but the rates of production are different. The initial conversion of propane on H-MFI occurs mainly via protolytic cracking involving C–C bond scission with subsequent desorption of methane and ethene, but recent investigations on alkane conversion on H-MFI have shown that the protonium ion decomposes 2–3 times faster via C–C cleavage (protolytic cracking) than by protolysis of a C–H bond which yields propene and H₂ [28]. Using Figs. 7 and 8, we derive an ethene/propene ratio of about 3.7 over H-MFI at low conversion which confirms that C–C bond cleavage of propane prevails over C–H protolysis under our experimental conditions. When Cu is added to H-MFI forming Cu-MFI, the rate of protolytic cracking of propane to methane and ethene decreases by a factor of about 3.5 and more propene is produced probably via direct dehydrogenation of propane on ionic copper sites. Similar trends can be seen in Figs. 7 and 8 for CuO/H-MFI but the effects are slight due to the low degree of ion-exchange of Cu in this material so that protons still dominate propane transformation

pathways. The propane product distributions over all three catalysts are detailed in Table 2 at similar degrees of conversion near 5 wt%. The Cu-MFI aromatic yield is about one order of magnitude higher than for both H-MFI and CuO/H-MFI in this low conversion region. The Cu-MFI catalyst is remarkably active and selective for propane dehydrogenation and aromatization (especially to benzene) while the transformation of propane over H-MFI and CuO/H-MFI is typical of distributions obtained over acidic catalysts. The production of aromatics on Cu-MFI is even higher than the aromatics produced with the classical Ga-MFI (1 Ga/1 framework Al) catalyst. 3.97 wt% and 3.41 wt% aromatics were obtained with Cu-MFI and Ga-MFI respectively under the same experimental conditions. An acidic component of Cu-MFI can be detected but its action accounts for only a small fraction of the reaction products. The dominance of benzene among the aromatic hydrocarbons is also a specific feature of Cu-MFI and such high selectivities for benzene production from propane have never been reported even for classical light paraffin aromatization catalysts such as Ga/MFI or Zn/MFI. It should be noted, however, that there is a decline in the aromatic production at higher times on stream which we attribute to changes in the active state of the catalyst, particularly the reduction of Cu cations to copper metal since the catalyst is subjected to a heavily reducing environment under reaction conditions. However, the Cu-MFI catalyst which was purposely reduced (Cu-MFI/reduced) still showed a rather high selectivity toward aromatics from 1-PA (see Table 1). The reduction process probably produces finely dispersed metallic copper which acts with zeolitic protons as an effective bifunctional catalyst. Metallic copper should demonstrate appreciable hydrogenolysis activity resulting in high methane and ethane yields from propane which was not observed in our catalytic or thermal analysis experiments over Cu-MFI which further suggests that Cu in Cu-MFI is in a cationic state.

Table 3
Reaction of propene over Cu-MFI at 748 K

Reaction time (ks)	1.02	5.1
Conversion (wt%)	44.05	74.07
Product distribution (wt%)		
methane	0.17	0.41
ethene	8.79	14.40
ethane	0.10	0.83
propane	4.02	6.83
butanes	0.97	3.68
butenes	41.39	16.7
pentanes	0.21	0.66
pentenes	8.26	2.80
C ₆	7.10	3.17
C ₇	0.21	0.40
Aromatics	28.78	50.12
Aromatic distribution		
benzene	11.81	19.31
toluene	34.19	44.76
C ₈ -aromatics	37.30	29.36
C ₉ ⁺ -aromatics	16.70	6.57
Hydrogen/carbon ratio	1.91	1.84

3.3.2. Propene conversion

The high aromatization activity of the Cu-MFI catalyst was also confirmed for the propene reaction. Table 3 summarizes the product distribution obtained at two different conversion levels. At the shorter reaction time, C₂–C₆ alkenes dominate the reaction product, while further reaction shifts the product distribution toward aromatics which become the most abundant products. Remarkably low alkane contents were observed which suggests that aromatization does not occur through consecutive reactions of cracking and hydrogen transfer, requiring the production of 3 moles of paraffins for every mole of aromatics produced from olefinic feeds. We presume that dehydrogenation and cyclization reactions on copper cations account for this feature of the catalyst. Unlike the propane reaction, propene conversion does not yield benzene as the major aromatic hydrocarbon, which can probably be explained by the higher conversion and reactivity of propene compared to propane conversion where thermodynamics limit the dehydrogenation of propane. In addition, oligomerization and cracking reactions are more favorable with a propene reactant which results in

the presence of C₂–C₇ alkenes which can react further to yield a variety of aromatic hydrocarbons. Aromatic hydrocarbons may also undergo interconversion reactions which skew the distribution.

The H/C ratio of the products (Table 3) deserves special attention since values below the H/C ratio of the propene feed (H/C = 2) have been measured. Thus, molecular hydrogen is also a product during propene conversion.

3.4. The active state and the mechanism of hydrocarbon conversion on Cu-MFI

The formation of Cu-MFI probably occurs via solid state ion exchange of copper species which replace protons in H-MFI as suggested by the following:

1. TPR with H₂: TPR has provided evidence for the deaggregation of the CuO phase by detecting the consumption of bulk CuO. Since the amount of CuO reacted far exceeds the stoichiometric limit imposed by Cu²⁺ ion-exchange (Eq. 1), copper must be driven into H-MFI as the Cu⁺ cation.
2. TA of 1-propanamine: a strong decrease in the proton content of H-MFI is clearly registered by TA of 1-PA. Moreover, protons can be restored to a certain extent by hydrogen reduction (Eq. 6), as evidenced by 1-PA TA spectrum which resembles the spectrum for protons. Thermal analysis of 1-PA also provided the first indications of the specific catalytic action of copper cations for condensation and cyclization reactions.
3. Propane conversion: the extent of protolytic cracking which leads to methane and ethene from propane is in our opinion a reliable indicator of the proton content of MFI. A comparison of the rate of this reaction for H-MFI and Cu-MFI suggests that at least 75% of the H⁺ sites in H-MFI must have been removed during the high temperature treatment of the CuO/H-MFI mechanical mixture. The fact that we have created a remarkably active and selective catalyst indicates the presence of cat-

ionic copper and hence the advance of the ion exchange process we term RSSIE.

According to recent reviews on catalysts for the aromatization of light hydrocarbons (e.g., [29]), Cu-modified zeolites have never been considered as potential candidates for this reaction. This is understandable since ionic copper can generally be reduced easily under the conditions of the aromatization process (high temperature, presence of H_2). However, the redox chemistry of Cu-exchanged zeolites may be complicated [30] and temperatures higher than 700 K are apparently needed to convert ionic copper in MFI to Cu^0 .

We have observed high activity and selectivity for the dehydrocyclodimerization reactions of propane and propene over Cu-MFI prepared by RSSIE and here we will discuss briefly some mechanistic aspects of propane and propene conversion on this catalyst. We should first point out that we are aware that not all proton sites of the zeolite have been replaced by copper, but a very large fraction of the anionic sites are occupied by Cu cations which promote dehydrogenation reactions. Like Ga-MFI catalysts, copper cations facilitate dehydrogenation of propane to propene and this process likely proceeds with the participation of copper cations acting as Lewis acid centers [6,12,18]. The neighboring basic oxygen anions appear to be equally important components of the dehydrogenation reaction [30,31,11,18,13]. In addition, Cu ions may be similar to Ga and Zn ions in MFI where the rate limiting step for light paraffin aromatization is the removal of H-atoms from the zeolite surface as H_2 and metallic centers act as hydrogen 'portholes' [32,11].

However, the role of Cu is clearly not restricted to the dehydrogenation of propane to propene. Propene undergoes further oligomerization and aromatization on Cu which may occur through the successive abstraction of hydrogen and formation of an adsorbed allylic species. Whether the oligomerization occurs by coupling of two allylic species or by the interaction of an alkene and an allylic species is not yet clear. Previous work on the 1-propanamine reaction over Cu-MFI [21,33] indicates that the Cu cation can bring together more

than one reagent molecule even at relatively high temperatures and this is an important feature which facilitates the processes of hydrocarbon chain enlargement. We propose that the ability of the Cu^+ zeolitic cation to coordinate multiple reagent molecules is also essential for alkene dehydrocyclodimerization. Furthermore, we attribute the high selectivity to benzene observed in propane conversion on Cu-MFI to the specific action of Cu^+ cations. This is in accordance with the recent discovery [18] that alkali-exchanged MFI shows low activity in propene conversion but high selectivity for benzene production among the aromatic hydrocarbons. Cu-MFI produced by reductive solid-state ion-exchange yields a much more active aromatization catalyst with an exceptionally high selectivity for benzene from propane.

4. Conclusions

Catalysts prepared by high temperature treatment of CuO mechanically mixed with H-MFI show high activity and selectivity for the aromatization of propane and propene. An unusually high selectivity for benzene is observed during propane conversion. Catalytic studies coupled with TPR and thermal analysis of 1-propanamine provide evidence for the key role of the Cu cations in the aromatization reaction.

Acknowledgements

The authors gratefully acknowledge the financial support of the Department of Energy (Grant No. DE-FG05-92ER14291) and the Exxon Education Foundation.

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