Proton-poor, gallium- and indium-loaded zeolite dehydrogenation catalysts

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Received 15 December 1997; accepted 29 April 1998

The catalytic (propane dehydrocyclization) and reduction behaviors of near 1 : 1 cation (Ga, In)/framework-Al MFI zeolites were examined under conditions where the materials were initially either in fully protonated or zero-protonated states. Reductions at appropriate temperatures proceeded up to ∼100% exchange of protons for reduced univalent cations. Further aqueous exchange of alkali (K^+) or alkaline earth (Ba^{2+}) cations increased the selectivity for dehydrogenation reactions at little or no sacrifice in overall activity.

Keywords: zeolites, dehydrocyclization, gallium, indium, alkali exchange

1. Introduction

The replacement of Pt by Ga or Zn as a dehydrogenation component in MFI represented a great advance in dehydrocyclization catalyst development. Ga has the advantage (over Zn) of lower volatility in H_2 at high temperatures. There are many patents and publications on Ga- and Zn-modified MFI and several reviews (e.g., [1–4]). The observation that the method of introducing Ga into MFI has only a small effect on the properties of the catalyst [5,6] led Gnep et al. [7] to assume that Ga-MFI is truly bifunctional. Ga_2O_3 in the catalyst presumably acts as a dehydrogenation component, which ensures a sufficient rate of dehydrogenation but low hydrogenolysis activity. Later, a synergistic effect of Ga_2O_3 and zeolitic protons for propane dehydrogenation was proposed [8,9], and, similarly, a back-spillover mechanism involving migration of monatomic hydrogen onto Ga_2O_3 [10].

The classical concept of polyfunctional catalysis deals with at least two distinct active sites catalyzing distinct reaction steps [11]. For example, 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 arose from earlier work here [12–15]. A solid-state reaction occurs between Ga_2O_3 and H-MFI to form Ga^+ cations in the zeolite pore structure:

$$(1/2)Ga_2O_3 + H_2 + H^+Z^- \rightarrow Ga^+Z^- + (3/2)H_2O \quad (1)$$

where Z^- is an anionic zeolite site. This finding was later confirmed by others [3,16–18].

Carli et al. [17] suggested that the role of H-MFI is to provide “activated” hydrogen able to reduce Ga_2O_3 at low temperature. Meitzner et al. [18] 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 in large numbers, 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 [19,20], finding that catalyst activity displayed a maximum when plotted versus the fraction of sites occupied by Ga; no formation of aromatics was observed in the absence of Ga or in the absence of protons at 803 K and high space velocity. The maximum was observed at Ga/framework Al $\approx 0.4 : 1.0$.

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 [21–23] – in other words, in almost all reactions involved in making alkenes and aromatics from alkanes. The question then arises: For what roles are the zeolite’s protonic sites truly necessary? The main objective of this work is to develop more selective dehydrogenation catalysts based on the combination of zeolite and post-transition metals (M), but with few or none zeolite protonic sites. The starting zeolite is a standard MFI, loaded with the post-transition metals Ga or In. We will show that the reduced metals alone, inside the zeolite, are apparently sufficient to catalyze all relevant dehydrocyclization reactions. This is accomplished by careful delineation between fully and partly (slightly <1 : 1 M/framework Al) loaded Ga-MFI or In-MFI catalysts.

In this work we used partial loading of basic cations (K^+, Ba^{2+}) on some catalysts in order to better eliminate residual protons. The MFI zeolite is almost 100% exchanged with Ga, In, Cu, etc., using solid-state ion-exchange techniques [13,24–27]. Available evidence suggests that much or all of the hydrogenolysis activity may be caused by a small residue (<5% of framework Al based on past work) of protonic sites in the zeolites, and that these sites cannot be exchanged (especially with Ga^+) except in ultra-pure environments and temperatures >820 K [27]. Therefore, we sought to obviate the need for 100% proton replacement by exchanging some alkali or alkaline earth ions into the metal-containing zeolites, after an initial reduction with H_2 in order to disperse the metals as much as possible. Following the alkali/alkaline earth aqueous ion exchange, we again reduced these materials, in order to eliminate (by reaction (1)) any protons re-introduced adventitiously. In this second high-temperature reduction, the extent of replacement of, say, K^+ by Ga^+, is far less certain; previous work suggests such a process is difficult even at 850 K, because of the non-volatility of the product oxide [28].

2. Experimental

Most of the catalysts were synthesized starting with fully exchanged H-MFI from PQ Corporation (Lot CBV-3020 with framework $SiO_2/Al_2O_3 = 43$). One catalyst (“0.95Ga”) and the Ga-containing samples for the NMR work used, as starting material, a UOP H-MFI, framework $SiO_2/Al_2O_3 = 40$. The SiO_2/Al_2O_3 ratio was determined by 1-propanamine adsorption on acid sites as described elsewhere [21–25]. Post-transition metal addition to the H-MFI was by mechanical mixing with the oxides. Reagent-grade In_2O_3 or Ga_2O_3 was mechanically mixed with dry H-MFI for 1 h (In) or 3 h (Ga) in a stainless-steel ball mill. All catalysts were initially dried in flowing He at 673 K for at least 6 h. The metal-loaded catalysts were reduced (except where noted) in 30% H_2/70% He at 848 K for 6 h (Ga-MFI, gallosilicate), or at 673 K for 4 h (In-MFI). An initial reduction always took place prior to any aqueous ion exchange with K^+ or Ba^{2+}. The aqueous exchanges were at ambient temperature for 24 h using the nitrate (0.1 M) with a large water/zeolite ratio, followed by filtration and water washing. Three exchange ratios were used: one well below exchange capacity, another with 10% excess salt, and the third with a large excess of the salts for comparative purposes.

Elemental analyses for Al and K or Ba (by ICP) were performed at Gulf Coast Analytical Laboratories (Baton Rouge, LA); duplicate analyses agreed to within 10%. In the TGA experiments, a catalyst sample ($\sim$10–15 mg) was loaded into the microbalance (Perkin-Elmer TGA7), dried in flowing He at 773 K until constant weight was reached, returned to 673 K in He, then reduced in flowing 30% H_2/ 70% He with a 5 °C/min ramp to the stated reduction temperature, followed by a 3 h final hold. Duplicate analyses agreed to within 5%. In pulse H_2 chemisorption experiments (Micromeritics Pulse Chemisorb 2700), the pretreatment procedures were similar, but with 300–600 mg loads. The H/M determination was made at 273 K, after reductive pretreatment, using UHP N_2 (BOC) carrier gas in conventional manner.

The ^{29}Si MAS-NMR experiments were performed on a Bruker MSL 200 MHz instrument using a 7 mm rotor at 5 kHz spin rate, with a 90° ^{29}Si pulse of 5 μs, high-power ^{1}H decoupling and 3 s relaxation delay. The IR spectra were taken in the transmittance mode using an IBM IR-30 FTIR. The zeolites were pressed into self-supporting waters, 6.5 mg/cm^2, which were loaded into a controlled atmosphere quartz IR cell and outgassed (<0.1 Pa) overnight at 773 K prior to further treatment. All spectra were taken at <0.1 Pa.

We used a standard microreactor system [25] with a quartz tubular reactor (1.25 cm i.d.) for the kinetics experiments. The system was capable of mixing and metering three gases to the reactor: propane, hydrogen (UHP, Liquid Carbonic), and helium (UHP, Liquid Carbonic). Propane was the model hydrocarbon reactant, helium was used as a diluent (12 kPa propane at total pressure 101 kPa), while hydrogen was mixed with helium to reduce the catalysts. A typical catalyst load was 200 mg, and typical weight-hourly-space velocities (WHSV, g(reactant)/(g(cat) h)) were from 1 to 9 (varied to keep conversion low), with a temperature range 723–773 K.

Gas samples to two GC’s (HP 5890 and HP 5880, FID detectors) were analyzed by a 30 m DB-1 (J + W) column to separate C_5 and higher hydrocarbons, and by a 30 m Al_2O_3-coated capillary (Alltech) column to separate C_1–C_4 hydrocarbons. Further details are in a thesis [29]. The selectivities were computed on a mols of carbon basis.

Prior to reaction, the catalysts were pelletized and ground to 20–40 mesh, oven-dried at 470 K, and loaded into the reactor. For those materials which had been ion-exchanged with basic cations, an additional reduction just prior to the reaction experiment was necessary; it was similar to the first reduction.

3. Results and discussion

In all results, catalysts based on the MFI zeolite are designated as, e.g., 1.2In, listing the elemental reduced metal cation and the approximate ratio of mols of this cation to the mols of framework Al in the zeolite. The amounts of K and Ba in base-exchanged catalysts were (from elemental analysis): $K/Al = 0.051$, $Ba/Al = 0.023$. These numbers are for samples exchanged using 10% stoichiometric excess of basic cation; therefore, replacement of intrazeolitic Ga by this process was minimal, close to 5% replacement in both cases. Because all of the K- and Ba-containing catalysts were, therefore, of similar composition, they are denoted K/Ga-a, -b, -c for materials ion-exchanged using less than stoichiometric K^+, $\approx$stoichiometric K^+, and a large excess of K^+ in the aqueous exchange solutions, respectively. The nomenclature for the Ba-containing samples is similar.

Table 1
TGA reduction experiments.

Sample	Reduction temp. (K)	Mass loss (%)		Metal reduced (%)
		Theoretical	Actual	
1.0Ga	848	1.75	1.70	97
0.83In	673	1.43	1.37	96
0.83In	823	1.43	1.59	111
1.0In	673	1.70	1.79	106
1.0In	848	1.70	1.95	115
Ba/Ga-a	848	1.06	0.75	71
Ba/Ga-b	848	1.06	0.78	73
Ba/Ga-c[a]	848	1.06	0.75	71
K/Ga-a	848	1.06	0.60	57
K/Ga-b	848	1.06	0.26	25
K/Ga-c[b]	848	1.06	0.30	28

[a] Used 11-fold excess Ba^{2+} in ion exchange.
[b] Used 36-fold excess K^+ in ion exchange.

3.1. Catalyst characterization

We followed the progress of the H_2-reductions of Ga and In by TGA; results are listed in table 1. The reduction reaction in the absence of basic cations was verified previously [13,15,24–27] and is shown as equation (1). In table 1, the “Mass loss (%), Theoretical” column for Ga- and In-MFI is based upon this stoichiometry. The “Metal reduced (%)” column is computed as the ratio of actual to theoretical loss, and is approximately the fraction of metal reduced to the 1+ formal oxidation state.

The 1.0Ga catalyst at 848 K and the In catalysts at 673 K show the expected metal reduction behavior. This is in agreement with previous work showing that In_2O_3/H-MFI is reduced at a lower temperature than Ga_2O_3/H-MFI [30]. The In catalysts at 823 K show greater than 100% reduction; also unlike Ga-MFI [15], with In-MFI it proved impossible to restore the sample to the initial weight of In_2O_3/H-MFI upon prolonged oxidation. Such behavior suggests reduction at 823 K of at least some of the In to its elemental state, with subsequent evaporation of metal atoms from surface. Somewhat similar sublimation behavior was found previously for Te-loaded zeolites [31]. Hydrogen reduction at near 800 K to In^0 for an In-containing Y-zeolite was confirmed by an XPS study [32], although Pt was also present. Such high-temperature reduction was previously determined to be undesirable for dehydrogenation catalysis [33]. At 673 K, the In reduces to the 1+ oxidation state, which is conducive to dehydrogenation catalysis. However, these materials reduce further while on-line at the higher temperatures characteristic of alkane dehydrogenation; therefore, In-containing catalysts are far less stable than Ga-containing ones in this application.

The reduction reaction in the presence of basic cations is not well understood, and previous work suggests Ga or In cannot easily displace alkali ions even at 850 K [28], while purely alkali-exchanged zeolites (no Ga or In) show no reductive weight loss whatsoever. At ambient temperature (actually, at as high as 773 K for Ga^+ [25]) the Ga^+ and In^+ are re-oxidized even in trace O_2 to dispersed metal oxides and $[GaO]^+$ ions [18]. These ions may have been partly or completely replaced by K^+ or Ba^{2+}. However, previous work on trivalent aqueous ion exchange into zeolites [34] suggests it unlikely that intrazeolitic Ga or In in the $[MO]^+$, $[M(OH)_2]^+$, or highly dispersed oxidic state could be extracted by water. The results from the elemental analyses support this hypothesis. We previously confirmed the difficulty of true aqueous exchange for Ga^{3+} using an XRD analytical technique [15], which showed that >75% of the Ga was still extra-crystalline after a conventional aqueous “ion exchange” followed by calcination.

If the second reduction of the catalysts, after aqueous exchange, were similar to reduction with no base present, it would follow the stoichiometry:

$$[GaO]^+Z^- + H_2 \rightarrow Ga^+Z^- + H_2O \tag{2}$$

This reaction would hold for the roughly 95% of Ga which was not displaced by K^+ or Ba^{2+}. The displaced Ga (5% maximum) would be reduced according to reaction (1). In table 1, the theoretical mass loss percentages for Ba/Ga and K/Ga are based on maximum conversion for this reduction reaction (equation (2)). It is clear that Ga reduction does take place to some extent, but is incomplete for both Ba- and K-containing materials. This is possibly because some of the Ga counterions were not oxidized during the aqueous ion exchange, or because there is some pore blockage associated with the added K or Ba. However, the key result listed in table 1 is that the amount of weight loss upon this second reduction was independent of how much excess Ba^{2+} or K^+ was used in the ion-exchange solution, supporting the conclusion that Ga and In were not lost to the solution during the ion exchange.

The percentage of theoretical metal reduction does increase somewhat for the K/Ga materials, as more K^+ is used in the exchange solution, up to the stoichiometric amount. Pore blockage may have been a problem with the more concentrated solutions, even though the total amounts of K^+ in K/Ga-a, -b, and -c are not significantly different. A pore mouth poisoning argument here is consistent with catalytic results presented in the next section.

We further examined these reductions at high temperature using H_2 pulse chemisorption. After reduction with a continuous H_2 stream (673 or 773 K for 3 h, In catalysts; 773 K for 15 h, K/Ga-b and 1.0Ga), there was no adsorption of pulsed H_2 at these same temperatures. This is indicative of complete reduction because >20 μmol/g was adsorbed prior to any water evolution in the unreduced catalysts. The H_2 adsorption results at 273 K for both reduced and unreduced catalysts are shown in table 2. Here we see that completely unreduced and fully reduced materials alike show little or no adsorption of H_2 at 273 K. However, the In-containing catalysts reduced at high temperature (where In metal forms) do show H_2 reduction. As these catalysts are cooled in even traces of O_2, a dispersed metal oxide should form inside the zeolite by analogy with Ga [18,25]. Therefore, we suggest that the dispersed metal oxide state is associated with the low-temperature H_2 adsorption. There

Table 2
H_2 adsorption at 273 K.

Sample	Reduction temp. (K)	Reduction time (h)	H_2 adsorbed (μmol/g)	H/M[a]
1.0Ga	n.r.[b]	n.r.	0	0
1.0Ga	848	24	0.13	3.7×10^{-4}
1.0In	n.r.	n.r.	0	0
1.0In	673	3	0	0
1.0In	693	3	0.14	4.1×10^{-4}
1.0In	848	6	7.8	0.023
1.2In	673	3	0	0
1.2In	848	6	14	0.034
K/Ga-b	n.r.	n.r.	0	0
K/Ga-b	848	6	11	0.033
Ba/Ga-b	848	6	2.0	6.0×10^{-3}

[a] Mols H atoms/mols metal atoms.
[b] Not reduced.

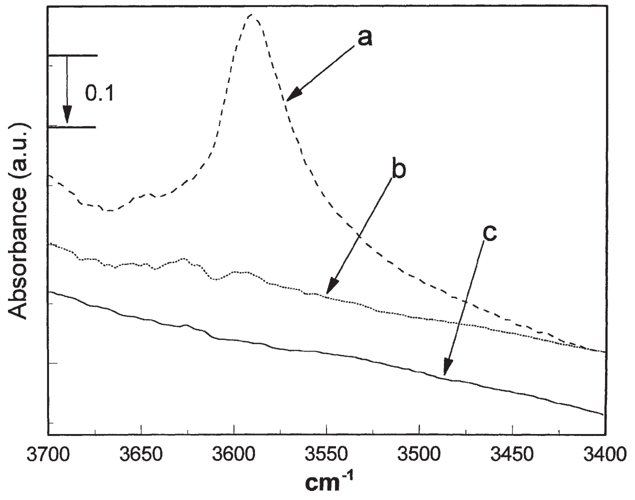

Figure 1. FTIR spectra under vacuum of the In-MFI catalyst 1.0In: (a) dried at 773 K; (b) 1 h reduction at 673 K; (c) same as (b), but 1 h additional reduction at 823 K.

is support for this suggestion in the H_2 adsorption behavior of the K- and Ba-containing catalysts (table 2), which are even more likely to contain some dispersed intrazeolitic $(GaO)_x$ because of the known difficulties in effecting Ga displacement of alkali as zeolitic counterions.

FTIR spectra of the 1.0In catalyst (figure 1) showed that ν_{OH} at 3610 cm^{-1} completely disappeared upon reduction, even at 673 K. The FTIR results for Ga-containing MFIs (figure 2) also showed complete disappearance of the bridged ν_{OH} band at ca. 3600 cm^{-1} upon standard reduction for K- and Ga-containing zeolites (either K/Ga-a or K/Ga-b). However, the band could not be fully eliminated for 1.0Ga, in agreement with previous work [25]. Therefore, although few protons are present in fully reduced Ga-MFI, almost none are present in the reduced alkali/alkaline earth ion-exchanged materials. Also, reduction of Ga- or In-containing catalysts was not accompanied by any significant change in the framework Si/Al ratio, as measured by ^{29}Si MAS-NMR (table 3). Only high-temperature treatment in O_2- or water-containing gases caused observable dealumination for such materials, and such treatments were avoided in these catalytic studies. Basically, the samples tested as catalysts show all the characteristics, when first put on stream in the fully reduced state, of highly crystalline zeolites with almost no protonic sites; they contain Ga^+ (or In^+) zeolitic cations and highly dispersed GaO_x (or InO_x) extraframework material within the pores.

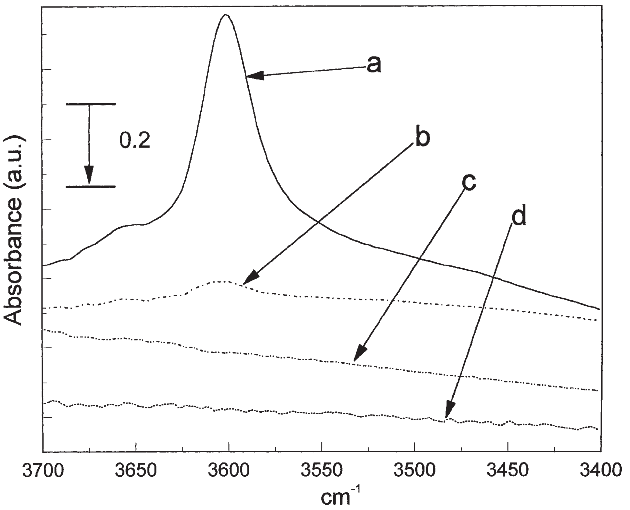

Figure 2. FTIR spectra under vacuum of Ga-MFI catalysts: (a) 1.0Ga, dried at 773 K; (b) 1.0Ga, 1 h reduction at 723 K, then 2 h reduction at 823 K; (c) K/Ga-a, 1 h reduction at 823 K; (d) K/Ga-b, 1 h reduction at 823 K.

Table 3
Si/Al from ^{29}Si NMR.

Sample	Treatment	Si/Al
H-MFI (UOP)	not reduced	26
0.95Ga	848 K reduction, 12 h	27
0.95Ga	800 K oxidation[a] (2 kPa O_2, 4 h)	35
0.95Ga	800 K steaming[a] (9 kPa H_2O, 4 h)	38
0.95Ga	800 K oxidation[a] (30 kPa O_2, 12 h)	40
0.95Ga	800 K steaming[a] (9 kPa H_2O, 12 h)	51
1.0Ga	848 K reduction, 6 h	20
0.83In	673 K reduction, 4 h	20
0.83In	673 K oxidation[a] (30 kPa O_2, 2 h)	40

[a] After reduction.

3.2. Catalytic behavior

When propane contacts a reduced metal/zeolite, many reactions can take place. The following have been proposed as reactions occurring at low conversion [33,35]. They are consistent with the observed product distribution:

(1) $C_3H_8 \rightarrow C_2H_4 + CH_4$

(2) $C_3H_8 \rightarrow C_3H_6 + H_2$

(3) $C_3H_6 + C_3H_8 \rightarrow i\text{-}C_4H_8 + C_2H_4 + H_2$

(4) $C_3H_6 + C_3H_8 \rightarrow C_6H_6 + 4H_2$

(5) $2C_3H_6 + C_3H_8 \rightarrow C_7H_8 + C_2H_6 + 3H_2$

(6) $C_2H_6 \rightarrow C_2H_4 + H_2$

(7) $i\text{-}C_4H_{10} \rightarrow i\text{-}C_4H_8 + H_2$

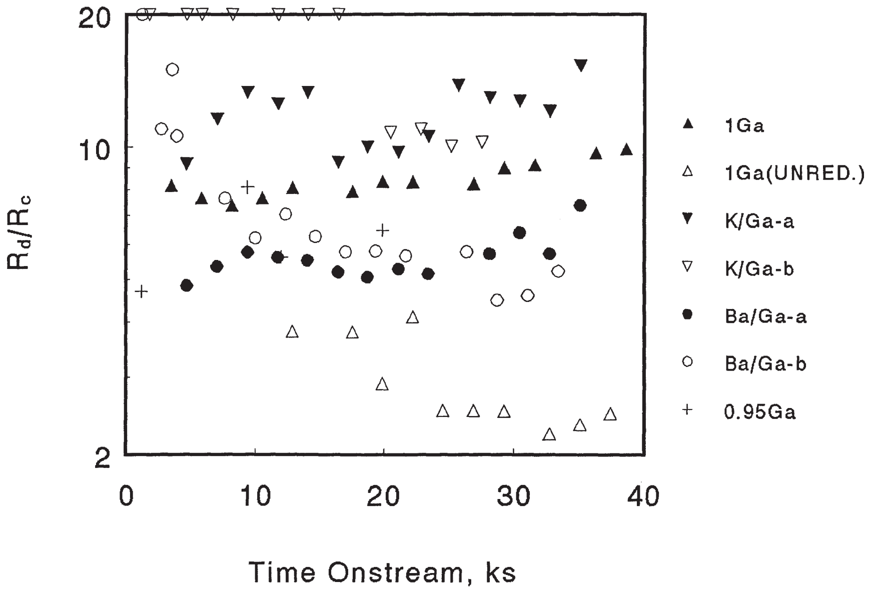

Figure 3. Propane dehydrocyclization, Ga-MFI catalysts; 723, 748 and 773 K, propane partial pressure = 12 kPa, WHSV = 1–9 h^{-1}.

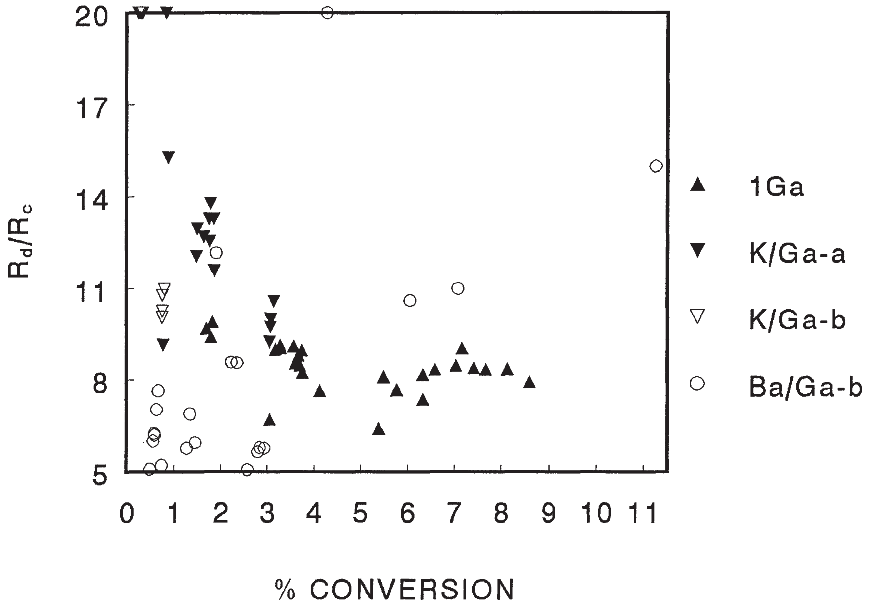

Figure 4. Propane dehydrocyclization, Ga-MFI catalysts of higher dehydrogenation selectivity; conditions same as in figure 3.

The primary undesirable cracking reaction is reaction (1). Reactions (2)–(7) are all dehydrogenations, and so desirable to differing extents. The ratio of the rates of reactions (2)–(5) to that of reaction (1) gives the ratio of overall dehydrogenation reaction rate to cracking reaction rate (R_d/R_c). Reactions (6) and (7) are excluded because they are not primary.

Because the conversions in these experiments are typically kept <5%, this rate ratio can be related to product ratios; in other words, the reactor is "differential" with rates directly proportional to the amounts of the products observed. Therefore, an estimate of R_d/R_c accounting for reactions (1)–(7) is as follows:

$$R_d/R_c = \left(M_{C_{3=}} + 2M_{C_4} + 2M_B + 3M_T\right)/M_{C_1}, \qquad (3)$$

where M_{C_3} represents moles of propene product, M_{C_4} moles of C_4's, M_B moles of benzene, M_T moles of toluene, and M_{C_1} moles of methane. C_8 and higher hydrocarbons were negligible at these conversions. The formulation and use of this ratio has also been discussed elsewhere [27].

In figures 3–5, results for propane microreactor experiments performed using Ga, K/Ga and Ba/Ga MFI catalysts are shown; figures 4 and 5 are basically selectivity versus conversion plots for catalysts, typically more selective than reduced 1Ga (figure 4), or less selective (figure 5). The experiments consisted of cycling through three temperatures (723, 748, 773, 748, 723 K, etc.) repeatedly. There are 2–3 data points at each temperature before moving to the next temperature. It is clear upon examining figure 3 that the se-

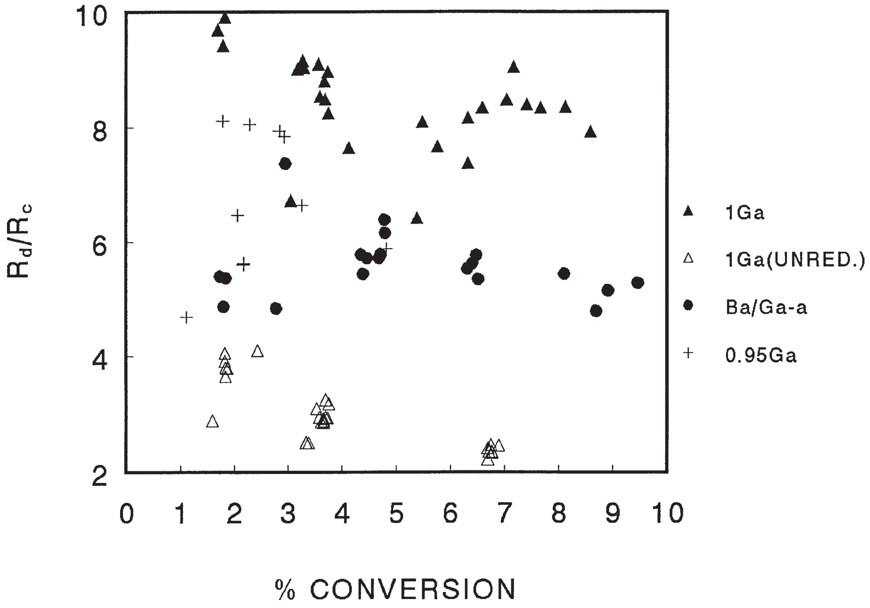

Figure 5. Propane dehydrocyclization, Ga-MFI catalysts of lower dehydrogenation selectivity; conditions same as in figure 3.

lectivity (R_d/R_c) depends more on the state of catalyst deactivation, as a function of time on-stream, than on temperature or conversion in the 723–773 K range. Catalysts such as 1Ga, K/Ga-a and Ba/Ga-a remain roughly constant in selectivity (data almost horizontal in figure 3). Catalysts such as Ba/Ga-b and 0.95Ga deactivate more rapidly; selectivity decreases monotonically with respect to time on-stream. However, the conversion is not decreasing monotonically, because of the temperature cycling.

First we note that, as shown previously, unreduced catalysts (1.0Ga) have relatively low selectivity (figure 5). Therefore, the superior selectivities of K/Ga-a, K/Ga-b and (at short time on stream) Ba/Ga-b cannot result from the fact that the available Ga was not reduced to a formal 1+ oxidation state, or that it remains in some highly dispersed, but not exchanged, oxidic state. Second, we note that the higher selectivities of these materials are not merely artifacts of lower propane conversions than for 1.0Ga, because for Ba/Ga-b the conversions at short times were actually greater (figure 4, data at >4% conversion). Furthermore, for K/Ga-a the selectivities at 1.5–3% conversion were all greater than for 1.0Ga at similar conversions (figure 4).

The above results are remarkable considering how true acid-catalyzed reactions in zeolites are poisoned by replacement of even a small percentage of the protons by alkali, with K^+ being a particularly effective poison [36]. Also, deuterium cross exchange studies have shown that the alkali cations cannot activate C–H bonds at these conditions [37], so these cannot be considered active sites for this reaction. We are left with the conclusion that the almost complete removal of protonic sites, as shown by the FTIR and TGA results, actually promotes the desired dehydrogenation reactions of these supposedly "bifunctional" catalysts. The results comparing 0.95Ga and 1.0Ga (figures 3 and 5) suggest the same thing. We further note that these reactions were run under highly reducing conditions, where the protonic sites are most prone to solid-state exchange (figures 1 and 2). However, our results certainly do not rule out as active sites intracrystalline hydridogallium and indium cations as active sites, as has been suggested by others [18,35]. Such sites would be formed by the interaction of H_2 and the M^{1+} cations.

The behavior of the K/Ga-b catalyst (figure 4) suggests that there was some difference in structure relative to K/Ga-a. The previous suggestion of more pore blockage for K/Ga-b was made on the basis of the TGA reduction results, but it is consistent with these results (lower activity for K/Ga-b) as well. However, the K/Ga-b was extremely selective; there was no measurable methane in the product stream for $\approx$20 ks; the R_d/R_c of 20, shown in figure 3, is just a minimum estimate based on our detection limits for methane at such low conversions. We note that for unreduced Ga-MFI or H-MFI catalysts methane is detected at even lower conversions [27]. The present data suggest that the small amount of methane generated by reduced Ga-MFI catalysts with Ga/Al $\approx 1:1$ is due to residual protolytic action. A similar finding regarding no methane production in high-loading zeolites was recently reported for the reaction of ethane over Zn-MFI [38].

Therefore, it appears that enhanced R_d/R_c with little sacrifice in activity occurs upon partial alkali exchange (possibly alkaline earth exchange as well although the data are more ambiguous) and almost-complete proton replacement in the zeolite. With Ga-MFI and no alkali we found it impossible to eliminate 100% of Brønsted sites, except using specially purified gases; the incompleteness of the reductions has been quantified both by TGA reductions and FTIR, as in figure 2 and past work [25–27].

For In-MFI, TGA reduction data [27] suggest that a more complete reductive solid-state exchange of In^+ is possible. Therefore, overloading of In might produce the same effect as partial alkali exchange. This appeared to be the case as

Table 4
Initial propane reaction data[a], In-MFI.

Sample[a]	Reduction conditions	Conversion (%)	R_d/R_c
1.2In	n.r.[b]	1.5	16
1.2In	673 K, 4 h	10	1600
1.0In	n.r.	1.7	0.37
1.0In	673 K, 4 h	2.4	1.1
0.83In	n.r.	1.0	0
0.83In	673 K, 4 h	5.2	0.51
0.83In	773 K, 4 h	2.1	0.23

[a] $T = 723$ K, WHSV $= 1.0$ h^{-1}, average of data from 1 to 6 ks time on-stream.
[b] Not reduced.

the data of table 4 show. It is seen that the % conversion and R_d/R_c both increased when the catalyst was reduced at 673 K; reduction at higher temperatures and longer times on stream at reaction conditions produced opposite effects. Again, this is likely a consequence of the reduction of some In to the metal. Higher loadings of In, to the point where all IR-detectable bridged –OH groups disappeared, resulted in both higher activity and higher R_d/R_c. Overloading of Ga did not produce a similar effect, because 100% reductive solid-state exchange (as seen from the TGA reduction curves) still was not possible.

The hydrogen-transfer capability of reduced In-MFI catalysts underwent continuous deactivation; this was evident from long-term (>50 ks) experiments at 803 K, where aromatics production ceased, the ethane/ethene ratio decreased, and ethene/methane increased to >2. This deactivation, accompanied or caused by reduction to In metal which takes place on stream, probably explains the differences between our data and that of Fejes et al. [39], whose catalysts were not pre-reduced. The latter data showed high selectivity to aromatics and low selectivity to cracking products and, therefore, must have been taken only for short times on-stream.

4. Conclusions

(1) For highly loaded post-transition metal zeolites, a higher metal loading (to at least 1/1 M/Al) increases both overall activity and the ratio of the rates of dehydrogenation to cracking reactions. Catalysts with a small but measurable number of zeolite –OH groups are poorer dehydrogenation catalysts. This finding does not agree with bifunctional theories of such catalysis, at least as they are presently formulated.

(2) It is possible to retain highly dispersed $(GaO)_x$ and $(InO)_x$ inside MFI under aqueous exchange conditions, even with excess alkali or alkaline earth cations in the exchange solutions.

(3) The exchange of some alkali or alkaline earth cations into the metal-loaded MFI zeolites can increase the ratio of the rates of dehydrogenation to cracking reactions, probably through the elimination of residual strongly acidic (Brønsted) sites.

(4) MFI zeolites with high In loadings are initially active and selective dehydrogenation catalysts, but on-line reduction of In to the metal under dehydrocyclization reaction conditions results in deactivation.

Acknowledgement

The authors gratefully acknowledge the financial support of the Department of Energy (Grant #DE-FG05-92ER14291) and the Exxon Education Foundation. One of us (MGB) acknowledges the support of the Louisiana Engineering Quality Support Fund/DOE Undergraduate Student Research Experience Program.

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