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Gallium-loaded zeolites for light paraffin aromatization: evidence for exchanged gallium cation active centers

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Abstract

It is shown that certain metal-loaded zeolites (e.g., Ga-MFI) initially prepared as separate metal-containing and zeolite phases are reducible, resulting in solid-state transfer of the metal to the zeolite. The final material is similar to those initially prepared as 'unsegregated' by methods such as aqueous impregnation. Reduction occurs either through appropriate pretreatment or onstream in certain hydrocarbon reactions. First, preparation methods leading to one or the other type of material are examined. Then it is shown that reduced catalysts give far higher ratios of dehydrogenation to cracking rates (for alkanes) than either segregated or unsegregated but unreduced systems. The product distributions of the propane reaction at low partial pressure and low conversion are also reviewed, and new data presented for unsegregated, reduced catalysts. There are great differences in the distribution obtained using reduced 1/1 metal/Al catalysts from corresponding distributions for the H-form zeolites or for segregated systems. The differences suggest a mechanism which may be entirely independent of catalysis by protons.

Keywords: Gallium-loaded zeolites; Light paraffin aromatization; Gallium cation active centers

1. Introduction and overview

Gallium-loaded zeolites are known to be active for the aromatization of light paraffins upon which the Cyclar process is based [1–3]. Many formulations of Ga-containing zeolites are known, but the overwhelming majority of useful materials are based upon the Ga/MFI system and we will focus on such materials here. These materials may also be useful for other chain-building and dehydrogenation reactions, for example the transalkylation of aliphatic amines [4] and in NO_x reduction using, for example, CH_4 [5].

In this paper, we classify metal-containing zeolite formulations as either segregated or unsegregated with respect to the method by which the metal and the zeolite are initially prepared. Examples of segregated materials include those studied by Le Van Mao and co-workers, who describe their materials as hybrid catalysts [6–11], the mechanical mixtures studied originally by Guisnet and co-workers [12,13] then later by Price and co-workers [14–19] and others [20–22], and materials prepared by vapor deposition of $GaCl_3$ onto H-MFI [23–25]. Unsegregated

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materials are those where Ga is deposited nearly uniformly within MFI, and they include aqueous impregnates, and gallosilicates and galloaluminosilicates isostructural with aluminosilicate MFI. These formulations have been studied by a broad range of researchers.

Whether or not Ga and MFI remain segregated under reaction conditions is of primary importance. The Ga oxide and acid sites of MFI are thought to act according to a bifunctional reaction mechanism whenever both types of sites are present; whether or not this synergistic interaction occurs over long distances is of great interest. It is thought that Ga as a dispersed oxide accelerates dehydrogenation by increasing the rate of H_2 recombinative desorption [26–29], while cyclo-oligomerization of olefins is thought to occur on the zeolite's Bronsted acid sites [13,30]. However, a number of researchers have provided evidence in support of catalyst transformations which occur via pretreatment or under reaction conditions which result in Ga^+ replacing H^+. Such a transformation has broad implications for the reaction mechanism because it greatly affects the relative acid strength.

We have observed that reduction of impregnated or mechanically mixed Ga_2O_3/H-MFI catalysts with H_2 or hydrocarbons is an effective method for incorporation of Ga^+ into the cationic positions of the zeolite framework [14–17]. We and others have also studied the relationship between initial activity and pretreatment method for Ga_2O_3/H-MFI alkane aromatization catalysts. It was found that reduction with H_2 is the most beneficial pretreatment, again giving Ga^+ cations within the zeolite prior to reaction [15,19,31,32]. The reduction of Ga_2O_3 appeared to be kinetically limited by the number of available cation sites in the host zeolite [15,33].

It is noteworthy that high surface area Ga_2O_3 and steamed gallosilicates (with little measurable Bronsted acidity) by themselves can react propane to propene, and aromatize dienes, 1-hexene, cyclohexene and methylcyclohexene at significant rates over the range 770–870 K [13,34,35]. For alkanes C_3 and larger, the formation of aromatics, while sensitive to H_2 partial pressures [36,37], is less sensitive to the almost complete absence of protons [15–17,37]. Zeolitic Ga cations, with enhanced Lewis acid strengths resulting from the electron-withdrawing nature of the zeolite, may therefore catalyze almost the entire transformation. It was recently observed that Ga_2O_3/silicalite gives the same product distribution (mostly cracking products) as H-MFI at the same conditions [31]. The only thing in common between these two materials is the absence of Ga in reducible cationic form.

For intimate mechanical mixtures of Ga_2O_3 and H-MFI, the Ga_2O_3 reduction and dispersion in the zeolite can be represented as follows [15]:

$$Ga_2O_3 + 2H_2 \rightarrow Ga_2O + 2H_2O \quad (1)$$

$$Ga_2O + 2H^+Z^- \rightarrow H_2O + 2Ga^+Z^- \quad (2)$$

This dispersion by reduction has been confirmed in a variety of FTIR [37,38], STEM [39], EXAFS [28] and XPS [40–42] studies, and has been extended to include $Ga(NO_3)_3$ aqueous impregnates [43–46] and gallosilicates which contain extraframework Ga as an artifact of the preparation and calcination procedure [47]. Reduced catalysts are far more active for alkane dehydrogenation (relative to protolytic cracking reactions) than unreduced Ga_2O_3/H-MFI mixtures and other segregated catalysts [14,15,31,48]; this will be demonstrated conclusively here using both new and past results at low conversion, but it should be noted that beneficial effects of reducing Ga-containing zeolites were noted some time ago in the patent literature [49].

Our recent results are consistent with a hypothesis that only a few zeolite proton sites, in conjunction with nearby Ga^+ sites, are needed to generate adsorbed alkyl chain carriers [37], which rapidly undergo dehydrogenation, oligomerization, and dehydrocyclization [25,27,50]. The catalytic cycle can of course be perpetuated by an H-transfer reaction of arenium, benzylic or similar carbenium ion with the alkane feed, especially at high conversions. We further explore this hypothesis in the following discussion, while also trying to explain why great differences in the catalytic behavior of Ga/MFI and related materials can exist even at similar metal/framework Al (M/Al) ratios.

2. Segregated materials

The discussion of this class of materials should begin with the distinction that these materials are initially segregated. Treatments can be applied which result in transformation to single-phase materials. An important aspect of the discussion of segregated materials is the conditions which are favorable for such transformations to occur.

Perhaps the best way to begin the discussion is to consider a class of segregated materials which are unlikely to undergo transformation to a homogeneous gallium-containing phase under typical pretreatment or catalytic reactor conditions. We consider this class to be the materials termed ‘hybrid’ by Le Van Mao and co-workers [6–11]. Typically, these materials are prepared by extrusion of a physical mixture of a Ga-containing co-catalyst, H-MFI, and a binder. The Ga-containing co-catalyst is usually a dried and calcined mixture of aqueous $Ga(NO_3)_3$ and colloidal silica. The effect of the preparation of the co-catalyst is to bind the gallium into an amorphous silica matrix which is relatively stable to the effects of hydrogen or hydrocarbon reducing agents. Indeed, treatment of a mechanical mixture of the Ga-containing co-catalyst and H-MFI in *n*-butane at 813 K for 10 h resulted in virtually no transfer of Ga into the zeolite; when the MFI crystals were retrieved from the mixture, they exhibited catalytic behavior virtually identical to H-MFI [9]. In a later publication [51], the possible transfer of Ga was further checked by treating a similar mechanical mixture at 813 K for 3 h in H_2, then separating the mixture by sieving. The resulting MFI phase contained less than 0.2% Ga_2O_3 which corresponded to less than 5% of the total initial gallium. Clearly, the 0.2% Ga_2O_3 residual could have resulted from imperfect sieving.

Buckles and Hutchings [21,22] have noted similar behavior with physical mixtures of Ga_2O_3 and H-MFI, reporting catalytic activities for these materials as being greater than the sum of the activities of the individual materials. They also separated the physical mixtures after treatment both with H_2 and with hydrocarbon under reaction conditions, and noted that the MFI component obtained after the separation process was chemically and catalytically similar to the original H-MFI used to make the mechanical mixture. This result prompted the researchers to claim ‘reversible formation of a catalytically active site’ [21]. However, Buckles and Hutchings have noted the ‘materials were mixed using gentle agitation in a glass tube’ [22], so that the post-reaction separation was possible. In contrast to our previous findings that intimate mechanical mixtures (prepared by intense ball-milling) undergo an activation process when placed on a propane feedstock at reaction conditions [14], Buckles and Hutchings noted that the increase in activity with time onstream for their mechanical mixtures ‘is not substantial’ [21]. These observations all point to the conclusion that transfer of gallium into the zeolite is minimal.

We should also note the pioneering work of Gnep et al. [13], who were among the first to test physical mixtures of Ga_2O_3 and H-MFI for light alkane aromatization. Unfortunately, the details of the mixing process were not reported, direct H_2 reduction was not applied, and post-reaction analysis was not performed; there is therefore not enough evidence to judge whether or not Ga transferred into the zeolite. However, the lack of a slow increase in the catalytic activity with time onstream, and the fact that careful attention to the intimacy of the mixture must be made for successful transfer suggests that, like the materials of Buckles and Hutchings, transfer did not take place.

Next, we would like to consider some segregated materials which do undergo transformation into a single phase, and discuss why the transformation process takes place. Kwak and Sachtler [24] have reported on materials prepared from a physical mixture of $GaCl_3$ and H-MFI. The physical mixture was heated at 473 K for 2 h, then 773 K for an additional 2 h. Prior to catalytic reaction, the material was treated in the reactor at 853 K, in O_2 for 1 h, then in H_2 for 2 h. As $GaCl_3$ melts at 351 K and boils at 474 K, these heat treatments will allow migration of the $GaCl_3$ to the zeolite where it can absorb, adsorb, or react. Thus Kwak and Sachtler have termed this process 'chemical vapor deposition'. Whether or not the $GaCl_3$ enters the zeolite pores during the initial heat treatment stage, and at what point reaction between $GaCl_3$ and protons of the zeolite occurs is not important to the discussion at hand. The important point is that $GaCl_3$ undergoes a close physical interaction with H-MFI by this process, and such an interaction is required before transformation can take place. We should further emphasize that at our present understanding of the process, the 'degree of intimate contact' which must be achieved cannot be quantified, but clearly a gentle agitation of two phases, such as that described by Buckles and Hutchings, is insufficient. Kwak and Sachtler also provided the second component for a successful transfer of Ga, which is reduction. In their case, direct H_2 reduction was used, but for a truly intimate mixture, the hydrocarbon feedstock is a suitable reducing agent.

Mechanical mixtures of Ga_2O_3 with H-MFI undergo a relatively slow activation period when placed on propane feedstock at typical aromatization conditions, but the transient activation period can be eliminated by pretreatment in H_2 [14]. Later we proposed a solid-state ion-exchange process for the interaction of Ga_2O_3 with H-MFI which included Ga^+ replacement of zeolitic protons [15]. Since intimacy of the mechanical mixture is of paramount importance, we should note that these initial studies used a mechanical mixture prepared by ball-milling Ga_2O_3 with H-MFI for 3 h. We later reported findings regarding the degree of ball-milling required to achieve substantial transfer of Ga [33]. For materials with 10 wt% Ga_2O_3, marked improvements in both the rate and ultimate degree of Ga_2O_3 reduction were observed as ball-milling time was increased to 3 h, after which both the rate and ultimate degree of reduction reached a plateau. This result itself suggests that the materials of Buckles and Hutchings, which were characterized as gently mixed, will not undergo reduction.

Our experiments measuring migration rates (by TGA, during reduction) of initially segregated systems find the rates dependent on temperature [15], amount of Ga present [46], amount of contact surface between MO_x and zeolite crystals [37], and crystal size of MO_x [52]. How slow the migration can be under typical reaction conditions can be seen in Fig. 1, where data were taken using pelletized mixtures of H-MFI and dried β-Ga_2O_3 or In_2O_3, after initial ball-milling. Total conversion and aromatics yield of the Ga_2O_3/MFI was still increasing after 90 ks onstream. These data were taken using a flow microreactor (see Experimental section).

A synopsis of the potential for segregated materials to undergo transformation to a single

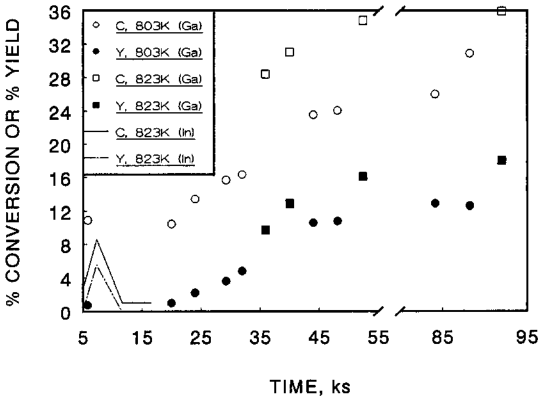


Fig. 1. Propane % conversion (C) and % yield to aromatics (Y) for initially unreduced mechanical mixtures of Ga_2O_3/H-MFI (UOP) and In_2O_3/H-MFI (UOP), C_3 partial pressure = 12 kPa, WHSV = 1.0 h^{-1}. The Ga/Al and In/Al molar ratios are 1/1. Mixing by ball-mill for 3 h (Ga) or 1 h (In).

phase material is as follows. Systems can be designed with high or low reduction potential. Highly intimate mixtures will undergo transformation when reduced, but poorly mixed systems and systems that bind gallium in a separate phase can remain segregated even under rather severe conditions.

3. Unsegregated materials

The broad types of Ga-containing catalytic systems which we will term unsegregated include materials treated with aqueous Ga salts and gallosilicates with the MFI framework topology. For this class of materials there is a wealth of evidence that, under reaction conditions, Ga zeolitic cations exist and are responsible for most of the catalytic activity.

The strong Lewis acidity associated with reduced Ga-cations at lattice sites has been measured through changes in EPR intensity upon adsorption of electron donors [53], in IR frequency of adsorbed pyridine [54] or CO [27], in NH_3 TPD [24], and in thermal analysis of adsorbed 1-PA [4]. All studies suggest the presence of strongly acidic sites in reduced Ga-MFI, even when FTIR data indicate almost no zeolite proton sites [37]. Perhaps the strongest direct evidence that H-MFI catalysts impregnated with $Ga(NO_3)_3$ undergo Ga reduction and solid-state ion exchange was provided by NEXAFS/EXAFS studies [28]. X-ray absorption near edge measurements detected reduction of Ga by H_2 or propane at reaction conditions, and EXAFS has shown that Ga is highly dispersed and mostly in the zeolite pores after reduction. The relationship of impregnated to Ga_2O_3 mechanically mixed systems is clear; impregnated materials yield Ga_2O_3 in intimate contact with H-MFI after any heat treatment breaking down the nitrate ion; the high initial rates of reduction for impregnates are consistent with this view [19,33,43]. We also observed no substantive differences in catalytic behavior between $Ga(NO_3)_3$ impregnates and Ga_2O_3 mechanical mixtures once transfer of Ga into the zeolite was complete.

Gallosilicates with MFI topology also contain Ga zeolitic cations under reaction conditions [47]. Extraframework Ga_2O_3, in intimate contact with the zeolitic framework, results from uncrystallized synthesis material or by accidental or purposeful removal from the framework.

4. Cataytic behavior of segregated vs. unsegregated materials

4.1. Experimental

Some additional data on propane conversion were necessary to delineate the behavioral differences in these materials as discussed below. The data were taken at propane partial pressures of 12–14 kPa with 90–100 kPa of He diluent using either a flow microreactor [37] or a batch recirculation reactor [4,52]. Operating procedures and analytical procedures for GC were exactly as described in these references. Selectivities to products and conversions of propane were computed on the basis of moles of carbon; yield is the product of selectivity and conversion. The starting zeolites were fully exchanged H-MFIs from PQ (lot CBV-3020 with framework $SiO_2/Al_2O_3 = 43$) and UOP (framework $SiO_2/Al_2O_3 = 40$). The framework ratios were determined using the 1-propanamine adsorption/desorption technique as described elsewhere [4,37].

The metal addition to H-MFI was by mechanical mixing. Initially, the appropriate quantity of Ga or In was ball-milled for 3 h (Ga) or 1 h (In) in the presence of the H-MFI. In the course of the work we found that the rate of reduction of Ga was more dependent on the aggregate size of Ga_2O_3 than H-MFI, and so it was more efficient to ball-mill the Ga_2O_3 alone for 24 h, then mix with H-MFI briefly in an agate mortar [52]. This new procedure did not affect the final weight upon reduction, which for all Ga and In catalysts followed the stoichiometry (to ±5% by weight) of the solid-state reactions (1)–(2). The times required for complete reduction at 848 K (Ga) or 673 K (In), and the final weights, were determined using a Perkin-Elmer TGA7 microbalance as described previously [4,15,33,37]. In the discussion below we denote an unreduced mechanical mixture as, for example, Ga_2O_3/MFI and a fully reduced material as, for example, Ga-MFI.

5. Results and discussion

In alkane dehydrogenations, the total alkane conversion is greatly affected by extraneous factors such as particle size, feed purity, framework Si/Al ratio, etc., making catalyst comparisons on this basis unreliable [37,52]. We have found that a relative dehydrogenation/cracking activity (R_D/R_C) is a better indicator of cation replacement, one which we have duplicated working with slightly different preparations. An estimate of R_D/R_C in a series-parallel network of propane dehydrogenation reactions was computed from a simple model of the overall reactions at low conversion and low propane partial pressure, similar to one proposed previously [55]:

$$C_3H_8 = C_2H_4 + CH_4 \tag{3}$$

$$C_3H_8 = C_3H_6 + H_2 \tag{4}$$

$$C_3H_6 + C_3H_8 = i-C_4H_8 + C_2H_4 + H_2 \tag{5}$$

$$C_3H_6 + C_3H_8 = C_6H_6 + 4H_2 \tag{6}$$

$$2C_3H_6 + C_3H_8 = C_7H_8 + C_2H_6 + 3H_2 \tag{7}$$

$$C_2H_6 = C_2H_4 + H_2 \tag{8}$$

$$i\text{-}C_4H_{10} = i\text{-}C_4H_8 + H_2 \tag{9}$$

The above reaction sequence is also justified based on the following observations from present and recent [52] work with reduced M/Al = 1 catalysts:

(a) the ratio of moles ($C_1 + C_4$) products to moles (ethane + ethene) is close to 1 when aromatics are in low concentration, and is < 1 otherwise;

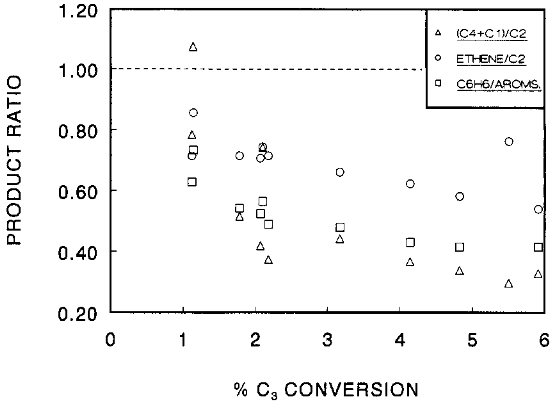


Fig. 2. Key product ratios for 1/1 (molar) Ga/Al Ga-MFI catalyst from conversion of propane (12–14 kPa, 748–803 K). Catalyst prepared by ball-milling Ga_2O_3 for 24 h, mixing with H-MFI (PQ) in agate mortar, then reduction with 25 kPa H_2/75 kPa He at 848 K for 3 h.

(b) the isobutane/*n*-butane and isobutene/(1- and 2-butene) ratios are large;

(c) benzene is the primary aromatic product at low conversion.

Data summarizing the key ratios ($C_1 + C_4$)/C_2, ethene/C_2, and benzene/aromatics for a 1/1 Ga/Al Ga-MFI are in Fig. 2; for Ga-MFI the ratios rapidly decrease from 1.0 with increasing conversion. For this reason In-containing analogs of Ga-MFI are especially useful in verifying reaction (5), because they are less active and also relatively inactive for aro-

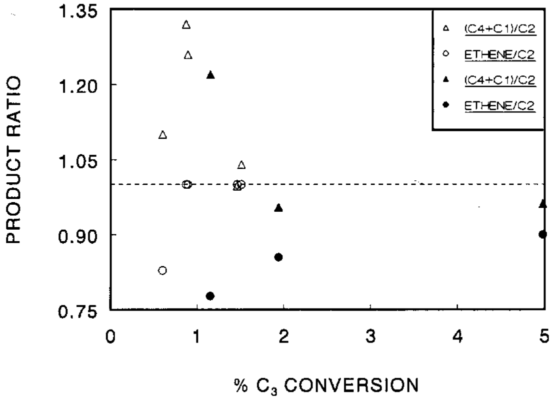
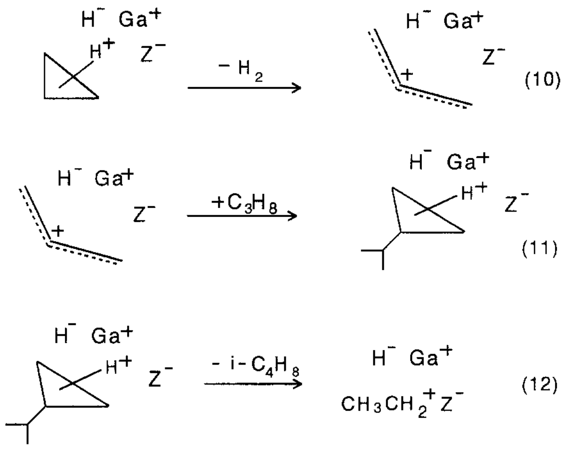


Fig. 3. Key product ratios for 1/1 (open symbols) and 0.8/1 (filled symbols) In/Al molar ratio In-MFI catalysts from conversion of propane (12 kPa, 723–803 K). Catalysts prepared same as in Fig. 1, followed by reduction with 25 kPa H_2/75 kPa He at 673 K for 3 h.

matics formation (more C_4s). Product distribution data for In-MFI catalysts in Fig. 3 again show a trend to an average of 1 for the key ratios, at low conversion.

Preliminary data suggest that the above product distributions at low conversion are also characteristic of catalysts prepared by wet impregnation and gallosilicates, for Ga-, In-, and Cu-guest metals. Our equilibrium calculations support the hypothesis that the product distribution at low conversions arises from a few specific reactions rather than any general equilibration of hydrocarbon products. For example, the iso/n-butane and iso/2- or 1-butene preferences of 1/1 M/Al (M = Ga, In, or Cu) MFI catalysts are far in excess of equilibrium thermodynamic ratios. Using the ASPEN PLUS® [56] global Gibbs free energy minimization routine, we determined (at 723–773 K and pressure < 15 kPa) these ratios, allowing formation of all C_2–C_7 alkanes, alkenes, cycloalkanes and cycloalkenes. The predicted iso/n-butane equilibrium ratios are slightly < 1, while the equilibrium isobutene/(2- and 1-butene) ratios are 1. The total C_4/C_2 equilibrium ratios are less than 0.05.

It is possible that each reaction (5)–(7) is really a combination of a few rapid serial reactions which cannot be distinguished easily. Reaction (5), for example, might occur as propane dehydrogenation in series with the classical Bronsted acid-catalyzed dimerization/β-cracking sequence for hydrocarbon disproportionation [57–59]. However, the primary product nature of isobutene can be rationalized even if it is assumed that propane rather than propene reacts with a carbenium ion. For example, the reaction to isobutene on a Lewis acid–base pair site might take place as shown in Scheme 1 (Z^- represents an anionic site of the zeolite lattice).



Scheme 1.

A similar mechanism for formation of a carbonium ion during the disproportionation of butane was recently proposed to explain such kinetics on Mordenite with extraframework Al [60]. The cyclopropane-type intermediate is consistent with the rapid scrambling of propane 2-^{13}C observed prior to the appearance of products in NMR studies [50]. Attack of the secondary carbon on an allylic intermediate in step (11) is consistent with the preponderance of iso-C_4 products we observed, the excess of ^{13}C at the tertiary position of the isobutane product, and the apparent commonality between the intermediates for ^{13}C scrambling and butane formation [50]. Assuming reversibility of step (5), the scheme is also consistent with observed rapid deuterium incorporation in propene from a propene/D_2 feed [29].

The possibility of a different mechanism for highly exchanged, Ga-loaded zeolites than for H-form zeolites is in fact suggested by our kinetics data; the total butane formation rate from propane for a typical H-MFI is $< 5\%$ that of the corresponding reduced 1/1 Ga/Al catalyst at $< 3\%$ conversion [52], and a very low iso/n-C_4 ratio is characteristic of H-MFI [24,61]. However, further study would be necessary to rule out the more conventional dimerization/β-cracking mechanism, or the alternative proposed by Huang and Kaliaguine [62] to explain their results on alkali-exchanged zeolites. Here it was assumed that an attack of propene would occur at the α-position of a σ-bonded C_3-alkyl. While plausible, this mechanism would not explain Derouane's [50] results.

In the set of proposed initial reactions, (4)–(7)

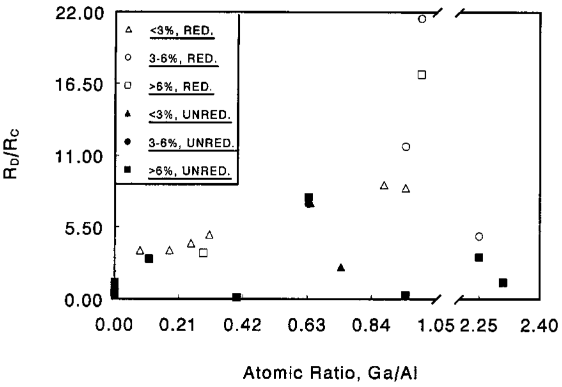


Fig. 4. Dehydrogenation/cracking rate ratio calculated according to Eq. (13) using various Ga-containing MFI catalysts and H-MFI, as described in text. New data for reduced materials at Ga/Al = 1 and 0.95 (molar) were taken using catalysts prepared same as in Fig. 2.

can be identified as dehydrogenations, leading to an estimate of R_D/R_C as follows:

$$R_D/R_C = (M_{C3=} + 2M_{C4} + 2M_B + 3M_T)/M_{C1} \tag{13}$$

where $M_{C3=}$ is moles of propene product, M_B moles of benzene product, etc. This ratio should be low when either a low extraframework Ga/(framework Ga or Al) ratio is present, or when the extraframework Ga is unreduced. Examining results for the propane reaction for just the Ga_2O_3/MFI (unreduced), Ga/MFI (reduced) and H-MFI systems, we prepared Fig. 4 using data from sources where the following information was available: (a) detailed product distribution at low propane conversion; (b) some measure of extraframework Ga/(framework Al) ratio; (c) information on catalyst pretreatment.

Such information can be found for H-MFI [15,24,27,31,34,55,61], for Ga_2O_3/MFI [3,13,15,34,48], and for extensively reduced Ga-MFI [15,24,25,27,31,34,48,52]. Some gaps in the graph were filled in with new data taken as discussed previously. Gallosilicates were excluded because, as discussed previously, it is difficult (impossible?) to ascertain the framework Ga composition after typical thermal treatments prior to reaction, unless post-treatment characterization is performed [47].

Fig. 4 raises several interesting points. First, the reduced Ga/MFI data follow a relatively smooth curve except in the vicinity of Ga/Al = 1.0. Second, the non-reduced (Ga_2O_3/MFI) materials always fall at or below the Ga/MFI smooth curve (at Ga/Al = 0.63 the non-reduced and reduced data almost exactly coincided). The R_D/R_C estimator for the non-reduced but unsegregated materials cannot describe a smooth curve because in this case the dehydrogenation rates are strongly dependent upon the time onstream at which product sampling took place (see Fig. 1) and the propane partial pressure. In other words, the reduction of Ga^{3+} in intimate mixtures, using H_2 produced in the dehydrogenation reactions, takes place during the microreactor experiments if we start with unreduced materials.

The third conclusion from Fig. 4 is that the optimum R_D/R_C occurs at Ga/Al ~ 1, and that at this composition R_D/R_C depends on factors other than Ga/Al and extent of Ga^{3+} reduction. One of these factors is dealumination. Our ^{29}Si MAS-NMR results suggest that long-term exposure to H_2 at > 800 K, while necessary to completely reduce Ga^{3+}, also increases framework Si/Al gradually. This causes mismatches between the amounts of Ga and framework Al. Using combined FTIR and adsorption measurements, it has recently been shown [63] that non-framework Al from thermal treatment can be highly dispersed. Therefore replacement of Ga^+ by oxyaluminum cations may result in decreased dehydrogenation selectivity with respect to time onstream, a decrease we continually observe.

We have also found that (in ethane aromatization) R_D/R_C, and overall yield to aromatics, can vary in the presence of small amounts of O_2 or H_2O in the feed. For Ga-MFI these impurities act to restore Bronsted sites in the zeolite through the reactions [19,23,24,37]:

$$[GaH_2]^+Z^- + O_2 \rightarrow [Ga(OH)_2]^+Z^- \tag{14}$$

$$H_2O + [Ga(OH)_2]^+Z^- \rightarrow Ga(OH)_3 + H^+Z^- \tag{15}$$

$$2Ga(OH)_3 \rightarrow Ga_2O_3 + 3H_2O \quad (16)$$

$$2Ga^+Z^- + O_2 \rightarrow 2[GaO]^+Z^- \quad (17)$$

$$Ga^+Z^- + H_2O \rightarrow [GaO]^+Z^- + H_2 \quad (18)$$

$$H_2O + [GaO]^+Z^- \rightarrow [Ga(OH)_2]^+Z^- \quad (19)$$

At ~ 800 K, short times onstream and low water pressures the gallyl cations $[GaO]^+$ apparently predominate. There is no reason to assume that small quantities of O_2 and H_2O would not have similar effects on propane aromatization, especially in experiments using flow microreactors where the effects on the actual Ga^+/Al ratio would be cumulative until an equilibrium determined by the impurity concentrations of O_2 and H_2O had been reached. Because R_C is already very low at Ga/Al ~ 1, the spread of the R_D/R_C results in Fig. 4 is unsurprising. Finally, we note that the highest R_D/R_C values recorded in Fig. 4 were taken in the quartz batch recirculation reactor using carefully reduced and specially purified helium and propane feeds [52].

As previously discussed, segregated catalysts can be effectively 'locked' into this state by starting with poorly mixed, large crystal sources of both metal oxide and zeolite. For example, such a system was used by Buckles and Hutchings [22], although at a higher temperature and propane partial pressure than in Fig. 4. It gave R_D/R_C values of only ~ 1.5–2.2 at Ga/Al ~ 0.6. On the other hand, gallosilicates show high R_D/R_C even when not pre-reduced. Some extraframework Ga is typically present after synthesis [47], and thermal activation at > ~ 800 K removes some framework Ga [28,64]; this extraframework Ga is easily reducible under reaction conditions. Data for such materials [65,66] suggest $R_D/R_C > 7.5$ at 723 K with Si/Ga ~ 20. With pre-reduced catalysts [66], even higher values are observed ($R_D/R_C > 8.4$ at 773 K with Si/Ga ~ 21) [2]. And of course the addition of Ga to a gallosilicate in a post-synthesis step, followed by reduction, also increases R_D/R_C (= 0.40 at 773 K with Si/Ga = 45, but increasing to 3.1 after 1 wt% Ga added and H_2 reduction [31]).

The In_2O_3/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. For In_2O_3/MFI, the reduction of In^{3+} and subsequent exchange of In^+ is rapid even at 700 K [67,68], and there is some further reduction to In^0 at higher temperatures [67,69]. Therefore the In-containing material builds to its maximum activity rapidly (Fig. 1), then loses dehydrogenation activity as the In is further reduced. Only cracking activity remains. Our results for these materials further confirm that optimal dehydrogenation activity is closely associated with the exchanged M^{+1} state in the post-transition metals.

Examining Fig. 1, and considering the ease of occurrence of reactions (14)–(19), it seems safe to conclude that even in carefully pre-reduced materials the maintenance of a 100% Ga^+ exchange state would be difficult, and that unreduced Ga_2O_3/MFI catalysts could deactivate and/or dealuminate at a faster rate than Ga exchange could take place. Conversely, In_2O_3/MFI, with its rapid solid-state ion exchange, can sometimes appear more active than Ga_2O_3/MFI, which helps explain some previous results comparing the two materials [70].

6. Conclusions

It is incorrect to assert that only one type of catalytic behavior is characteristic of medium-pore zeolites with guest Ga and related cations. The observed behavior will differ depending on whether the material is unsegregated to begin with, segregated but 'locked', or initially segregated but in a dispersed fashion such that metal

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[2] Actually there was a small amount of Pt present in this catalyst (Pt/Ga = 0.035). But the R_D/R_C ratio was < 1 using a corresponding aluminosilicate with far more Pt.

migration takes place on experimental time scales.

Under conditions where Ga is locked into a separate phase from the MFI, evidence shows that a synergism may still take place, resulting in catalytic materials which are more active together than the separate components. However, this does not preclude that Ga can undergo transformation, and given the appropriate reducing conditions there is clearly a transfer of Ga to cationic sites up to a level approaching 100% exchange. This is the case with conventional Ga-MFI formulations, so that, either by design or under reaction conditions, the replacement of protons by gallium cations eventually takes place. Also, because segregated materials are active and long range synergism does take place still does not preclude short range synergism involving reduced Ga cations and the zeolite. It is this synergism which results in high ratios of dehydrogenation to cracking rates.

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