On the Mechanism of Propane Dehydrocyclization over Cation-Containing, Proton-Poor MFI Zeolite

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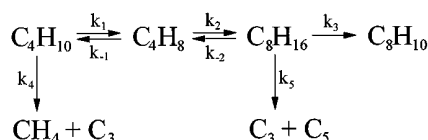
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The catalytic behavior of 1/1 cation (Ga, Cu, or In)/framework-Al MFI (MFI is terminology officially sanctioned by the International Zeolite Association, IUPAC commission) zeolite for propane dehydrocyclization was examined under conditions where the materials were initially either in fully protonated or fully metal-loaded states. Metal-loading was accomplished with reductive solid-state ion exchange, and under appropriate conditions, loadings nearing 100% exchange of protons for the reduced univalent cations could be achieved. Ga-MFI is stable to dehydrocyclization reaction conditions to at least ~800 K, but both In-MFI and Cu-MFI convert to a relatively inactive catalytic state under similar conditions probably by reduction. However, prior to this reduction, In-MFI and Cu-MFI are equivalent or superior to Ga-MFI for the formation of aromatics. The initial zero-protonated state for Ga-MFI was characterized by little or no C−C bond scission to methane, a high benzene/toluene ratio, and a strongly olefinic and branched C_4 fraction. On this basis, a reaction mechanism for this state not involving protons, and not bifunctional, is proposed. © 1998 Academic Press

INTRODUCTION

The Cyclar process for upgrading lower alkanes to aromatics (1, 2) exploits specific features of the Ga/MFI zeolite system to effectively catalyze dehydrocyclization reactions. The dehydrocyclization reaction of light hydrocarbons was discovered by Csicsery (3, 4). Pt/Al_2O_3 and other nonzeolitic catalysts have been studied but none have attained industrial significance because of rapid catalyst deactivation. Dehydrocyclization consists of several reaction pathways. The most important pathways have been summarized using the example of butane conversion (4):

$$C_4H_{10} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} C_4H_8 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C_8H_{16} \overset{k_3}{\longrightarrow} C_8H_{10}$$

$$\downarrow k_4 \qquad\qquad\qquad \downarrow k_5$$

$$CH_4 + C_3 \qquad\qquad C_3 + C_5$$

SCHEME 1

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Csicsery defined the kinetic requirements for an effective dehydrocyclization catalyst as:

   (i) fast dehydrogenation step: $k_1 > k_2$
   (ii) low hydrogenolysis activity: $k_1 \gg k_4$; $k_3 \gg k_4$
   (iii) dehydrocyclization of the dimers faster than both dimer cracking and dimer formation: $k_3 \gg k_2$; $k_3 \gg k_5$; $k_3 > k_2$
   (iv) temperature high enough to favor the equilibrium formation of dehydrogenation products.

Such vastly different catalytic requirements are difficult to satisfy using catalysts with a single type of active site. The main drawbacks of the bifunctional catalysts utilized by Csicsery were high hydrogenolysis activity and unrestricted condensation reactions, leading to polycyclic aromatics and consequent coking (4). The discovery of MFI zeolites offered an opportunity for improved catalyst stability, because steric or spatial constraints limit the product distribution to smaller hydrocarbons (5). Indeed, Pt/MFI catalysts showed resistance to coke formation, but the production of methane and ethane through hydrogenolysis reactions remained high (6, 7).

The replacement of Pt by Ga or Zn as a dehydrogenation component in MFI represented the next great advance in dehydrocyclization catalyst development. Ga has the advantage (over Zn) of lower volatility in H_2 at high temperatures. There are large numbers of patents and publications on Ga- and Zn-modified MFI and several reviews (e.g., (7–11)). The fact that the method of introducing Ga into MFI had only a small effect on the properties of the catalyst (8, 12) led Gnep *et al.* (13) to assume that Ga-MFI is truly bifunctional. Ga_2O_3 in the catalyst presumably acted as a dehydrogenation component, which assured a sufficient rate of dehydrogenation (k_1) but low hydrogenolysis activity (k_4). Later, a synergistic effect of Ga_2O_3 and zeolitic protons for propane dehydrogenation was proposed (14, 15), and, similarly, a back-spillover mechanism involving migration of monatomic hydrogen onto Ga_2O_3 (16).

The classical concept of polyfunctional catalysis deals with at least two distinct active sites catalyzing distinct reaction steps (17). Hence, finely dispersed Ga_2O_3 and the

proton sites of the zeolite might constitute independent components of a bifunctional catalyst. A postulate involving strong interaction and even chemical reaction between the catalytic components under dehydrocyclization reaction conditions was not published until 1990 (18, 19). Our previous work on Ga-containing MFI (e.g., (18–21)) revealed that a solid-state reaction occurred between Ga_2O_3 and H-MFI to form Ga^+ cations in the zeolite pore structure

$$\tfrac{1}{2}Ga_2O_3 + H_2 + H^+Z^- \rightarrow Ga^+Z^- + \tfrac{3}{2}H_2O \qquad [1]$$
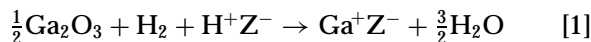
where Z^- is an anionic zeolite site. This finding was later confirmed by others (10, 22–24). Carli *et al.* (23) suggested that the role of H-MFI is to provide "activated" hydrogen able to reduce Ga_2O_3 at low temperatures. Meitzner *et al.* (24) postulated that reduced Ga is present in dispersed form without Ga nearest neighbors, possibly at higher temperatures as a monomeric hydride coordinated to basic oxygens within zeolite channels. In cases where Ga and H^+ sites coexist, a bifunctional catalyst system is probably a correct definition. Kwak and Sachtler examined the impact of the Ga/H^+ ratio in Ga/MFI catalysts prepared by chemical vapor deposition on the conversion of propane and propene to aromatics (25), finding that catalyst activity displayed a clear maximum when plotted versus the fraction of sites occupied by Ga; this is typical for bifunctional catalysts. No formation of aromatics was observed in the absence of Ga or in the absence of protons at $530°C$ and high space velocity.

Returning to the industrial Ga/MFI catalyst, note that the Cyclar process converts LPG into about 65 wt% aromatics, 6 wt% hydrogen, and 29 wt% fuel gas with an aromatics distribution of 30 wt% benzene, 42 wt% toluene, 20 wt% xylenes, and 8 wt% heavier aromatics (2). Because the dehydrocyclization reaction has an optimum theoretical product distribution of 88 wt% benzene and 12 wt% hydrogen (from propane), there is considerable space for improvement of the Cyclar catalyst. The mechanism of hydrocarbon transformation, involving cracking, oligomerization, and cyclization (k_2, k_3, k_5 in Scheme 1), is already understood in the case of proton-containing acidic zeolites. However, the catalytic features of the metal component for light alkane dehydrocyclization are not well understood. Other than its postulated participation in hydrogenolysis, dehydrogenation, and hydrogenation, the metal component might also participate in oligomerization and cyclization (26–28).

We report here on MFI catalysts which have been prepared by solid-state ion exchange, such that they are virtually devoid of protons. However, complete proton removal has apparently eluded our efforts and these residual protons may still affect the reaction of the intermediate olefins by well-known mechanisms. Nonetheless, these systems shed new light on the action of different zeolitic cations on hydrocarbon conversion processes.

EXPERIMENTAL

A. Catalysts

The catalysts were based on H-MFI (PQ Corporation CBV-3020) with a reported elemental SiO_2/Al_2O_3 molar ratio of 26. It was initially in the fully protonated state. The proton content was determined by 1-propanamine thermal desorption and, assuming that H^+/framework-Al = 1, a SiO_2/framework-Al_2O_3 ratio of 43 was calculated.

Metal loading of Cu, Ga, and In was accomplished by mechanical mixing. Pure CuO, Ga_2O_3, and In_2O_3 reagent grade chemicals were used as the metal source materials. CuO and In_2O_3 were mechanically mixed with H-MFI for 6 and 1 h respectively in a stainless-steel ball-mill described previously (19) to form materials we term CuO/H-MFI and In_2O_3/H-MFI, respectively. Ga_2O_3/H-MFI was prepared by first ball-milling the pure Ga_2O_3 for 24 h in a stainless-steel ballmill, then the Ga_2O_3 was mixed with the H-MFI by hand in an agate mortar. Since previous experiments have indicated that the details of the ball-milling process are important in the process of transferring Ga into the zeolite, we separately tested some of these hand-mixed samples for efficient transfer of Ga.

Pretreatment of the three metal catalysts was performed differently in all three cases. For CuO/H-MFI (Cu/Al = 1.0), the mechanical mixture was spread on a quartz tray and calcined at 973 K for 16 h after drying and a slow ramp rise to temperature. The procedure has been described previously in detail (19). The purge gas was argon, which was passed through an elemental copper trap at 773 K to remove trace O_2. We refer to this calcined material as Cu-MFI. Prior to catalytic reactor experiments, Cu-MFI was heated in a batch recirculation catalytic reactor (described below) at 423, 573, and 823 K for 0.5 h at each temperature under vacuum (1 Pa), then cooled to reaction temperature under vacuum.

Ga_2O_3/H-MFI (atomic ratio Ga/framework Al = 1) was treated in the batch recirculation catalytic reactor at 423, 573, and 823 K for 0.5 h at each temperature, then the material we term Ga-MFI was formed by further treatment with a 25 kPa H_2/80 kPa He mixture at 848 K for 3 h. In_2O_3/H-MFI was treated similarly by drying at 423, 573, and 823 K for 0.5 h at each temperature followed by cooling to reaction temperature. In-MFI samples were studied in both the recirculating reactor system and a tubular flow reactor system described below. Further treatments were accomplished in the tubular flow reactor in varying manners as described subsequently.

B. Microbalance Reduction

A Perkin–Elmer TAC7 microbalance was used to follow the progress of reduction of Ga_2O_3/H-MFI and In_2O_3/H-MFI. Samples of 10–15 mg were first dried

(Ga$_2$O$_3$/H-MFI) by temperature programming from 298–848 K at 20 K/min in flowing He. After equilibration at 848 K for Ga$_2$O$_3$/H-MFI, 25% of the He purge stream was replaced with H$_2$ and an isothermal reduction curve was generated. The In$_2$O$_3$/H-MFI samples were dried at 673 K and then reduced at either 673 or 848 K.

C. Propane Dehydrocyclization Reactions

The catalytic conversion of propane was performed using two different reactor systems. The first was a batch recirculating reactor system described in detail elsewhere (30). The system consisted of a magnetically operated piston pump, a check-valve arrangement, mixing volume, and reactor section, all of which could be evacuated. Samples were periodically withdrawn by expansion through a traced line into a preevacuated sample loop on a chromatographic sampling valve attached to an HP 5890-II chromatograph which was equipped with a PONA column and FID detector. A 25-mg H-MFI sample (wet basis) was charged into the reactor and amounts of Cu-, Ga-, and In-containing catalysts were charged so that the number of framework-Al atoms was equal to that of the H-MFI charge.
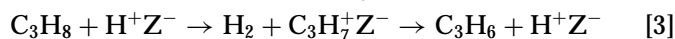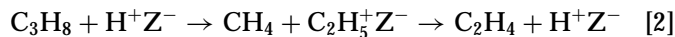
After catalyst pretreatments were completed, the system was evacuated and the reactor section brought to 748 K, backfilled with pure He at 110 kPa, and isolated. The remainder of the recirculation loop was filled with 14 kPa propane and 100 kPa He. The reaction was initiated by diverting the propane/He feed through the reactor section. The propane feed contained 0.01 wt% propene and 0.04 wt% isobutane; corrections for these impurities were made in calculating product distributions.

The other reactor system consisted of an upflow tubular reactor of stainless steel, i.d. 1.0 cm and length 20 cm, containing 0.5–1.0 g catalyst on a quartz wool bed. The system components, gases used, and product analysis were the same as in a previous study (31). All samples were purged after other pretreatments for at least 0.5 h in He flow at the initial reaction temperature, just prior to a reaction experiment.

RESULTS

A. H-MFI

Results for propane conversion over H-MFI are given in Table 1. The product distribution is typical of that reported by others (13, 25, 32–35). At low conversions (<1%) the primary reactions involve protolytic cracking induced by strong Bronsted acid sites of H-MFI:

$$C_3H_8 + H^+Z^- \rightarrow CH_4 + C_2H_5^+Z^- \rightarrow C_2H_4 + H^+Z^- \quad [2]$$

$$C_3H_8 + H^+Z^- \rightarrow H_2 + C_3H_7^+Z^- \rightarrow C_3H_6 + H^+Z^- \quad [3]$$

The mole ratio of reaction 2/reaction 3 at 0.52% conversion was about 3 which also agrees with other researchers

TABLE 1

Propane Conversion on H-MFI at 748 K

Time (ksec):	1.50	3.96	7.32	9.78	14.10	19.50	76.56
Conversion (wt%):	0.52	1.10	2.01	2.69	3.93	5.43	21.52
Turnovers[a]:	1.03	2.18	3.99	5.33	7.79	10.78	42.69
Selectivity (wt%)							
Methane	21.97	25.87	26.13	25.75	26.05	25.67	25.36
Ethene	40.46	49.09	48.48	47.49	45.76	43.03	18.59
Ethane	1.26	1.17	2.18	2.69	3.31	4.53	10.71
Propene	23.51	20.58	19.62	18.79	18.28	18.61	15.22
Butanes				0.57	2.16	3.09	12.83
Butenes			0.57	1.58	2.61	3.22	4.62
C$_{5+}$				0.65	0.54	2.00
Aromatics			1.27	1.19	1.14	1.35	10.68
Aromatics distribution (wt%)							
Benzene			35.79	49.22	45.19	43.48	24.63
Toluene			64.21	50.78	54.81	56.52	48.42
C$_8$							24.40
C$_{9+}$							2.55
Weight ratios:							
Methane/ethene	0.54	0.53	0.54	0.54	0.57	0.60	1.36
Ethane/ethene	0.03	0.02	0.04	0.06	0.07	0.11	0.58
Butanes/butenes				0.36	0.83	0.96	2.78
Isobutane/butane					0.88	0.61	0.69

[a] Moles of propane converted/mole of framework Al.

(13, 32–33, 35). Hydrogen transfer reactions, for example,

$$C_2H_5^+Z^- + C_3H_8 \rightarrow C_2H_6 + C_3H_7^+Z^- \rightarrow C_3H_6 + H^+Z^-, \quad [4]$$
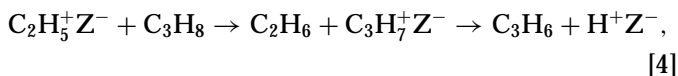
are clearly not present in the early stages of reaction as evidenced by the lack of ethane. However, at longer times hydrogen transfer plays an important role in chain propagation and cyclization as evidenced by an increasing saturated/unsaturated hydrocarbon ratio and a parallel rise in aromatics (Table 1).

B. Ga$_2$O$_3$/H-MFI

Results of the catalytic reaction of propane over unreduced Ga$_2$O$_3$/H-MFI mechanical mixtures are given in Table 2. The product distribution at the initial period of reaction (<20 ks) is virtually identical to the H-MFI material. Bulk Ga$_2$O$_3$, therefore, appears to have no specific activity for propane conversion at these conditions. However, at higher conversions (>10%), deviations between the product distributions over Ga$_2$O$_3$/H-MFI and over H-MFI are apparent. Ga$_2$O$_3$/H-MFI gives a lower yield of olefins (including propene) and paraffins, and a much higher yield of aromatics compared to H-MFI at about 76 ks. This confirms our previous work where mechanical mixtures of Ga$_2$O$_3$ with H-MFI showed a strong enhancement in dehydrocyclization activity with increased time on stream (18). We suggest that the catalyst undergoes transformation under
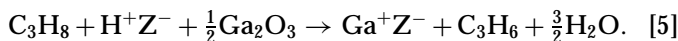
TABLE 2

Propane Conversion on Ga$_2$O$_3$/H-MFI at 748 K

Time (ksec):	1.2	3.96	7.32	9.78	14.1	19.5	76.44
Conversion (wt%):	0.37	1.08	2.00	2.65	3.83	5.36	21.03
Turnovers[a]:	0.75	2.20	4.08	5.43	7.83	10.96	43.02
Selectivity (wt%)							
Methane	24.41	25.42	23.94	24.04	24.04	23.95	24.71
Ethene	42.51	46.85	45.07	44.50	42.88	39.82	13.98
Ethane		1.22	1.99	2.19	3.32	4.07	9.41
Propene	32.97	26.53	24.28	23.46	21.74	20.89	10.08
Butanes			1.91	1.78	2.69	3.64	7.96
Butenes			1.70	2.78	3.26	3.99	2.54
C$_{5+}$					0.78	1.01	1.03
Aromatics			1.09	1.00	1.31	2.60	30.28
Aromatics distribution (wt%)							
Benzene			41.56	45.86	46.02	33.12	32.86
Toluene			58.44	54.14	53.98	46.41	46.53
C$_8$						20.47	18.27
C$_{9+}$							2.34
Weight ratios:							
Methane/ethene	0.57	0.54	0.53	0.54	0.56	0.60	1.77
Ethane/ethene		0.03	0.04	0.05	0.08	0.10	0.67
Butanes/butenes			0.96	0.64	0.83	0.91	3.13
Isobutane/butane			2.42	1.12	0.81	0.63	0.59

[a] Moles of propane converted/mole of framework Al.

these conditions via reaction 1, and that hydrogen for reaction 1 is supplied by reaction 3, which is known to be an initial step of the propane reaction over H-MFI. An interesting possibility is the sum of reactions 1 and 3 given by:

$$C_3H_8 + H^+Z^- + \tfrac{1}{2}Ga_2O_3 \rightarrow Ga^+Z^- + C_3H_6 + \tfrac{3}{2}H_2O. \quad [5]$$

The carbonium ion, $C_3H_9^+$ (formed through the action of H$^+$ on C_3H_8) could provide an active form of hydrogen to reduce Ga$_2$O$_3$, which is stable to hydrogen treatment at these temperatures in the absence of H-MFI (19). Reaction 5 is also consistent with a slightly higher selectively for propene at < 1% conversion, which is observed over Ga$_2$O$_3$/H-MFI compared to H-MFI. The transfer of Ga into H-MFI is relatively slow, but higher transfer rates can be achieved with In, as will be discussed shortly.

C. Ga-MFI

The process of gallium transfer into H-MFI can be accomplished via H$_2$ reduction as already noted (reaction 1). Our previous studies relied upon ball milling Ga$_2$O$_3$ with H-MFI and the ball-milling operation was identified as critically important for successful transfer of Ga into the zeolite. However, we have been interested in other effective techniques for making the mechanical mixtures, especially those which would allow us to make small quantities (<1 gram) of material. We therefore prepared

microcrystalline Ga$_2$O$_3$ by ball-milling for 24 h, and tested this material as a Ga$_2$O$_3$ source for MFI-based propane dehydrocyclization catalysts. Figure 1 shows the results of isothermal reduction of four samples containing 8.1, 9.8, 11.8, and 15.2 wt% Ga$_2$O$_3$ on H-MFI corresponding to 1.26, 1.55, 1.91, and 2.57 Ga/framework-Al, respectively. These samples were prepared by hand-mixing the microcrystalline Ga$_2$O$_3$ with H-MFI in an agate mortar for 0.6 ks. Note that all materials undergo reduction to virtually the same extent. Clearly, bulk reduction of Ga$_2$O$_3$ in excess of the stoichiometric amount given by reaction 1 does not occur. This result also suggests that, at least for the particular materials we have at our disposal, the important aspect of ball-milling is to reduce the Ga$_2$O$_3$ particle size whether H-MFI is present or not during ball-milling.

The catalysts described here were pretreated *in situ* so that a highly reduced and dry state was maintained, and then used immediately after pretreatment so there was virtually no opportunity for slight impurities in a purge gas or residual vacuum to reoxidize the sample. A high degree of proton replacement was achieved for Ga-MFI which is important for maintaining a reduced state of gallium as suggested by Meitzner *et al.* (24) who observed reverse oxidation of Ga by protons upon cooling the catalysts. Table 3 gives the results of propane conversion over Ga-MFI and the essential features are summarized in Fig. 2. At 0.27% conversion, the only product detected was propene. Aromatics were clearly a secondary product which agrees with previous observations for materials with a high degree of proton replacement with Ga (15, 25, 34). Also of interest is the distribution among aromatic products. The first detectable aromatics at 1.14% conversion favor the benzene
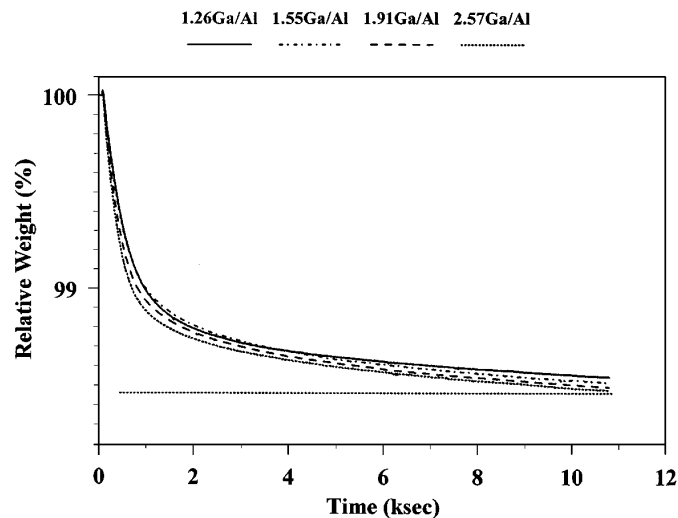

FIG. 1. Isothermal reduction curves for Ga$_2$O$_3$/H-MFI mechanical mixtures at 848 K in 25% H$_2$/75% He reagent gas. The horizontal line represents the theoretical relative weight for reduction to the Ga$^+$ exchange state for 1.00 Ga of the 2.57 Ga/framework-Al material.

TABLE 3

Propane Conversion on Ga-MFI at 748 K

Time (ksec):	0.6	2.40	4.44	6.84	9.12	13.68	16.44	19.02	25.80	63.00	65.70
Conversion (wt%):	0.27	1.14	2.10	3.17	4.14	5.91	6.89	7.82	10.09	20.89	21.69
Turnovers[a]:	0.54	2.34	4.29	6.48	8.47	12.08	14.09	15.99	20.64	42.73	44.37
Selectivity (wt%)											
Methane		0.86	0.95	1.40	1.60	1.58	1.63	1.79	1.92	2.98	2.99
Ethene		4.49	9.10	12.40	13.81	14.19	13.68	13.30	11.69	6.52	6.29
Ethane		0.81	3.36	6.81	8.96	12.96	14.64	16.32	19.23	29.17	29.52
Propene	100.00	83.28	65.82	52.90	45.51	36.29	32.36	29.29	23.90	12.08	11.55
Butanes			2.96	3.49	3.19	3.57	3.53	3.48	3.34	2.93	2.87
Butenes		8.27	11.96	11.68	10.71	8.30	7.58	6.70	5.36	2.58	2.51
Butadiene			0.009	0.016	0.016	0.015	0.015	0.018	0.011	0.011	0.011
C_{5+}					0.54	0.52	0.53	0.59	0.63	0.41	0.50
Aromatics		2.26	5.85	11.30	15.69	22.62	26.07	28.51	33.83	43.38	43.75
Aromatics distribution (wt%)											
Benzene		69.99	51.79	43.00	38.00	36.54	36.01	35.76	34.95	37.43	37.71
Toluene		30.01	39.74	42.16	44.15	43.88	43.52	43.79	43.56	43.42	43.36
C_8			8.47	14.84	16.54	17.48	18.25	17.89	18.79	17.03	16.84
C_{9+}				1.31	2.11	2.22	2.56	2.70	2.11	2.08	
Weight ratios:											
Methane/ethene		0.19	0.10	0.11	0.12	0.11	0.12	0.13	0.16	0.46	0.48
Ethane/ethene		0.18	0.37	0.55	0.65	0.91	1.07	1.23	1.64	4.47	4.69
Butanes/butenes			0.25	0.30	0.30	0.43	0.47	0.52	0.62	1.14	1.14
Isobutane/butane			6.88	7.02	7.75	4.44	3.84	4.36	3.45	1.53	1.46

[a] Moles of propane converted/mole of framework Al.

fraction by more than 2/1. But after about 4% conversion, the weight fraction of toluene surpasses that of benzene and significant quantities of C_{8+} aromatics are evident. Perhaps the most notable difference between reduced Ga-MFI and unreduced Ga-containing materials is in the yield to ethane, which is a secondary product of the reaction and increases in a fashion parallel to aromatics. On a molar basis, ethane becomes the most populous product at about 10% conversion, which is contrary to findings for unreduced Ga-containing MFI (13, 33). In other behavior different from either H-MFI or Ga_2O_3/H-MFI, propane converts to far more C_4 hydrocarbons, at short reaction times, over Ga-MFI. The C_4 fraction is strongly olefinic over Ga-MFI, and butadiene is a detectable product; no butadiene could be detected over H-MFI. The isobutane/n-butane ratio is much higher on Ga-MFI than H-MFI or Ga_2O_3/H-MFI.

D. Cu-MFI

Table 4 gives the results for propane dehydrocyclization over Cu-MFI. The catalyst was very active initially as can be seen by a 1.24% conversion at 1.02 ks compared to 1.14% conversion for Ga-MFI at 2.40 ks. Propene again was the initial product, and aromatics begin to appear quickly. A small amount of protolytic C–C cracking is also apparent, as can be seen by the small yields of ethene and methane in 1/1 molar ratio at low conversion.

The aromatics production is very unusual. Benzene strongly dominated the initial aromatic products. If we ex-

amine the propane/propene-free product, we note extraordinary aromatic selectivities of 69 wt% at 1.24% conversion, 73 wt% at 2.61% conversion, and 76 wt% at 3.48% conversion. Cu-MFI, however, undergoes further reduction at longer times on stream. This is evidenced by a continuous increase in methane/ethene selectivity. Up to about 4% conversion, methane/ethene molar ratios are near 1/1, indicative of protolytic C–C bond rupture. The proton
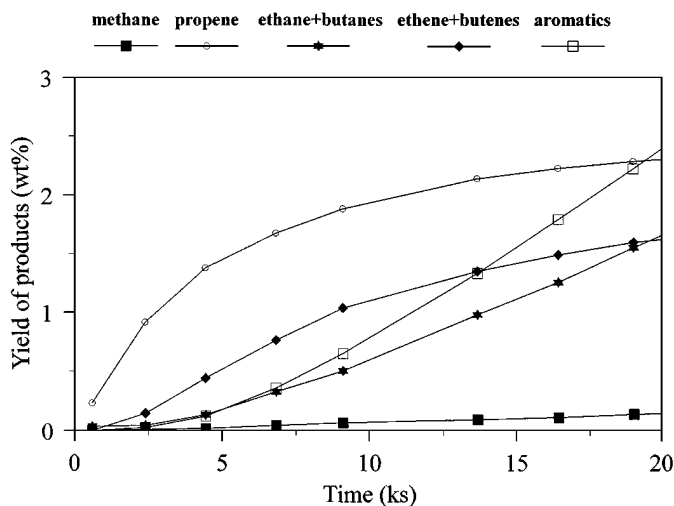

FIG. 2. Reaction of propane over Ga-MFI at 748 K in the batch reactor system.

TABLE 4

Propane Conversion on Cu-MFI at 748 K

	1.02	3.6	6.06	8.52	15	22.92	58.38	61.38	79.2	84.9	144.8
Time (ksec):	1.02	3.6	6.06	8.52	15	22.92	58.38	61.38	79.2	84.9	144.8
Conversion (wt%):	1.10	2.61	3.48	4.11	5.47	6.77	10.65	11.51	12.74	13.56	19.18
Turnovers[a]:	2.28	5.40	7.19	8.50	11.30	13.99	22.01	23.79	26.34	28.02	39.65
Selectivity (wt%)											
Methane	2.02	3.43	3.71	4.11	5.16	6.18	10.44	11.31	12.62	13.91	17.65
Ethene	4.40	6.28	7.28	8.10	9.49	10.44	12.08	12.23	12.48	12.86	12.88
Ethane		0.47	0.65	0.48	0.99	1.74	4.93	5.49	6.63	7.52	11.53
Propene	79.74	61.69	49.94	42.66	29.92	21.66	9.72	8.73	7.69	7.25	6.33
Butanes						0.28	0.58	0.89	1.00	1.13	1.28	2.03
Butenes		0.36	0.33	0.37	0.48	0.69	0.79	0.88	0.75	0.75	0.93
C_{5+}						0.09	0.09	0.04	0.06	0.10	0.46
Aromatics	13.85	27.82	37.92	44.29	53.69	58.62	61.04	60.31	58.62	56.32	48.19
Aromatics distribution (wt%)											
Benzene	84.78	85.67	79.97	78.86	75.51	73.18	66.43	64.98	63.27	62.68	58.09
Toluene	15.22	14.33	14.57	16.03	18.02	19.71	25.02	25.96	27.42	27.98	32.19
C_8			4.96	4.70	6.04	6.55	8.00	8.59	8.86	8.83	8.86
C_{9+}			0.50	0.41	0.43	0.56	0.55	0.47	0.45	0.51	0.86
Weight ratios:											
Methane/ethene	0.46	0.55	0.51	0.51	0.54	0.59	0.86	0.92	1.01	1.08	1.37
Ethane/ethene		0.08	0.09	0.06	0.10	0.17	0.41	0.45	0.53	0.59	0.90
Butanes/butenes					0.57	0.84	1.13	1.14	1.52	1.72	2.19
Isobutane/butane					0.65	0.65	0.53	0.47	0.51	0.52

[a] Moles of propane converted/mole of framework Al.

population increases steadily by reduction:

$$\tfrac{1}{2}H_2 + Cu^+Z^- \rightarrow Cu^\circ + H^+Z^- \qquad [6]$$
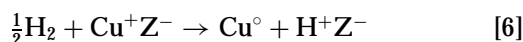
Thus, we expect catalytic action characteristic of H-MFI as the reduction progresses. This reduction should yield metallic copper finely dispersed in the zeolite, which would promote hydrogenolysis of propane to yield ethane and methane; their selectivities increase markedly at >5% conversion. However, the increasing ethane and methane yields and the growing methane/ethene ratio at >5% conversion are also partly explained by the involvement of olefins in hydrogen transfer reactions, leading to aromatics and saturated products similar to what is observed for H-MFI.

E. In₂O₃/H-MFI

The indium analog of Ga_2O_3/H-MFI was also investigated for propane dehydrocyclization, and transfer of In into the zeolite by the action of the reacting propane was apparently rapid compared to the same process for Ga_2O_3/H-MFI. This is in agreement with early work showing that In_2O_3/H-MFI could be reduced at a much lower temperature than Ga_2O_3/H-MFI (36).

Figure 3 shows the products of the propane reaction starting with the unreduced but dried material, and only three hydrocarbon products (methane, ethene, and propene) were observed. Evidence of some protolytic C–C scission is seen in the ethene and methane yields as previously dis-

cussed, but the ethene/propene ratio was only 1.2, compared to 2–3 for H-MFI. The difference arises from rapid transfer of In into the zeolite, exchanging for protons. Taking into account the total volume of the batch reactor and the initial pressure of propane, we estimate that after 45 ks into the reaction 14 μmol of C_3H_6 has been produced. This compares favorably to 17 μmol of cationic sites in the catalyst charge. Thus, all products of the reaction can be explained by assuming that the fully reduced catalyst has
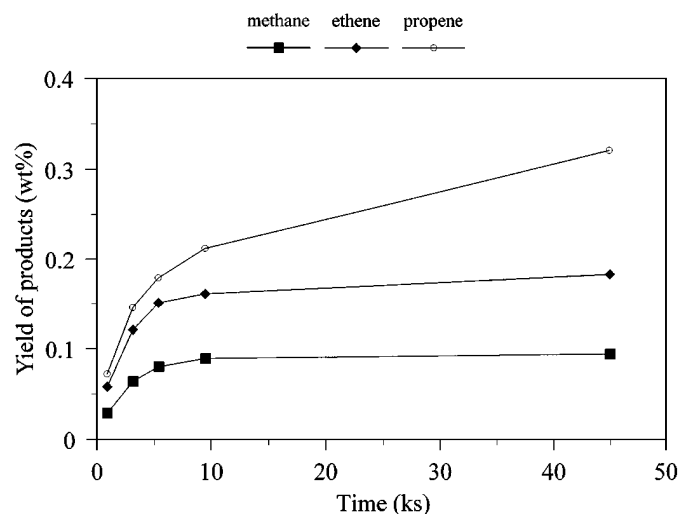

FIG. 3. Reaction of propane over In₂O₃/H-MFI at 748 K in the batch reactor system.

little activity compared to protons, that propene is largely the result of indium oxide reduction analogous to reaction 5, and that ethene and methane result from the initial action of H^+ prior to substantial reduction of In and proton exchange for In^+.

The In_2O_3/H-MFI system is more complex than its Ga counterpart owing to the instability of the In^+ state in the MFI zeolite at temperatures characteristic of alkane dehydrogenation. Although microbalance reductions at 673 K apparently proceeded smoothly to the In^+-exchange state (Fig. 4), there were additional weight losses of ~0.2 wt% at a higher reduction temperature of 848 K. Also, unlike Ga-MFI (37), with In-MFI it proved impossible to restore the initial weight of In_2O_3/H-MFI upon prolonged oxidation. Such behavior suggests reduction at 848 K of at least some of the In to its elemental state, with evaporation of metal atoms from the surface. Somewhat similar sublimation behavior was found previously for Te-loaded zeolites (38). Hydrogen reduction at near 800 K to $In°$ for an In-containing Y-zeolite was confirmed by an XPS study (39), although Pt was also present. The replacement of H^+ by In^+ at lower temperatures is suggested both by the present microbalance reduction data and by work using pyridine adsorption as an acid site probe (40).

The catalytic behavior of In_2O_3/H-MFI is observed in the batch reactor system in the first few data points of Fig. 3. The behavior of reduced (to In^+) In-MFI can only be observed at short times in the flow reactor, as in Fig. 5; the flow reactor experiments were all at 803 K, 12–14 kPa propane in the feed (balance He to 102 kPa), and propane WHSV = $1.0 \, h^{-1}$. The catalyst reduced at 673 K is capable of production of aromatics in a fashion similar to Ga-MFI, with Ga also in the +1 exchange state; however, the catalyst reduced at 848 K is a disproportionation and cracking catalyst only.
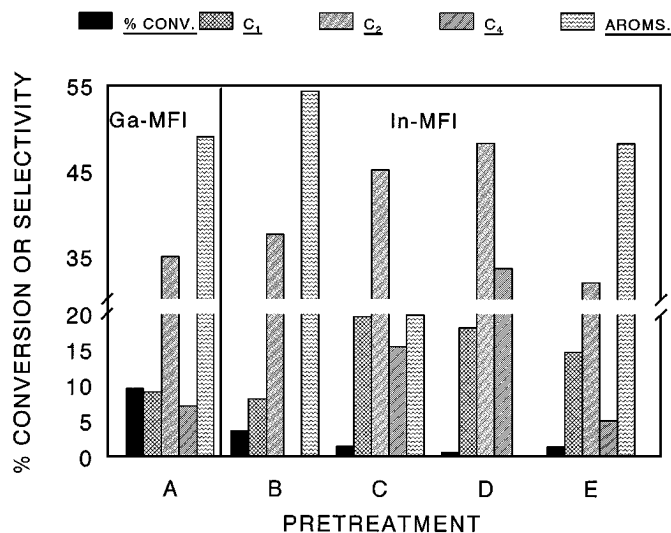

FIG. 5. Initial conversion and product distribution (mol% carbon) for reaction of propane over Ga-MFI and In-MFI at 803 K in the flow reactor system. Pretreatments are (balance is He): (A) 30% H_2, 848 K, 6 h; (B) 30% H_2, 673 K, 3 h, then He, 673 K, 12 h; (C) 30% H_2, 673 K, 3 h; (D) 30% H_2, 848 K, 3 h; (E) 30% H_2, 848 K, 3 h, then 30% O_2, 823 K, 2 h.

The In–MFI catalyst reduced at 673 K became similar in product distribution to its counterpart reduced at 848 K after a few ks onstream with propane feed at 803 K. For example, the product distribution over In-MFI (In/framework-Al = 1.0) reduced at 673 K had shifted after 4.7 ks onstream to no aromatics and 34% C_4's (on a carbon basis). A similar shift in product distribution was observed when a lower In loading was used (In/framework-Al = 0.83). However, an In-containing catalyst treated with 30% O_2/He at either 673 or 823 K, after initial high temperature reduction, gave a product distribution remarkably similar to Ga-MFI (Fig. 5). Note that long-term treatment with He of the material reduced at high temperature resulted in a similar product distribution; a slight O_2 impurity in the gas was probably the cause. However, these reoxidized In-MFI materials proved no more stable for reaction of propane than the other In-containing catalysts.

The results of Fig. 5 suggest that O_2 in the feed may be able to stabilize the more active In^+ state. This hypothesis was tested in experiments which showed enhanced aromatics formation for either In-MFI catalyst (In/framework Al = 1.0 and 0.83), when O_2 was present in the feed at <10 kPa (Fig. 6, conditions same as Fig. 5). The samples here were taken consecutively about 1.5 ks apart. There was also a beneficial effect of the O_2 on total conversion; however, it appeared that catalyst deactivation was accelerated by O_2 at the higher partial pressures used.

Regarding deactivation, the hydrogen-transfer capability of the reduced In-MFI catalyst continuously deactivated; this was evident from long-term (>50 ks) experiments at 803 K where the ethane/ethene ratio decreased while the
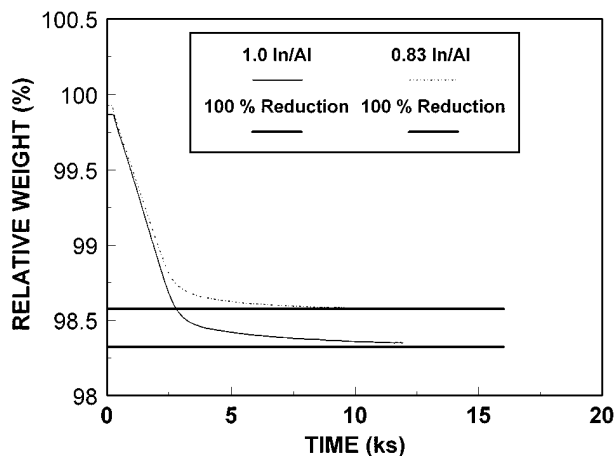

FIG. 4. Isothermal reduction curves for In_2O_3/H-MFI mechanical mixtures at 673 K in 25% H_2/75% He reagent gas. The heavy horizontal lines represent theoretical relative weights for reduction to the In^+ exchange state for 1.0 In/framework-Al and 0.83 In/framework-Al.
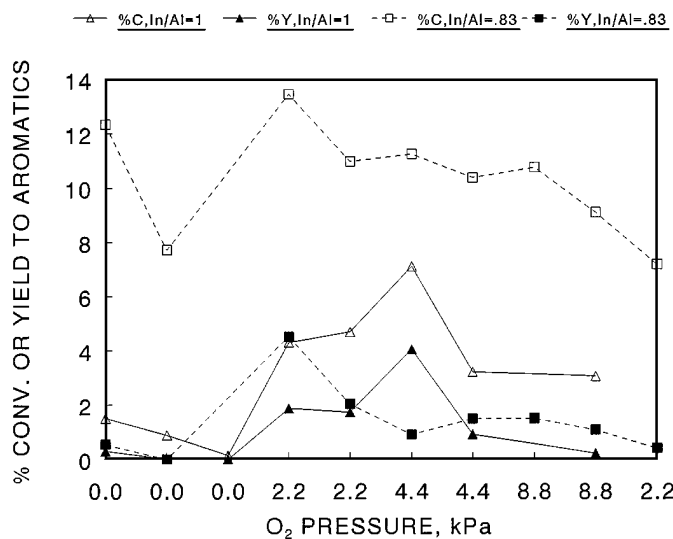
FIG. 6. Propane reaction at 803 K over In-MFI with O_2 in feed in the flow reactor system. Yield is the product of conversion and selectivity, on a mol% carbon basis. Pretreatment was with 30% H_2/70% He for 3 h at 673 K.

ethene/methane increased to >2. This deactivation, accompanied or caused by reduction to In metal which takes place onstream, probably explains the differences between our data and that of Fejes *et al.* (41), whose catalysts were not prereduced. The latter data showed high selectivity to aromatics and low selectivity to cracking products, both with and without O_2 present, and therefore must have been taken at short times onstream only.

In summary, the results for In_2O_3/H-MFI show that separate phases of In_2O_3 and H-MFI, or of the In^+-exchange state of MFI, are not stable under the working conditions of light alkane dehydrocyclization. The propane reaction causes transformation of H-MFI from a strongly acidic system to an active dehydrogenation material characterized by replacement of H^+ with In^+, and then to a relatively inactive material with (probably) reduced In metal present.

DISCUSSION

The catalytic systems reported in this paper were carefully chosen so that activity arising from zeolitic protons and zeolitic cations other than protons might be separately evaluated. Figure 7 compares yields of CH_4 from propane in the batch reactor experiments, and we provide this plot as evidence that the Ga-MFI sample is largely devoid of protons. We believe that the CH_4 yield is a good indicator of the relative proton populations of the catalysts based on the following thinking. For all the catalysts depicted in Fig. 7 except Ga-MFI, in the range of conversion depicted, the methane/ethene molar ratio is virtually equal to one as required by reaction 2, and protons are known to promote this type of behavior. For Ga-MFI, there is a complication in

that ethene/methane > 1, but the excess ethene apparently comes from cracking of a dimeric C_6 species as evidenced by simultaneous appearance of butenes (Table 3), and we assume that residual protons in Ga-MFI promote reaction 2 parallel to other reactions occurring at other catalytic sites. We note that the methane selectivities reported here for H-MFI and unreduced Ga_2O_3/H-MFI (which we expect to have a high proton content) are in full accord with previous work on similar materials (13, 19, 25, 33–35, 38, 42), so the very low selectivities found for Ga-MFI at short times are significant and suggest a very low proton content. A similar finding was recently reported for the reaction of ethane over Zn-MFI (43). Previous studies (21, 44, 45) have also reported low proton contents of similar materials. As Fig. 7 indicates, however, there are residual protons which will promote reactions of intermediate olefins in all the materials, but we believe that the high ratio of Me^+/H^+ will result in catalysis largely reflecting the action of Me^+ especially in the early stages of paraffin conversion.

Iglesia and co-workers (24, 38) have written a mechanism for desorption of hydrogen from Ga-containing MFI which requires the action of both protons and Ga-cation sites. A mechanism such as this, though possibly valid in the previous studies where a Ga/H^+ ratio of about 1/4 was used, may not be applicable for the Ga-MFI used in this study because of the proton-poor environment. Also, mechanisms which postulate separate zeolite and Ga-containing regions (e.g., 13, 33) are certainly not applicable because of the absence of a separate Ga-containing phase in our case. We therefore believe that consideration of a new mechanism involving only Ga sites is warranted because of the high Ga^+/H^+ ratio of materials in this study, though we do not suggest that such a mechanism should be favored over
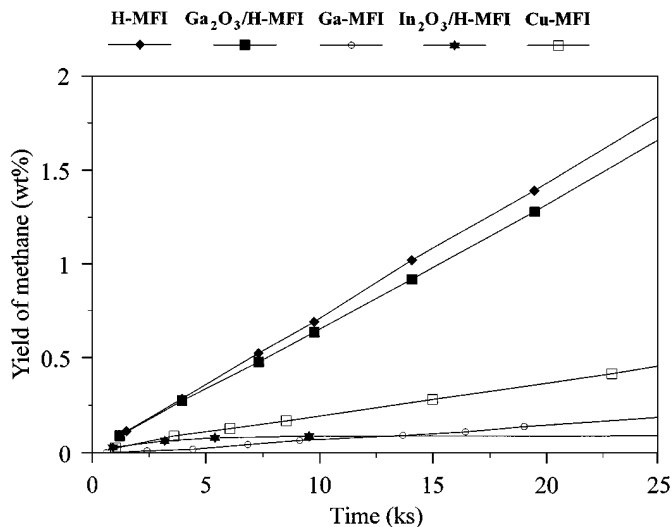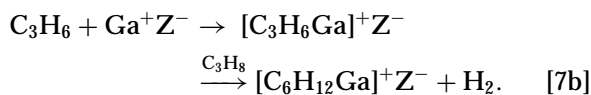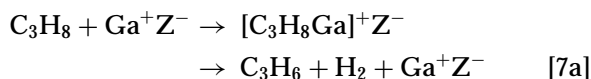

FIG. 7. Comparison of methane yields from the propane reaction at 748 K over H-MFI, Ga_2O_3/H-MFI, Ga-MFI, In_2O_3/H-MFI, and Cu-MFI, in a batch reactor.

other proposed mechanisms for materials with modest H^+ contents. In rethinking the mechanism, some existing proposals need careful consideration. First, Meitzner *et al.* (24) agreed that reduced Ga is coordinated to basic oxygens in the zeolite. The essential part of their and others' (25, 28) proposed mechanisms for the initiation reaction relies upon a $Ga^{\delta+}$ ($\delta \approx 1$)/Ga^{3+} redox cycle also involving zeolitic protons; it therefore cannot be used in its entirety in explaining our results. Second, Huang and Kaliaguine (26) proposed a mechanism for propene conversion on alkali–metal exchanged zeolites which involves polarization of C–H bonds on metal–oxygen acid–base pairs. This mechanism may be closely related to our results, since alkali-exchanged zeolites are largely devoid of protons, and the alkali–metal cations also exist in the 1^+ oxidation state. Third, Derouane *et al.* (46) proposed a mechanism involving Ga^{3+} cations, basic oxygen anions, and a proton which combines with propane forming a cyclopropyl cation and resulting in reduction of Ga^{3+} to Ga^+. Again, the essential features cannot be operative in our case because of the proton-poor environment, but the acid–base metal–oxygen pairs are obviously present in the reduced catalysts.

Though we emphasize that we believe conventional mechanisms on materials which contain a Me/H^+ balance are valid and operative, we suggest that the important aspects of catalytic activity in the case of proton-poor catalysts can be derived from the acid–base pair action of Ga^+ and neighboring basic oxygen anions associated with the zeolite framework which we generally denote as Z^-. This proposal arises from work of Kazansky (47, 48) who reported that such Lewis sites should be considered as acid–base pairs with their neighboring oxygen anions. We expect that oxygen anion neighbors of Ga^+ cations are more strongly basic than those surrounding Ga^{3+} cations. Because our results suggest that the controlling mechanism for proton-poor materials does not involve C–C bond rupture, we instead suggest a chain mechanism involving ions formed by the action of acid–base pairs on propene, similar to that recently proposed for initial reactions of ethane on Zn-MFI (43). The propene arises initially either as a trace impurity in the feed, or by a trace of protolytic activity, or by direct reaction with reduced Ga. Representative reactions are

$$C_3H_8 + Ga^+Z^- \rightarrow [C_3H_8Ga]^+Z^-$$
$$\rightarrow C_3H_6 + H_2 + Ga^+Z^- \qquad [7a]$$
$$C_3H_6 + Ga^+Z^- \rightarrow [C_3H_6Ga]^+Z^-$$
$$\xrightarrow{C_3H_8} [C_6H_{12}Ga]^+Z^- + H_2. \qquad [7b]$$

Consideration of other possible paths is also warranted. Alkenes might couple with another propene molecule to transform to higher oligomers via the mechanism proposed by Huang and Kaliaguine (26), where participation of the neighboring oxygen anions is important. The formation and

decomposition of $[C_3H_xGa]^+Z^-$ in reactions [7a] and [7b] might also occur simultaneously with another decomposition path represented by reaction 8:

$$[C_3H_8Ga]^+Z^- \rightarrow C_3H_6 + H^+Z^- + GaH. \qquad [8]$$
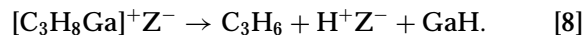
In this case, another path of chain propagation would be participation of the $C_3H_7^+$ carbenium ion in classical acid catalysis via addition of propene, forming C_6 surface carbenium ions which can crack, continue to add alkene molecules, or participate in hydrogen transfer reactions producing alkanes. It is difficult to quantify the contributions of these differing pathways for chain propagation, but our data suggest that chain growth via the Brønsted acid catalyzed process (sometimes termed conjunctive polymerization) is strongly restricted at least at short reaction times. For Ga-MFI, the high production rate of ethane, which parallels aromatics formation, and the high isobutane/*n*-butane ratio indicate rapid hydrogen transfer or hydrogenation of ethylene over Ga species (49). The production of methane at longer times onstream for Ga-MFI indicates that $C_3H_7^+$ ions become more prevalent.

Figure 8 shows that for Ga-MFI only a short induction period for accumulation of alkenes is necessary for aromatics production to begin. Such a period might even be absent for Cu-MFI where there is a higher rate of aromatics production at short times. Replacement of protons by Ga^+ leads to a high initial benzene content in the aromatic fraction, and for Cu-MFI benzene selectivity is even higher and benzene remains the dominant aromatic over a wider conversion range. The high benzene selectivity is not accompanied by increased methane formation, thus C_6-hydrocarbon precursors must be dominant in the oligomerization
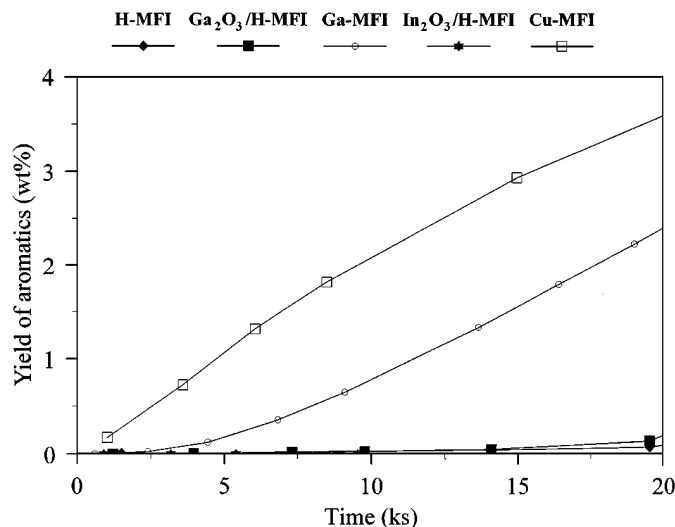

FIG. 8. Comparison of aromatics yields from the propane reaction at 748 K over H-MFI, Ga_2O_3/H-MFI, Ga-MFI, In_2O_3/H-MFI, and Cu-MFI, in a batch reactor.

product. This contrasts with the acid-catalyzed case where the oligomer precursors lead to toluene as the major aromatic product—as noted even for Ga-MFI at longer times onstream. The appearance of butadiene in the product can also be explained in light of a proton-poor environment, similar to the case for weakly acidic borosilicates (10). In summary, for the proton-poor Ga-MFI catalyst, we suggest that propene itself through reaction 7 is the more likely precursor to oligomers than the $C_3H_7^+$ carbenium ion which is generally considered to promote oligomerization in acid-catalyzed reactions. In the case of alkali–metal-exchanged zeolites which are weaker Lewis acids than Ga-containing zeolites, desorption of the C_6-oligomer occurs (26). For the Ga-MFI proton-poor system, we do not find C_5 and higher aliphatics in the product, so C_6-oligomers continue to undergo dehydrogenation and rearrangement yielding aromatics.

Initial rates of propene formation over Cu-MFI are higher than Ga-MFI probably because Cu^+ a is more efficient metal for dehydrogenation of hydrocarbon species. This is consistent with a recent investigation of the 1-propanamine reaction on Ga-MFI, Cu-MFI, and In-MFI (50) where we showed that the effectiveness of dehydrogenation of 1-propanamine followed the sequence $Cu \gg Ga > In$. In reaction [7], the mechanism of hydrogen desorption has not been specified, but evidence accumulated to date suggests that for proton-rich materials there is a recombination of H^+ produced by the decomposition of $C_3H_7^+$ and H^- which comes from metal hydrides (24). For example,
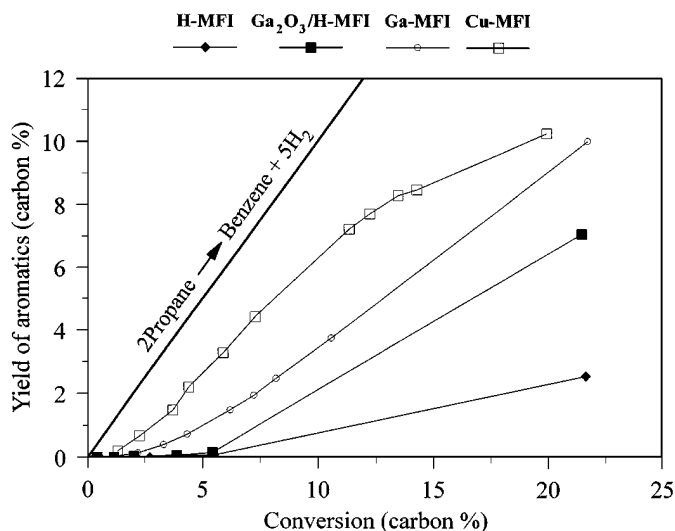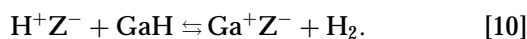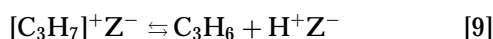
$$[C_3H_7]^+Z^- \rightleftharpoons C_3H_6 + H^+Z^- \qquad [9]$$

$$H^+Z^- + GaH \rightleftharpoons Ga^+Z^- + H_2. \qquad [10]$$

In the above mechanism, GaH is formally nonionic, but presumably maintains a partial positive charge because of its proximity to the electron-withdrawing zeolite framework. Reaction [10] suggests a dynamic equilibrium between Ga^+ and H^+ sites, and could be used to explain why we have been unable to prepare a material which has a proton content below detectable limits after a short time onstream.

Industrial application of Ga/MFI has already taken place, and the practical potential of Cu-MFI can be noted by an examination of Fig. 9 which compares the selectivity of Cu-MFI for aromatics production to other catalysts. Note the extremely high selectivity to aromatics prior to significant reduction of Cu^+ to Cu°. A reference curve for direct production of benzene from propane is included, and at the early stages of reaction, benzene production over Cu-MFI nearly parallels the ideal case. This suggests that if the Cu^+ state could be stabilized in MFI, the resulting catalyst would be far more selective than any Ga-containing material.

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H-MFI   Ga₂O₃/H-MFI   Ga-MFI   Cu-MFI

FIG. 9. Dependence of aromatics yields on propane conversion at 748 K over H-MFI, Ga₂O₃/H-MFI, Ga-MFI, In₂O₃/H-MFI, and Cu-MFI, in a batch reactor.

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