

Structure and function of metal cations in light alkane reactions catalyzed by modified H-ZSM5

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Abstract

The rate of propane dehydrocyclodimerization to form C_6 + aromatics is limited by a sequence of irreversible dehydrogenation reactions leading to propene, higher alkenes, dienes, trienes, and aromatics. Quasi-equilibrated acid-catalyzed cracking, oligomerization, and cyclization reactions of alkene intermediates occur in sequence with these dehydrogenation reactions. Each dehydrogenation reaction is in turn limited by the rate of elementary steps that dispose of H-atoms formed in C–H bond activation steps. The rate of C–H bond activation, recombinative hydrogen desorption, and propane chemical conversion have been measured from the rates of isotopic redistribution and chemical conversion during reactions of C_3H_8/C_3D_8 and D_2/C_3H_8 mixtures on H-ZSM5, Ga/H-ZSM5, and Zn/H-ZSM5. Isotopic studies show that C–H activation steps are fast during steady-state propane dehydrocyclodimerization on H-ZSM5, Ga/H-ZSM5, and Zn/H-ZSM5.

Ga and Zn species increase the rates of propane chemical conversion, recombinative hydrogen desorption, and deuterium incorporation from D_2 into reaction products. Disposal of hydrogen formed in C–H bond activation steps occurs by transfer of H-atoms to unsaturated species to form alkanes or to Ga and Zn species, which catalyze the recombinative desorption of H-atoms to form dihydrogen (H_2). The sequential release of several H-atoms during a propane dehydrocyclodimerization turnover limits the rate and selectivity of this reaction on H-ZSM5.

In-situ X-ray absorption studies suggest that Ga and Zn species reside at cation exchange sites as monomeric cations and that recombinative desorption involve reduction–oxidation cycles of such cations during each dehydrocyclodimerization turnover. These monomeric species form directly during exchange of Zn ions from solution onto H-ZSM5. Ga^{3+} species, however, do not exchange directly from solution onto H-ZSM5, but instead form extrazeolitic Ga_2O_3 crystals. Ion exchange occurs during subsequent contact with propane or hydrogen at 700–800 K via vapor phase exchange of volatile Ga^{1+} species.

Keywords: Structure and function; Metal cations; Light alkane reactions; Modified H-ZSM5

1. Introduction

The selective conversion of light (C_1 – C_4) alkanes to alkenes, aromatics, and dihydrogen

via non-oxidative routes significantly expands the range of feedstocks available to form these useful petrochemicals and fuels. Dehydrocyclodimerization reactions of light alkanes were first reported in a series of papers by Csicsery [1–5]. These studies showed that the conversion of propane to aromatics occurs on Pt/Al_2O_3

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catalysts with low selectivity (18.7%) at high temperatures (833 K). The use of metal-exchanged zeolites to catalyze dehydrocyclodimerization reactions was first reported by British Petroleum researchers [6,7]; these reports disclosed the preferred use of Ga as the exchanged cation in H-ZSM5.

Since these initial reports, many studies have focused on the use of medium-pore pentasil zeolites. H-ZSM5 catalyzes the conversion of light alkanes to aromatics with low selectivity because of fast cracking side reactions [8–12]. H-ZSM5 catalysts are uniquely resistant to deactivation at the high temperature and low hydrogen concentration required for favorable dehydrocyclodimerization thermodynamics. H-ZSM5 catalysts also provide the basis for the M-forming catalytic reforming process reported by Mobil, a process that uses the alkene products of cracking reactions to alkylate benzene and toluene to higher octane aromatics [13,14].

The introduction of Ga [15–36], Zn [37–42], and Pt [43–47] species into H-ZSM5 increases the rate and selectivity of aromatization reactions and inhibits cracking side reactions that lead to loss of carbon to undesirable products. These cations, however, also decrease the unique stability of H-ZSM5 and lead to significantly faster rates of catalyst deactivation during alkane dehydrocyclodimerization [29]. This undesired side effect of the promotion of H-ZSM5 with Ga, Zn, and Pt has led to the recent use of these materials in moving-bed reactors in the CYCLAR process jointly developed by British Petroleum and UOP [48,49].

The catalytic role and the structure and location of metal cations in light alkane aromatization remains the subject of intense controversy even after significant emphasis and numerous publications. Ono and co-workers [15,38] have proposed that metal cations catalyze the selective conversion of alkenes to aromatics, but do not participate in the activation of the light alkane reactants. Their proposal is based on the observed increase in aromatic synthesis rate and

selectivity as well as the decrease in the concentration of intermediate alkenes when Ga is added. Guisnet et al. [17,18,24,46] suggest on the basis of the higher initial rate of propene formation when Ga is added, that metal cations are exclusively involved in propane dehydrogenation and naphthene dehydrogenation steps, while the remaining required reaction steps occur via conventional acid catalysis on intrazeolitic Brønsted acid sites.

Mole et al. [37] proposed that Zn cations in H-ZSM5 catalyze the desorption of H-atoms formed during C–H bond activation steps as H_2 , while the remaining required steps occur on zeolitic acid sites. This proposal is consistent with kinetic and isotopic tracer studies for propane reactions on Zn- and Ga-promoted H-ZSM5 by Inui et al. [43,50], Le Van Mao et al. [19,21,41], and Iglesia et al. [22,26,28,29,42]. These studies suggest a synergistic requirement for both acid sites, in order to stabilize alkane adsorption and C–H bond cleavage, and ‘metal’ sites, in order to dispose of the resulting H-atoms. Meitzner et al. [26] and Biscardi et al. [42] have reported structural studies of Ga and Zn species by X-ray absorption during propane aromatization. These studies suggest that hydrogen desorption occurs by the cyclic reduction and oxidation of monomeric Zn and Ga species. X-ray absorption studies have also detected the reduction and migration of Ga species during reducing pretreatments and propane reactions [26]; this phenomenon has also been suggested by the reduction and catalytic measurements of Price et al. [20,23].

In this review of dehydrocyclodimerization catalysis on modified H-ZSM5, we discuss in detail the literature evidence for the function and the structure of metal cations and of Brønsted acid sites during the dehydrocyclodimerization of light alkanes on modified H-ZSM5 zeolites. We also present new mechanistic evidence for the critical role of hydrogen transfer and disposal during the dehydrogenation and aromatization of these light alkanes.

2. Experimental methods

2.1. Catalyst synthesis

Na-ZSM5 (Zeochem, Si/Al = 14.5) was converted to the ammonium form by exchange with a 0.67 M solution of ammonium nitrate at 333 K for 20 h. This sample was exchanged again, filtered, washed with deionized water, dried at 373 K for 20 h, and calcined at 773 K for 20 h in order to convert it to the protonic form (H-ZSM5).

Ga cations were introduced by incipient wetness impregnation into H-ZSM5 with a 0.065 M solution of gallium nitrate, after several unsuccessful attempts to achieve significant Ga concentrations by ion-exchange. This sample was then dried and calcined (773 K, 20 h). These Ga/H-ZSM5 catalysts were pretreated in flowing hydrogen at 773 K for 1 hour before catalytic reactions. Two Zn/H-ZSM5 samples were prepared, one by ion-exchange of H-ZSM5 with a 0.0065 M solution of zinc nitrate and the other by incipient wetness impregnation into H-ZSM5 with a 0.0065 M solution of zinc nitrate. Each sample was filtered, washed with deionized water, dried at 373 K for 20 h, and calcined at 773 K for 20 h.

2.2. Elemental analysis

The Si and Al content in H-ZSM5 was measured by inductively-coupled plasma atomic emission spectroscopy (ICP-AES). The atomic Si/Al ratio in the Zeochem material was 14.5. This value remained constant throughout all exchange procedures and thermal treatments of the samples. The sodium content of H-ZSM5 was less than 0.15 wt% (as Na). The Zn and Ga content in metal-exchanged H-ZSM5 was also measured by ICP-AES. The Zn content in ion exchanged Zn/H-ZSM5 was 1.3 wt%. Zn, which corresponds to a Zn/Al atomic ratio of 0.20 in this sample. The Zn content of the

impregnated Zn/H-ZSM5 was 2.8 wt% (Zn/Al = 0.41). The Ga/H-ZSM5 sample was measured to have a Ga content of 2.1 wt% (Ga/Al = 0.29).

2.3. X-ray absorption spectroscopy

The structure and chemical state of Ga and Zn species in calcined Ga/H-ZSM5 and Zn/H-ZSM5 samples were examined by in-situ X-ray absorption spectroscopy at the Ga and Zn K-edges. Experimental procedures are described in detail elsewhere [26,42]. Ga K-edges were fitted by linear combinations of spectra from well characterized Ga³⁺ compounds and from Ga metal. The resulting best fit gave the fraction of the Ga present in various reduced and oxidized states [51]. Catalytic tests were conducted during X-ray absorption measurements using an in-situ cell design previously described [52].

X-ray spectra include sharp increases in absorbance at 10368 eV (Ga K-edge) or at 9659 eV (Zn K-edge), which arise from the ejection of Ga (or Zn) 1s electrons. The energy region near this K-edge contains detailed information about the chemical environment, bonding symmetry, and oxidation state of the absorber [53]. The extended X-ray absorption fine structure (EXAFS) in the energy range slightly above the absorption edge ($\Delta E = +50$ eV) arises from scattering of ejected electrons by atoms near the absorber. This region contains information on the chemical identity and bond distances of atoms near the absorber.

2.4. Catalytic reaction studies

Kinetic and isotopic tracer studies were carried out in a gradientless batch reactor consisting of a shallow packed-bed reactor contained within a gas recirculation loop [22]. Reactants and products were recirculated at $2\text{--}10\text{ cm}^3\text{ s}^{-1}$ using a graphite gear micropump in order to maintain differential reactor conditions (< 2% conversion per pass). The reactor was evacuated

by mechanical and diffusion pumps isolated from the system by liquid nitrogen traps. The chemical and isotopic compositions of reactants and products were measured by capillary chromatography using flame ionization and electron-impact mass spectrometric detection methods. Deuterium and carbon-13 content in products were determined from mass spectrometric data using matrix techniques that correct for ion fragmentation and natural ^{13}C abundance [54,55].

Undeuterated propane (Matheson, instrument purity, > 99.5%), perdeuterated propane (Isotec, chemical purity > 99.0%, isotopic purity > 99.0%), deuterium (Matheson, C.P., chemical purity > 99.5%, isotopic purity > 99.0%), and propene (Matheson, C.P., > 99.0%) were used as reactants without further purification. 2- C^{13} -propane (Cambridge Isotopes, chemical purity > 98.0%, isotopic purity > 99.0%) was purged by freezing in liquid nitrogen and evacuating several times. Hydrogen (Matheson, C.P., > 99.99%) was purified using an oxygen trap (Matheson) followed by a 13X molecular sieve trap at room temperature. Helium (> 99.95%) was purified using a 13X molecular sieve trap at room temperature before use as an inert diluent in microreactor studies.

Propane reaction rates are reported as the molar rate of propane conversion per g-atom Al in the catalyst charge. This represents a rigorous measure of the turnover rate only if Al sites catalyze the rate-determining reaction steps in a bifunctional catalytic sequence. It can be easily converted to a turnover rate based on Ga or Zn species by dividing by the (M/Al) atomic ratio in each catalyst sample. Batch reactor data are presented as turnovers vs. time plots; their slope give turnover rates for the formation of each product. Hydrocarbon selectivities are reported on a carbon basis as the percentage of the converted propane that appears as each reaction product. Hydrogen selectivities are similarly reported as the percentage of the hydrogen in the converted propane that appears as various products, including H_2 .

3. Results and discussion

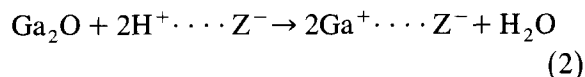
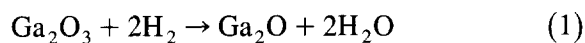
3.1. Structure of gallium species during catalyst synthesis and reaction

The beneficial effect of Ga on alkane aromatization rates and selectivity has been observed whether Ga ions are introduced by impregnation [16,26,28,29,33,35] or ion exchange techniques [15,18,22,23,32]. These effects are even observed when catalyst precursors consist of $\text{Ga}_2\text{O}_3/\text{H-ZSM5}$ physical mixtures [17,19–21,23,36] or of gallosilicates containing Ga species within framework positions in the pentasil structure [56–58]. In all cases, initial activation under reducing conditions appears to lead to the reduction of Ga^{3+} cations and to their migration from either extracrystalline or framework positions to cation exchange sites within zeolite channels [20,26]. In gallosilicates, reduction and migration of Ga species requires their extraction from framework position at high temperatures (> 973 K) [58].

Ion exchange procedures lead to the preferential deposition of Ga^{3+} species on the outer surface of zeolite crystals [20,23,26]. It appears that hydrated Ga^{3+} cations cannot enter the (0.55×0.57 nm) elliptical channels in ZSM5 during impregnation or ion-exchange [59]. During calcination, these extracrystalline Ga species convert to Ga_2O_3 crystals [20,23,26]. Ga_2O_3 reduces during pretreatment with hydrogen or during propane reactions at 773 K [20,23,26]. These reduced species appear to migrate into zeolite channels by surface diffusion processes that become possible for reduced Ga species at high temperatures. This reduction is confirmed by the shift in Ga K-edge energy to lower values detected by in-situ X-ray absorption measurements on Ga/H-ZSM5 during pretreatment in H_2 or propane dehydrocyclodimerization [26]. X-ray absorption studies also show that these reduced Ga species consist of monomeric Ga^0 or Ga^{1+} compounds [26]. Price et al. [20,23] and Meitzner et al. [26] have suggested that mobility may be induced by the

reduction of Ga_2O_3 to form volatile Ga_2O species.

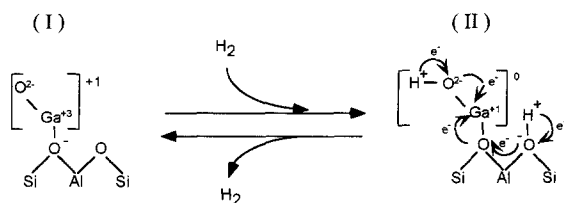
Gravimetric studies by Price and co-workers [20,23] have also shown that reduction occurs during hydrogen treatment by a sequence of steps involving the formation of Ga_2O from Ga_2O_3 and the migration and solid-state exchange between Ga_2O and protonic sites within zeolite channels (Eqs. (1) and (2)):



where Z represents oxygen atoms bridging Al and Si atoms in the zeolite framework.

Meitzner et al. [26] have detected by in-situ X-ray absorption the re-oxidation of reduced Ga^{1+} species to Ga^{3+} species upon cooling to room temperature even in H_2 or propane carrier gas, suggesting that the active form of Ga species can be detected only at reaction conditions.

We suggest that the steady-state product of the reduced Ga are neutral $[\text{GaOH}]$ species stabilized by interactions with basic oxygens within ZSM5 channels. These in-situ studies have suggested a reduction–oxidation mechanism for the desorption of H-atoms as H_2 during catalytic reactions of propane on Ga/H-ZSM5 (Eq. (3)):



where species (II) may account for the most

abundant form of Ga detected by in-situ EXAFS at reaction conditions.

3.2. Structure of zinc species during catalyst synthesis and reaction

In contrast with the results on Ga/H-ZSM5, Zn ions exchange directly onto intrazeolitic sites during contact with zinc nitrate solutions. Zn K-edge data were analyzed using Zn foil and ZnO as standards in order to detect the existence of Zn–Zn and Zn–O nearest neighbors and of Zn–Zn next nearest neighbors. These X-ray studies suggest that ion-exchanged Zn/H-ZSM5 (1.3 wt% Zn) contains only Zn–O nearest neighbors, suggesting that Zn is present as isolated Zn species at zeolitic exchange sites [42]. Direct exchange is apparently possible because of the smaller coordination sphere of divalent cations, such as Zn^{2+} , compared with those of Ga^{3+} cations.

Impregnation techniques lead to the formation of both exchanged Zn cations and of extracrystalline ZnO crystals, which can be detected by transmission electron microscopy and by Zn K-edge X-ray absorption [42]. Unlike Zn ion exchange, Zn K-edge studies using ZnO as a standard, suggest that Zn impregnated H-ZSM5 (2.8 wt% Zn) contains a small fraction of Zn–Zn next nearest neighbors, consistent with the presence of external ZnO crystals. These extracrystalline ZnO particles are poorly dispersed and do not significantly contribute to the rate of propane conversion or of recombinative hydrogen desorption [42]. In fact, impregnated Zn/H-ZSM5 (compared to ion exchange) results in lower propane conversion turnover rates,

Table 1

Propane turnover rates and aromatic selectivity on ion-exchanged (1.3%) and impregnated (2.8%) Zn/H-ZSM5

	Propane conversion turnover rate per Al site (10^{-3} s^{-1})	Aromatics selectivity (at 6% Conversion)
Ion-exchanged 1.3% Zn/H-ZSM5	5.1	25.4
Impregnated 2.8% Zn/H-ZSM5	2.0	24.7

773 K, 26.6 kPa C_3H_8 , balance He, 6.0% propane conversion.

suggesting that these ZnO species, formed during impregnation, may actually block zeolite channels and prevent access to some acid sites (Table 1). These external ZnO crystals also reduce and elute from the bed as gaseous Zn atoms during reduction in flowing hydrogen [42]. The reduction and vaporization of extracrystalline ZnO during reduction and reaction is confirmed by the presence of Zn metal films and H₂O droplets at the reactor exit. In contrast with the behavior of Ga₂O₃ during reduction, ZnO reduction does not appear to lead to migration into crystal channels or to solid state reactions with cation exchange sites, possibly because Zn lacks volatile intermediate oxides.

3.3. The effect of metal cations on propane conversion rate and selectivity

Propane conversion turnover rates and selectivities at similar conversions (8.6–9.6%) on H-ZSM5, Ga/H-ZSM5, and Zn/H-ZSM5 are shown in Table 2. Turnover rates for aromatics formation increase markedly when Zn or Ga are introduced within zeolite channels (Fig. 1). The selectivity to C₆–C₈ aromatics increases from 3.9% to 35.8% when Zn (1.3 wt%) is ion-exchanged onto H-ZSM5. The hydrogen selectivity to H₂ also increases from 4.6 to 30.5% when Zn is present (Table 2).

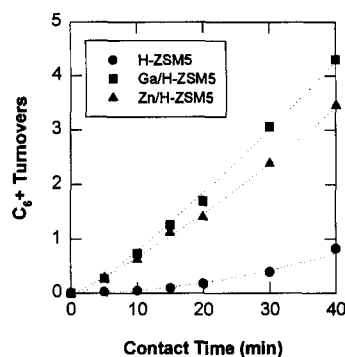


Fig. 1. C₆ + aromatic turnovers versus contact time from propane dehydrocyclodimerization reactions on H-ZSM5, 1.3% Zn/H-ZSM5, and 2.1% Ga/H-ZSM5 in a recirculating batch reactor [773 K, 26.6 kPa C₃H₈, balance He, turnover rates are given by slopes].

The presence of Ga or Zn species leads to an increase in the rate of H₂ formation via recombinative desorption of H-atoms formed in dehydrogenation steps (Fig. 2). In contrast, H-ZSM5 disposes of these H-atoms at significantly lower rates and predominantly by placing them within hydrogen-rich C₁ and C₂ alkanes. On H-ZSM5, hydrogen transfer reactions lead to the use of carbonaceous intermediates as stoichiometric sinks for the removal of the H-atoms formed in sequential dehydrogenation steps. Ga and Zn sites allow dehydrogenation reactions to occur without the requirement for concurrent crack-

Table 2

Propane turnover rates and product distribution on H-ZSM5, 2.1% Ga/H-ZSM5, and 1.3% Zn/H-ZSM5

	H-ZSM5	Ga/H-ZSM5	Zn/H-ZSM5
Aromatics turnover rate (per Al, 10 ⁻³ s ⁻¹)	0.1	2.3	1.8
Carbon selectivity (%)			
C ₁ –C ₂	62.3	29.3	25.8
Propene	24.9	30.8	32.9
C ₆ + aromatics	3.9	31.2	35.8
Benzene	1.2	12.3	15.1
Toluene	2.5	12.8	14.2
Xylene	0.1	4.9	5.5
Other	0.1	1.2	1.0
Hydrogen selectivity (%)			
Hydrogen (H ₂)	4.6	26.7	30.5
C ₁ –C ₂	66.7	29.2	26.2
Propene	18.7	23.1	24.5
C ₆ + aromatics	1.6	13.0	14.8

773 K, 26.6 kPa C₃H₈, balance He, 8.6–9.6% propane conversion.

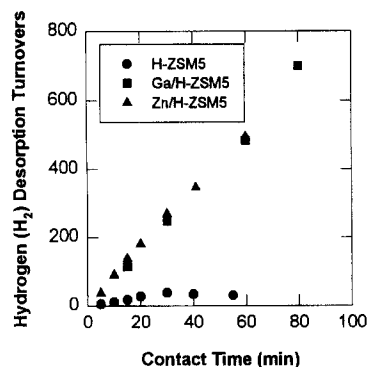


Fig. 2. Hydrogen (H_2) desorption turnovers versus contact time from propane dehydrocyclodimerization reactions on H-ZSM5, 1.3% Zn/H-ZSM5, and 2.1% Ga/H-ZSM5 in a recirculating batch reactor [773 K, 26.6 kPa C_3H_8 , balance He, turnover rates are given by slopes].

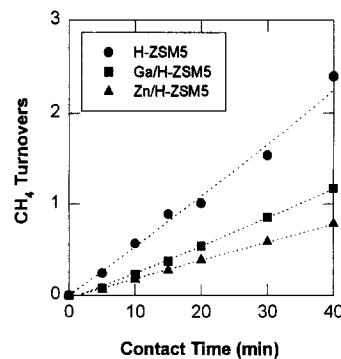


Fig. 3. Methane (CH_4) turnovers versus contact time from propane dehydrocyclodimerization reactions on H-ZSM5, 1.3% Zn/H-ZSM5, and 2.1% Ga/H-ZSM5 in a recirculating batch reactor [773 K, 26.6 kPa C_3H_8 , balance He, turnover rates are given by slopes].

ing. The addition of metal species to H-ZSM5 channels increase aromatic turnover rates and actually decrease cracking turnover rates (Fig. 3).

Mole et al. [37] first proposed on the basis of product distribution data that a large fraction of the H-atoms formed in dehydrogenation steps appears as H_2 on Zn/H-ZSM5. They suggested that Zn species introduce recombinative desorption sites for H-atoms into H-ZSM5 catalysts. Our recent isotopic tracer studies confirm this proposal [28,29,42].

We discuss later in this review three possible mechanisms that may account for this beneficial effect of metal cations on alkane dehydrocyclodimerization reactions.

(i) Zn and Ga species catalyze the initial dehydrogenation of propane to propene, while the remaining acid-catalyzed reactions of alkene intermediates occur on Brønsted acid sites within zeolite channels.

(ii) Zn and Ga species catalyze the recombinative desorption of H-atoms formed in an acid-catalyzed C–H bond activation reaction occurring as a first step in every dehydrogenation event required for an aromatization turnover.

(iii) Selective propane dehydrocyclodimerization occurs exclusively on Ga and Zn catalytic sites and the role of the H-ZSM5 component is

merely to protect these catalytic species against sintering and carbon deposits.

The first two hypotheses require the concurrent presence of acid sites and metal cations during reactions for light alkane dehydrocyclodimerization to occur with high selectivity.

3.4. The mechanism of propane dehydrocyclodimerization on H-ZSM5 zeolites

Reactions of propane on modified H-ZSM5 lead to the formation of a broad range of aromatics, alkanes, and alkenes (Table 2), suggesting the involvement of a complex reaction sequence. Aromatic products consist of a mixture of benzene, toluene, xylenes, and larger aromatics; the formation of these products requires several chain growth (oligomerization) and cracking events before aromatization. These oligomerization–cracking reactions lead to the formation of an ‘equilibrated’ mixture of unsaturated intermediates [60,61]. Cyclization and aromatization pathways become available as these intermediates acquire more than five carbon atoms.

Dehydrocyclodimerization reaction pathways have been extensively discussed in the literature primarily on the basis of observed effects of catalyst composition on reaction rate and selectivity. Recently, we have obtained more direct

evidence for the sequence of steps using isotopic tracer and exchange methods [22,26,28,29,42]. These methods have established the nature and the rate of individual reaction steps in this reaction sequence.

The initial propene intermediate, formed by dehydrogenation of propane, undergoes acid-catalyzed chain growth reactions within zeolite channels by oligomerization or addition to C_3 + carbocations. As the alkene chain lengthens, β -scission reactions become faster and ultimately establish a 'quasi-equilibrated' pool of alkene intermediates with a broad size distribution [60,61]. These alkene intermediates continue to undergo hydrogenation–dehydrogenation reactions, commonly described as hydrogen transfer, in which light alkenes accept hydrogen to form alkanes. C_6 + alkenes tend to dehydrogenate and cyclize to kinetically-stable and thermodynamically-favored aromatic products. Cracking of larger chains also occurs with the concomitant removal of hydrogen by its addition to light alkene products of cracking reactions. These individual mechanistic proposals suggest that propane dehydrocyclodimerization occurs via a complex sequence of dehydrogenation, oligomerization, cracking, and cyclization steps (Scheme 1). Below, we describe the experimental evidence for the role and rate of these individual steps during propane dehydrocyclodimerization.

3.5. Isotopic tracer studies of the initial formation of propene reactive intermediates

The rate of the initial dehydrogenation of propane and the intermediate and reactive nature of the propene formed in this reaction were probed by measuring the chemical and isotopic

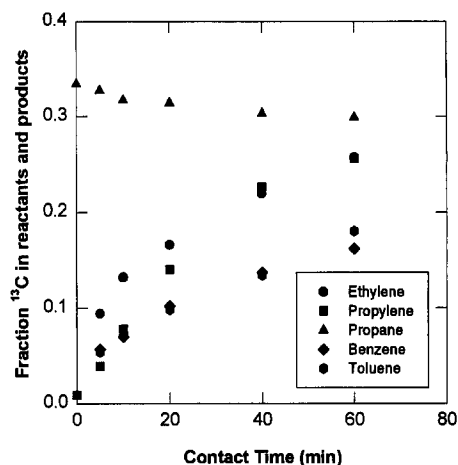


Fig. 4. ^{13}C content in reaction products of propene/ $2-^{13}C$ propane mixtures on H-ZSM5 in a recirculating batch reactor [773 K, 5.6 kPa C_3H_8 - $2-^{13}C$, 1.1 kPa C_3H_6 , balance He].

composition of reaction products formed from reactions of unlabeled propene and propane- $2-^{13}C$. The ^{13}C content in reaction products can be used to calculate the relative rates of propane and propene reactions and the fraction of the initial products (before isotopic scrambling within the reactant mixture) formed directly from either propane or propene molecules.

The isotopic content in reactants and products is shown in Figs. 4–6. On H-ZSM5, the ^{13}C content in propane decreases with increasing conversion (and contact time) because the pure propane- $2-^{13}C$ reactant is diluted by the unlabeled products of propene hydrogenation (Fig. 4). The ^{13}C content in propene increases with contact time because the initially unlabeled alkene is diluted by the labeled products of propane dehydrogenation. The aromatics and cracking products are initially unlabeled, consistent with their direct formation from the unlabeled propene in the feed. The isotopic content



Scheme 1. Reactions of propane on H-ZSM5-based catalysts.

in these products increases in parallel with that in propene, because they are formed from increasingly enriched propene.

The ^{13}C content is very similar in ethylene and propene products. Therefore, it appears that these reaction products are formed from a common pool of alkene intermediates and not from propane as expected from direct propane cracking. The ^{13}C content in toluene and benzene is slightly lower than in propene because of the fast initial formation of unlabeled large alkene intermediates, which are diluted slowly with time as the products of the enriched propane reactant begin to contribute to the observed products. On H-ZSM5, all aromatic products form only from propene, as shown by the lack of ^{13}C enrichment in initial reaction products (Fig. 4). These data show that alkenes are required intermediates in the conversion of propane on H-ZSM5 [42].

The addition of Ga (Fig. 5) and Zn (Fig. 6) to H-ZSM5 does not appear to perturb these reaction pathways. Initial reaction products do not contain ^{13}C and are formed predominantly from unlabeled propene molecules in the feed mixture. The rate of ^{13}C scrambling between propane-2- ^{13}C and unlabelled propene, however, is influenced by the presence of Ga and Zn. For example, the ^{13}C -content in propane

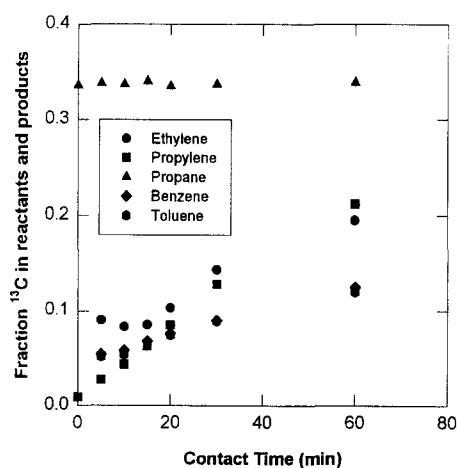


Fig. 5. ^{13}C content in reaction products of propene/2- ^{13}C propane mixtures on 2.1% Ga/H-ZSM5 in a recirculating batch reactor [773 K, 5.6 kPa C_3H_8 -2- ^{13}C , 1.1 kPa C_3H_6 , balance He].

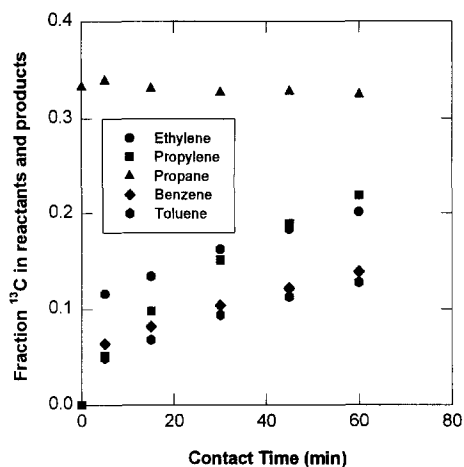


Fig. 6. ^{13}C content in reaction products of propene/2- ^{13}C propane mixtures on 1.3% Zn/H-ZSM5 in a recirculating batch reactor [773 K, 5.6 kPa C_3H_8 -2- ^{13}C , 1.1 kPa C_3H_6 , balance He].

decreases more slowly with increasing contact time on Zn/H-ZSM5 (Fig. 6) and on Ga/H-ZSM5 (Fig. 5) than on H-ZSM5 (Fig. 4), suggesting that the rate of propene ‘hydrogenation’ to propane decreases when Ga and Zn are added. This observation appears to contradict the expectation that metal cations would increase the rate of alkane dehydrogenation and of its reverse reaction (alkene hydrogenation). As we discuss below, this apparent contradiction arises because Ga and Zn cations also increase the rate of propene conversion to aromatics, a reaction that requires several sequential dehydrogenation steps, even more than they increase the rate of propane dehydrogenation to propene.

The rate of isotopic scrambling between propane-2- ^{13}C and unlabeled propene and the isotopic content of chemical reaction products can be used to calculate the relative rates of propene hydrogenation (r_{-1}) and conversion to other products (r_2) (Eq. (4)). In effect, one can obtain r_2 and r_{-1} values at various levels of conversion for H-ZSM5, Zn/H-ZSM5, and Ga/H-ZSM5 from these experimental results. The (r_{-1}/r_2) values for all three catalysts are shown in Fig. 7. This ratio is almost independent of conversion (contact time). The values of (r_{-1}/r_2) extrapolated to zero conversion are

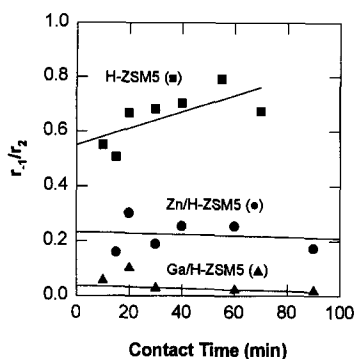
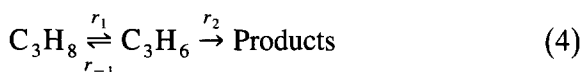


Fig. 7. Measurement of r_{-1}/r_2 in propene/2- ^{13}C propane mixtures on H-ZSM5, 1.3% Zn/H-ZSM5, and 2.1% Ga/H-ZSM5 in a recirculating batch reactor [773 K, 5.6 kPa C_3H_8 -2- ^{13}C , 1.1 kPa C_3H_6 , balance He].

0.55 (H-ZSM5), 0.23 (Zn/H-ZSM5), and 0.02 (Ga/H-ZSM5). In effect, Ga and Zn increase r_{-1} , and therefore the rate of its reverse reaction (r_1 , propane dehydrogenation), but they increase even more subsequent steps occurring at a rate r_2 . Therefore, Ga and Zn influence both the initial dehydrogenation step and the subsequent dehydrogenation steps that must occur to convert propane intermediates to aromatic products.



On all three catalysts, the (r_{-1}/r_2) ratio is less than unity (0.02–0.55), consistent with a non-equilibrated initial dehydrogenation step. In effect, this step becomes even more irreversible (r_{-1}/r_2 decreases) when Ga or Zn are introduced into H-ZSM5 catalysts, because required subsequent dehydrogenation reactions are more strongly influenced by these cations than the initial dehydrogenation reaction.

Carbocations are surface reactive intermediates (or at least activated complexes) in reactions catalyzed by Brønsted acid sites [62]. The two major mechanistic routes proposed for alkane conversion over H-ZSM5 involve the activation of propane by hydride abstraction from the reacting alkane by adsorbed carbenium ions (bimolecular) or by addition of protons to alkenes to form a carbenium ion (monomolecu-

lar) [63]. Reactions of propane-2- ^{13}C and unlabeled propene over H-ZSM5 were conducted to examine the relative contributions these mechanistic routes during propane dehydrocyclodimerization on H-ZSM5. Bimolecular reaction pathways would result in an increase in propane conversion turnover rates when propene is added to the propane reactants. If the rate of propane conversion remains unchanged when propene is added, the reaction proceeds via a monomolecular mechanism. Turnover rates for propane-2- ^{13}C conversion were found to be not catalyzed by the addition of unlabelled propene to propane-2- ^{13}C mixtures over H-ZSM5 (Fig. 8). This suggests that reactions of propane form carbocations via a monomolecular route. This also precludes the possibility that trace amounts of alkenes catalyze the initial activation of propane by providing $\text{C}_3 +$ carbocations as chain initiators.

An alternate monomolecular mechanism appears to be favored at high temperatures and low pressures [63] and leads to the direct protonation of a propane molecule to form carbonium ions (C_3H_9^+). This adsorption step is followed by carbonium ion decomposition into C_3H_7^+ and H_2 or C_2H_5^+ and CH_4 . Our isotopic studies support the activation of propane by a monomolecular route (Fig. 8), but provide no evidence for carbonium ion intermediates. On the contrary, H_2 produced during propane dehy-

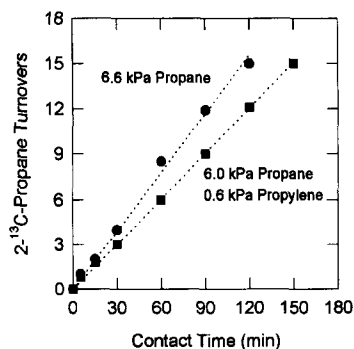


Fig. 8. Propane conversion turnovers versus contact time in propene/2- ^{13}C propane mixtures on H-ZSM5 in a recirculating batch reactor [773 K, 6.0–6.6 kPa C_3H_8 -2- ^{13}C , 0–0.6 kPa C_3H_6 , balance He, turnover rates given by slope].

dehydrocyclodimerization does not directly correlate with the propene produced over H-ZSM5, as expected by the mechanism proposed by Haag [63]. The lower than stoichiometric H_2 production may result from dissociative re-adsorption of H_2 and hydrogenation of alkene intermediates into alkanes. Isotopic evidence by Iglesia and co-workers [22,26,28,29,42] using C_3H_8/D_2 mixtures, however, confirms that the dissociative adsorption of gas phase deuterium over H-ZSM5 is minimal. Thus, our studies do not support the involvement of carbonium ion intermediates in propane dehydrocyclodimerization.

3.6. Formation and scission of carbon–carbon bonds

Reactions of positionally labeled alkanes can be used to study the mechanism of cyclization reactions [55,64,65]. Specifically, the analysis of the content and location of ^{13}C in the products of propane-2- ^{13}C reactions can establish the reaction pathways required for conversion of propene intermediates to stable aromatic products. For example, a simple cyclization of two propene-2- ^{13}C molecules formed from propane-2- ^{13}C would lead to benzene-1,4- ^{13}C .

On H-ZSM5, all products of propane-2- ^{13}C reactions contain a binomial distribution of ^{13}C -atoms, instead of the expected single isotopomer, even at very low conversions (Fig. 9). Disappointingly, all information on the location and content of ^{13}C -atoms in the propane-2- ^{13}C is lost during a dehydrocyclodimerization turnover on H-ZSM5. The ^{13}C atoms have exchanged positions not only within a single C_3 moiety, but among several. In effect, C–C bonds in propane have been broken and re-formed within a C_3 fragment and within much larger surface chains many times (> 10) in the time required for a dehydrocyclodimerization turnover. Such a turnover requires the formation of a C_6 or larger molecule, a process that involves oligomerization reactions, but also a significant number of cracking and rapid methyl

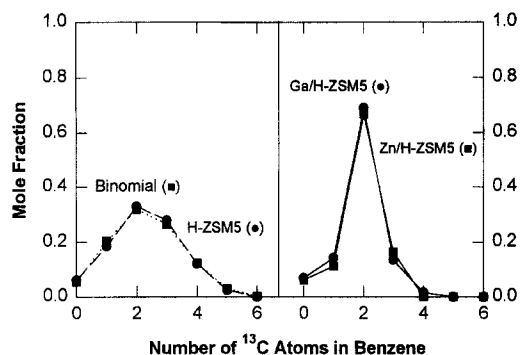


Fig. 9. ^{13}C distribution in benzene formed from propane-2- ^{13}C on H-ZSM5, 1.3% Zn/H-ZSM5, and 2.1% Ga/H-ZSM5 in a recirculating batch reactor [773 K, 6.7 kPa C_3H_8 -2- ^{13}C , balance He, $< 5\%$ conversion].

shift events. These oligomerization–cracking and isomerization reactions quickly establish an ‘equilibrated’ alkene mixture that is independent of the size of the alkene reactant [60,61]. Both chain length and methyl group position appear to reach equilibrium values. Another possible mechanism, recently proposed to explain similar scrambling during methanol conversion to light alkenes on H-ZSM5, involves the addition of alkenes directly to large carbocations, followed by β -scission without termination of the carbocation chain [66]. The broad carbon number distribution within aromatic products of propane reactions on H-ZSM5 (Table 2) is also consistent with extensive C–C bond formation and cleavage during dehydrocyclodimerization reactions.

Products of 2- ^{13}C propane reactions on 1.3% Zn/H-ZSM5 and 2.1% Ga/H-ZSM5 contain sharper ^{13}C distributions, with the predominant presence of benzene containing the expected two ^{13}C atoms (Fig. 9) [42]. Therefore, Ga and Zn ions increase the rate of removal of alkenes from these oligomerization–cracking cycles. This removal must occur by the formation of products, such as aromatics (and H_2) and alkanes, which are much less reactive than alkenes in acid-catalyzed reactions. The observed effect of Ga and Zn on dehydrocyclodimerization selectivity (Table 2) suggests that the stable products formed by these faster removal pathways are predominantly aromatics and H_2 .

3.7. Isotopic exchange in C_3H_8/C_3D_8 mixtures and C–H bond activation rates

Propane dehydrocyclodimerization reactions appear to involve a sequence of irreversible dehydrogenation reactions with interspersed rapid acid-catalyzed reactions that lead to chain lengthening and occasional ring closure. Each alkane dehydrogenation reaction involves at least two elementary reaction steps: the activation of C–H bonds and the disposal of the H-atoms formed in this reaction. The relative rates of C–H bond activation and hydrogen disposal can be independently measured during propane dehydrocyclodimerization by concurrent measurements of the isotopic content in products and reactants during reactions of C_3H_8/D_2 or C_3H_8/C_3D_8 mixtures [26,42].

For example, the cross exchange of D-atoms between C_3H_8 and C_3D_8 allows the measurement of the rate of C–H bond activation. The rapid appearance of $C_3H_{8-x}D_x$ molecules shows that reversible (quasi-equilibrated) C–H bond activation occurs during reaction; the rate of this reaction can be measured from the mole fraction of each propane isotopomer (C_3H_8 , $C_3H_7D_1$, $C_3H_6D_2$, ... C_3D_8) as a function of contact time in a gradientless batch reactor. This rate (reported as a turnover rate on the basis of Al atoms in ZSM5) was measured using C_3H_8/C_3D_8 reactant mixtures on all three catalysts. The reversibility of this C–H activation step can be determined by comparing the rate of C–H bond activation to the overall propane conversion turnover rate. The propane conversion turnover rate is measured from the total

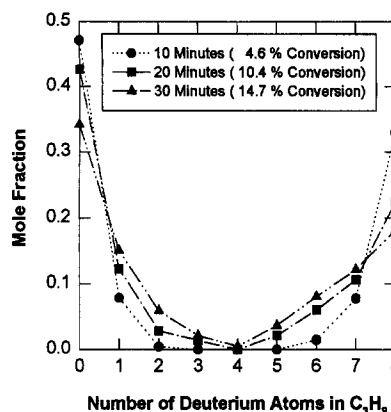


Fig. 10. Cross exchange of C_3H_8/C_3D_8 reactant mixtures on H-ZSM5. Deuterium distributions in 'unreacted' propane in a recirculating batch reactor [773 K, 3.56 kPa C_3H_8 , 3.10 kPa C_3D_8 , balance He, contact times in minutes, % propane conversion in parentheses].

molar rate of propane conversion (both C_3H_8 and C_3D_8) to products.

Significant cross exchange between C_3H_8 and C_3D_8 on H-ZSM5 occurs even at low chemical conversion levels (Fig. 10). C_3H_8/C_3D_8 cross-exchange occurs by stepwise transfer of single D or H-atoms, leading to statistical isotopomer distributions in both the mostly undeuterated and mostly deuterated components in 'unreacted' propane. Comparison of the rates of C–H bond activation and propane chemical conversion to products on H-ZSM5 suggests that C–H bond activation occurs much faster than propane conversion (Table 3). Thus, the C–H bond activation step is quasi-equilibrated and it does not limit the rate of the overall chemical conversion of propane on H-ZSM5. These data suggest that H-ZSM5 can activate C–H bonds very effectively, but it cannot dis-

Table 3

Overall propane conversion turnover and C–H bond activation rates on H-ZSM5, 1.3% Zn/H-ZSM5, and 2.1% Ga/H-ZSM5 (from cross exchange rates of C_3H_8/C_3D_8 mixtures)

	Propane conversion turnover rate per Al site (10^{-2} s^{-1})	C–H bond activation turnover rate per Al site (10^{-2} s^{-1})
H-ZSM5	0.06	2.0
Zn/H-ZSM5	0.13	1.9
Ga/H-ZSM5	0.18	2.1

773 K, 3.56 kPa C_3H_8 , 3.10 kPa C_3D_8 , balance He.

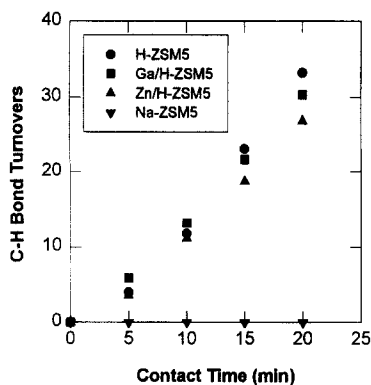


Fig. 11. C–H bond activation turnovers versus contact time (from cross exchange rates of C_3H_8/C_3D_8 mixtures) on H-ZSM5, 2.1% Ga/H-ZSM5, 1.3% Zn/H-ZSM5, and Na-ZSM5 in a recirculating batch reactor [773 K, 3.56 kPa C_3H_8 , 3.10 kPa C_3D_8 , balance He, turnover rates are given by slope].

pose rapidly of the hydrogen atoms formed in C–H bond cleavage. Thus, H-atoms are used to rehydrogenate and desorb carbenium ions from the surface. These data are consistent with the high (r_{-1}/r_2) ratios on H-ZSM5 compared with those on Ga and Zn modified samples because propane formation is one of these rehydrogenation reactions. Ga and Zn species remove H-atoms as H_2 and prevent these rehydrogenation reactions.

The presence of Ga and Zn species within zeolite channels leads to much higher propane conversion rates and aromatics selectivity (Table 2, Fig. 1). Yet, C_3H_8/C_3D_8 exchange data show that C–H bond activation rates on H-ZSM5 appear to be similar to those on Ga/H-ZSM5 and Zn/H-ZSM5 (Table 3, Fig. 11) [42]. Thus, the rate of C–H bond cleavage cannot limit the overall reaction rate, because the addition of Ga and Zn markedly increases the latter without dramatically increasing the rate of C–H bond activation. Surprisingly, C–H bond activation rates are independent of the addition of metal cations and appears to occur on Brønsted acid sites. This is supported by the lack of C_3H_8/C_3D_8 cross exchange over Na-ZSM5, which lacks such Brønsted acid sites. These two independent findings confirm the requirement for acid-catalyzed C–H bond activation in

propane dehydrocyclodimerization reactions and the presence of a similar number of Brønsted acid sites on all catalysts.

H/D ratios in the reaction products of C_3H_8/C_3D_8 mixtures provide indirect evidence for the relative rates of C–H bond activation and C–D bond activation (kinetic isotope effect). This information is obtained from the deuterium content in the unreacted propane mixture and from the deuterium content within reaction products. The ratio of the deuterium content in initial unreacted propane to the deuterium content in reaction products is related to the relative rate of which a C–H and C–D bond cleave. This C–H/C–D kinetic isotope effect (extrapolated to zero conversion) is 1.03 on H-ZSM5 and 1.2 on Ga/H-ZSM5 (Fig. 12).

The lack of a kinetic isotope effect (1.03) on H-ZSM5 may be explained as follows. The rate of C–H activation from C_3H_8 is greater than C–D activation from C_3D_8 due to the weaker C–H bond, but simultaneously, an unsaturated hydrocarbon would rather form a bond with an adsorbed D-atom than a H-atom. In other words, the breaking of the weaker C–H bond is accompanied by the formation of a stronger bond and in turn, canceling any observed kinetic isotope effect.

The appearance of a kinetic isotope effect (1.2) on Ga/H-ZSM5 is attributed to the ability for Ga species to recombine H-atoms. Unlike on

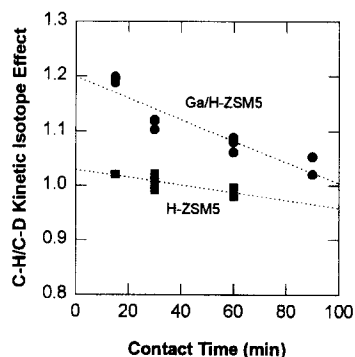


Fig. 12. Ratio of C–H/C–D bond activation (kinetic isotope effect) from C_3H_8/C_3D_8 mixtures on H-ZSM5 and 2.1% Ga/H-ZSM5 in a recirculating batch reactor [773 K, 3.56 kPa C_3H_8 , 3.10 kPa C_3D_8 , balance He].

H-ZSM5, the recombinative desorption of H-atoms and D-atoms on Ga/H-ZSM5 plays an important role. On Ga/H-ZSM5, the rate of C–H and C–D bond activation is similar to that on H-ZSM5, but the removal of H-atoms and D-atoms can, along with hydrogen transfer to unsaturated hydrocarbon fragments, can also be achieved by the recombinative desorption of these H- and D-atoms. This alternate H-disposal pathway can lead to a hydrogen surface pool which is not representative of the true H/D ratio due to the preferential desorption of D-atoms, which would leave a higher H/D ratio on the surface. This suggestion would lead to the observed normal kinetic isotope effect because an unsaturated hydrocarbon molecule would have a higher probability of forming a bond with a H-atom due to the greater H/D ratio on the surface.

3.8. Reversibility of hydrogen adsorption/desorption using C_3H_8/D_2 mixtures

The reversibility of the recombinative desorption step during propane dehydrocyclodimerization was probed by measuring the deuterium content in reaction products and in ‘unreacted’ propane using C_3H_8/D_2 mixtures as reactants [22,28,29,42]. A quasi-equilibrated desorption step would lead to complete mixing of D-atoms from D_2 and H-atoms from propane within the

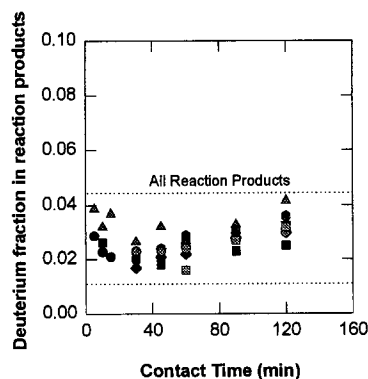


Fig. 13. Deuterium fraction in reaction products of propane/deuterium mixtures on H-ZSM5 in a recirculating batch reactor [773 K, 26.6 kPa C_3H_8 , 6.7 kPa D_2 , balance He].

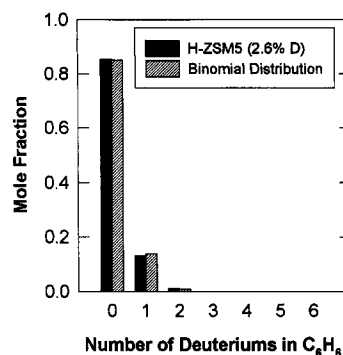


Fig. 14. Deuterium distribution in benzene product of propane/deuterium mixtures on H-ZSM5 in a recirculating batch reactor [773 K, 26.6 kPa C_3H_8 , 6.7 kPa D_2 , balance He, 4.6% propane conversion].

reaction products. These quasi-equilibrated adsorption–desorption steps would occur many times in the time required for one dehydrocyclodimerization turnover. In contrast, an irreversible recombinative desorption step would lead to the predominant presence of protium in reaction products because of the slow communication between gas phase (D_2) and surface pools of hydrogen isotopes.

On H-ZSM5, the deuterium content is very low in all products of C_3H_8/D_2 reactions (Fig. 13), suggesting that recombinative desorption steps are irreversible during propane dehydrocyclodimerization. The deuterium content is similar in all reaction products and it is almost independent of contact time (and conversion). Also, D-atoms are distributed statistically within each reaction product (Fig. 14). In other words, the distribution of D-atoms isotopomers within each product formed on H-ZSM5 obeys a binomial distribution because multiple exchange events with a common surface hydrogen pool occur during the formation of each reaction product.

This binomial distribution and similar D-content within all products suggest that all products accurately probe by multiple exchange with a well-mixed surface hydrogen pool with an isotopic composition of about 2–4% D and 96–98% H. The presence and statistical sampling of this well-mixed surface pool is consistent with

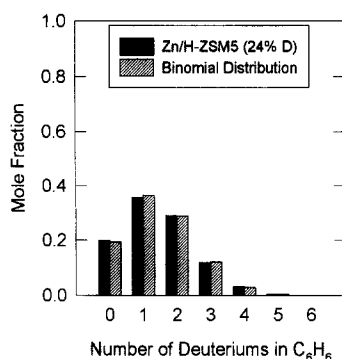


Fig. 15. Deuterium distribution in benzene product of propane/deuterium mixtures on 1.3% Zn/H-ZSM5 in a recirculating batch reactor [773 K, 26.6 kPa C₃H₈, 6.7 kPa D₂, balance He, < 2% propane conversion].

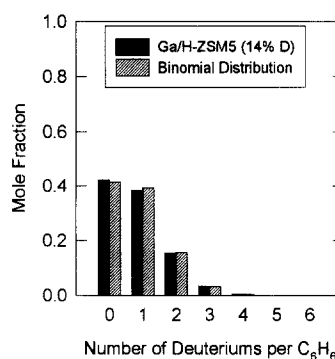


Fig. 16. Deuterium distribution in benzene product of propane/deuterium mixtures on 2.1% Ga/H-ZSM5 in a recirculating batch reactor [773 K, 26.6 kPa C₃H₈, 6.7 kPa D₂, balance He, < 2% propane conversion].

the oligomerization–cracking cycle that causes the rapid intermolecular scrambling of propane-2-¹³C products. Within this cycle, C–H and C–C bonds are broken and re-formed many times in their reaction path to products and their C–H bonds exchange thoroughly with surface hydrogen available as atoms, protons, or hydrides, or within carbocations. As a result, the deuterium content within reaction products becomes an accurate measure of the deuterium content within the surface hydrogen pool and of the rate of communication between this pool and a gas phase form of hydrogen.

The deuterium fraction within all reaction products is between 0.018–0.04 on H-ZSM5 and it is almost independent of contact time [28,42]. Therefore, the surface hydrogen pool initially contains between 2–4% deuterium and 96–98% protium, instead of the pure deuterium expected from full equilibration with the pure D₂ gas phase (Table 4). This surface pool contains predominantly protium atoms formed in C–H bond activation steps; the removal of these

protium atoms limits the rate of the required dehydrogenation reactions. As a result, products re-acquire H-atoms instead of D-atoms in the fast and reversible C–H bond activation steps that occur during propane conversion reactions. On H-ZSM5, the predominant hydrogen disposal pathway is by ‘attachment’ of H-atoms to surface hydrocarbon fragments, in steps that predominantly crack and hydrogenate these fragments and lead to hydrogen-rich light alkanes.

Deuterium atoms are also distributed statistically and the deuterium content is very similar within all products of C₃H₈/D₂ mixtures on Zn/H-ZSM5 and Ga/H-ZSM5 (Figs. 15 and 16), even though aromatic products are formed after a shorter residence time in oligomerization–cracking cycles. The deuterium fraction within all products, however, is much higher than on H-ZSM5 (e.g. toluene, Fig. 17). The deuterium fraction in toluene, obtained by extrapolation of the data in Fig. 17 to zero conversion, are 0.25 on Zn/H-ZSM5, 0.13 on Ga/H-

Table 4

Initial isotopic composition in toluene product of propane/deuterium mixtures on H-ZSM5, 1.3% Zn/H-ZSM5, and 2.1% Ga/H-ZSM5

	Deuterium fraction	Deuterium/hydrogen	H ₂ selectivity (%)
H-ZSM5	0.03	0.03	4.6
Ga/H-ZSM5	0.13	0.15	31.2
Zn/H-ZSM5	0.25	0.33	35.8

773 K, 26.6 kPa C₃H₈, 6.7 kPa D₂, balance He, < 2% propane conversion.

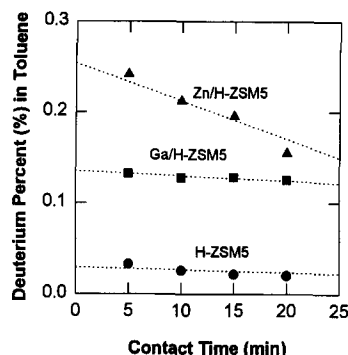


Fig. 17. Deuterium fraction in toluene product of propane/deuterium mixtures on H-ZSM5, 1.3% Zn/H-ZSM5, and 2.1% Ga/H-ZSM5 in a recirculating batch reactor [773 K, 26.6 kPa C_3H_8 , 6.7 kPa D_2 , balance He].

ZSM5, and 0.03 on H-ZSM5. On Zn/H-ZSM5, the D-content decreases as conversion increases because protium dilutes the deuterium content of the gas phase as deuterated reaction products are formed. Indeed, gas phase H_2 and HD are much more abundant and communicate more effectively with the reaction products when Ga and Zn are present in H-ZSM5 catalysts.

The addition of metal cations also increases the deuterium content in 'unreacted' propane (Fig. 18). The rate of incorporation of D-atoms into 'unreacted' propane provides an independent measure of the D-content in the surface pool [22,28,29,42]. Deuteration turnovers are calculated from the number of propane molecules that contain one or more deuterium

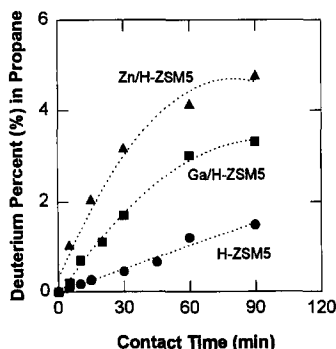


Fig. 18. Deuterium percent in 'unreacted' propane in propane/deuterium mixtures on H-ZSM5, 1.3% Zn/H-ZSM5, and 2.1% Ga/H-ZSM5 in a recirculating batch reactor [773 K, 26.6 kPa C_3H_8 , 6.7 kPa D_2 , balance He].

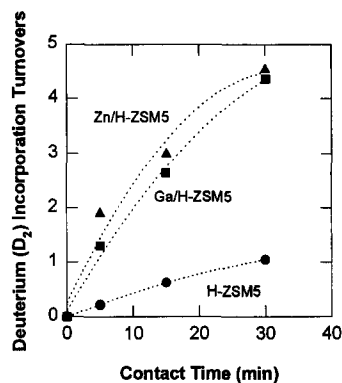


Fig. 19. Deuterium incorporation turnovers into propane molecules versus contact time from propane/deuterium mixtures on H-ZSM5, 1.3% Zn/H-ZSM5, and 2.1% Ga/H-ZSM5 in a recirculating batch reactor [773 K, 26.6 kPa C_3H_8 , 6.7 kPa D_2 , balance He, turnover rates are given by slope].

atoms. The addition of Ga and Zn increase the deuterium incorporation turnovers (Fig. 19). These turnovers reflect the rate of the reverse C–H bond activation step (r_{-1}) weighed by the probability that the hydrogen atom chosen from the surface pool to re-form the C–H bond is a D-atom. Ga and Zn cations increase propene hydrogenation rates (r_{-1}), however, these species increase r_2 proportionally more than r_{-1} , because of their promoting effect on subsequent dehydrogenation steps required to form aromatics from propylene. Therefore, Ga and Zn cations promote not only propane dehydrogenation, but even more effectively the subsequent removal of hydrogen as H_2 in reactions leading to the formation of highly unsaturated precursors (dienes, trienes, and cyclodienes) involved in cyclization steps.

Clearly, Ga and Zn species increase the reversibility of H-atom recombinative desorption steps and act as efficient 'portholes' [67] for the removal of H-atoms produced during C–H bond activation steps. Ga and Zn species increase the rate of both H-atom recombinative desorption and of H_2 dissociative adsorption during propane dehydrocyclodimerization reactions [22,28,29,42]. Adsorption–desorption steps, however, remain irreversible and not fully equilibrated even on Ga/H-ZSM5 and Zn/H-ZSM5. This H-atom disposal step remains the

rate-determining step for each sequential dehydrogenation reaction required to convert propane to aromatics. This is confirmed by the significant presence of protium within the surface pool during reactions of C_3H_8/D_2 mixtures on Ga/H-ZSM5 and Zn/H-ZSM5. Concurrent cracking steps are no longer required to remove most H-atoms formed in C–H bond activation steps and the selectivity to C_6 – C_8 aromatic products consequently increases when Ga or Zn ‘portholes’ are placed within H-ZSM5 channels.

Dent and Kokes [68] have previously shown that H_2 dissociates on Zn–O pairs during ethylene hydrogenation reactions on zinc oxide. Therefore, Zn cations must catalyze also the reverse of this process – the desorption of hydrogen during dehydrogenation reactions. Hydrogen appears to dissociate heterolytically with the partial reduction of the Zn^{2+} cations in ZnO. Thus, it is tempting to conclude that desorption during propane dehydrogenation on Zn/H-ZSM5 involves the recombination of $H^{\delta+}$ and $H^{\delta-}$ species and the concomitant re-oxidation of partially reduced Zn cations. Therefore, Zn (and Ga) cations within zeolite channels may act as momentary hydrogen acceptors that can dispose of the hydrogen by recombination with H-atoms stabilized by basic framework oxygens in H-ZSM5.

3.9. Availability of acid sites during propane reactions on H-ZSM5 and Ga/H-ZSM5

The presence of cationic Ga (and Zn) species within zeolite channels may displace protons and thus reduce the number of sites available for acid-catalyzed reactions. Several titration and probe reaction studies on H-ZSM5 and Ga/H-ZSM5, however, suggest that the density of acid sites does not decrease as metal loading increases within H-ZSM5 channels. For example, measurements of ammonia adsorption [15,16,18], *n*-alkane cracking rates [15,18,32], and *m*-xylene, cyclohexene, and 2-methyl-2-pentene isomerization rates [18,26,32] support this conclusion. One possible reason is that Ga

species have not exchanged during synthesis and remain as extracrystalline Ga_2O_3 or Ga_2O . In at least one of the studies cited above [26], however, the exchange has been verified independently by Ga K-edge X-ray absorption methods.

In contrast, Meriaudeau and Naccache [25,34,69] have reported a significant decrease in the intensity of O–H infrared bands when Ga is present within H-ZSM5 channels. These studies were performed at room temperature and suggest a displacement of protons by Ga cations during pretreatment. Kwak and Sachtler [27] detected the evolution of HCl during vapor phase exchange of H-ZSM5 with $GaCl_3$ caused by the exchange of Ga cations for protons. Kwak and Sachtler [31] also found that propane conversion rates initially increase with Ga content, but ultimately decreased as the Ga content reached Ga/Al values near 0.5. These findings may have been influenced by channel blockages at high metal loadings due to a different synthesis technique, which involved the chemical vapor deposition of $GaCl_3$ into ZSM5 channels.

Meitzner et al. [26] found the ammonia adsorption on H_2 pretreated Ga/H-ZSM5 also leads to a decrease in acid sites compared with H-ZSM5. This is contrary to previous researchers [15,16,18], who report a constant density of acid sites using ammonia adsorption. These several authors [15,16,18] did not pretreat Ga/H-ZSM5 samples with hydrogen before adsorption measurements and Ga species are unlikely to reside within zeolite channels, but as extrazeolitic Ga_2O_3 . Meitzner et al. [26] confirmed this finding by showing no decrease in Brønsted acid site density on non-pretreated Ga/H-ZSM5 catalysts during ammonia adsorption.

The reduction of Ga species and the accompanying formation of protons during reaction above 573 K may be responsible for these contradictory results. Specifically, Meriaudeau et al. [25,34,69] show that Ga cations replace protons by measuring the decreased intensity of O–H infrared vibrations at room temperature.

Indeed, independent X-ray absorption studies [26] confirm the formation of oxidized Ga^{3+} cationic complexes upon cooling samples to room temperature. Reduction treatments above 573 K, however, reduce Ga^{3+} complexes to Ga^0 or Ga^{1+} ; this reduction process occurs without water evolution and leads to the formation of H^+ species [26]. Thus, it appears that the addition of Ga and Zn species to H-ZSM5 does not decrease the density of acid sites at reaction conditions, but leads to a displacement of protons by oxidized Ga complexes near room temperature.

Dehydrocyclodimerization rate and selectivity increase as Ga atoms are transferred from extrazeolitic oxide crystals to isolated cation exchange sites [26]. Clearly, the proximity to acid sites, the high metal dispersion, and possibly the unique electronic structure of isolated Ga species induced by this migration improve the effectiveness of the catalytic hydrogen desorption function provided by Ga. In addition, the isolation of Ga species within zeolite channels prevents the formation of polymeric Ga metal, which would elute from the reactor as a liquid during catalysis above room temperature.

The reduction of Ga cations residing at intrazeolitic exchange sites can restore Brønsted acid sites by the formation of protons during H_2 pretreatment or catalytic reactions of light alkanes (Eq. (3)). This proposal suggests that cation exchange sites can be used for anchoring monomeric Ga species during synthesis, but protonic acid sites can be re-formed by appropriate reduction treatments or by the reductive environment during propane dehydrocyclodimerization. The reduction–oxidation of intrazeolitic Ga species has been confirmed by the X-ray absorption studies described in a previous report [26]. The adsorption–desorption process that accompanies this redox cycle has been detected by measurements of the appearance and disappearance of dihydrogen from the gas phase during thermal treatment of a Ga/H-ZSM5 sample previously pre-reduced in H_2 at 773 K for 4 h and cooled to room temperature.

Hydrogen adsorption–desorption data are consistent with Ga K-edge X-ray absorption data, which show Ga^{3+} forms during cooling of reduced samples to room temperature. During catalytic reaction of propane at 673–773 K, Ga^{3+} reduces to its active form (Ga^{1+}) in a process that occurs along with a significant increase in the rate of propane dehydrocyclodimerization reactions.

The cationic Ga complexes in exchange sites at room temperature must be present with a +1 charge, regardless of the formal oxidation state of the Ga atoms. This is required by the need to balance the net negative charge of a single cation exchange site isolated by significant distances from other exchange sites within zeolite channels. This is likely to lead to the formation of species such as $[\text{GaO}]^+$, where strongly bound oxygen atoms provide the required charge balance for Ga^{3+} ions exchanged during contact with Ga nitrate solution.

3.10. Synergy between metal cation and Brønsted acid sites in dehydrocyclodimerization reactions

Most literature reports suggest that propane dehydrocyclodimerization proceeds via a bifunctional route requiring the metal and acid sites to catalyze specific and distinct steps within the reaction sequence. The functions are C–C bond formation and cleavage, C–H bond activation, and hydrogen disposal. On H-ZSM5, hydrogen disposal proceeds by hydrogen transfer to hydrocarbon fragments, a process that leads to high cracking selectivities. On Ga/H-ZSM5 and Zn/H-ZSM5, hydrogen disposal proceeds predominantly through the recombinative desorption of H-atoms to form H_2 .

$\text{C}_3\text{H}_8/\text{C}_3\text{D}_8$ isotopic exchange data have shown that C–H bond activation steps are fast and quasi-equilibrated during steady-state propane dehydrocyclodimerization on H-ZSM5, Ga/H-ZSM5, and Zn/H-ZSM5. The C–H bond activation rate is independent of the presence of Ga and Zn cations and appears to occur on

Brønsted acid sites within zeolite channels. Additionally, C_3H_8/D_2 exchange data suggest that the turnover rate for hydrogen desorption increases with Ga or Zn introduction into ZSM5 channels and that this step is essentially irreversible during steady-state catalysis. These two independent findings provide evidence that propane dehydrogenation to propene is a concerted reaction requiring both acid sites and metal cation sites. The acid sites activate C–H bonds, while the metal sites remove the hydrogen species formed in these C–H bond cleavage steps via recombinative desorption of H-atoms as dihydrogen (H_2). This metal recombinative desorption function removes the hydrogen bottleneck on the surface and allows acid sites to turnover more efficiently without the requirement of hydrogen transfer and cracking reactions to form H-rich products. It also prevents the reversal of the initial C–H bond activation by rehydrogenation of surface species to re-form propane.

The oligomerization and cracking of light alkenes during propane dehydrocyclodimerization occurs readily on acid sites. Light alkenes can be converted to a mixture of lower and higher molecular weight alkenes via a sequence of acid-catalyzed shape-selective oligomerization and isomerization reactions over H-ZSM5 [60,61].

The aromatization of cycloalkenes formed after oligomerization and cyclization steps may also require a concerted reaction between acid and metal cation sites. The role of metal cations during reactions of methylcyclohexane on H-

ZSM5 and Ga/H-ZSM5 is consistent with the significant hydrogen removal requirements of such reactions. Methylcyclohexane turnover rates and selectivities on H-ZSM5 and Ga/H-ZSM5 are shown in Table 5. The selectivity to toluene increases from 29.5 to 40.3% with the introduction of Ga (2.1 wt%) into H-ZSM5 channels. The selectivity to H_2 also increases from 18.2 to 26.4% when Ga is present. The increase in hydrogen formation rate shows that Ga participates in the dehydrogenation of cycloalkanes by disposing of hydrogen via recombinative desorption of surface H-atoms as H_2 .

3.11. Role of the Ga and Zn cations during propane dehydrocyclodimerization on H-ZSM5

In a previous section, we mentioned three possible functions of exchanged metal cations, all of which have been proposed on the basis of literature results. Ono et al. [15,38] have proposed that Ga is not required for the initial activation of propane, but merely catalyzes the conversion of unsaturated intermediates to aromatics. This cyclization function was proposed on the basis of the observed decrease in intermediate alkene selectivities caused by the presence of Ga.

Our studies have confirmed the lower propene selectivity and the higher rate of propene aromatization on Ga/H-ZSM5 catalysts. We conclude, however, that Ga species also increase markedly the rate of propane conversion to propene. For example, the rate of propane conversion (to all products) (Fig. 20) increases by a

Table 5
Methylcyclohexane turnover rates and product distribution on H-ZSM5 and 2.1% Ga/H-ZSM5

	H-ZSM5	Ga/H-ZSM5
Turnover rate (per Al, $10^{-3} s^{-1}$)	2.2	5.1
Carbon selectivity (%)		
C_1 – C_5	36.4	30.3
Toluene	29.5	40.3
Hydrogen selectivity (%)		
Hydrogen (H_2)	18.2	26.4

773 K, 0.67 kPa methylcyclohexane, balance He, 35.4–36.1% methylcyclohexane conversion.

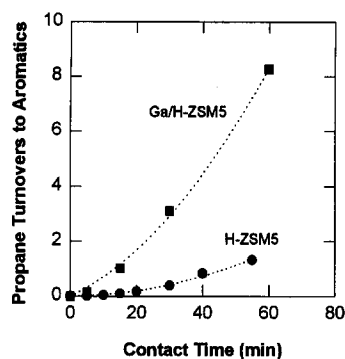


Fig. 20. Propane conversion turnovers to aromatic products versus contact time in recirculating batch reactor on H-ZSM5 and 2.1% Ga/H-ZSM5 [773 K, 26.6 kPa C_3H_8 , balance He, turnover rates given by slope].

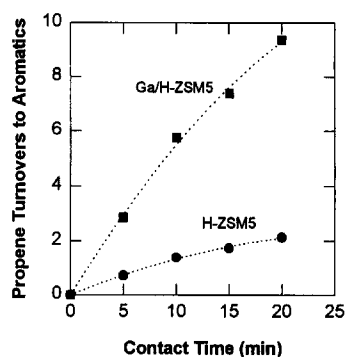


Fig. 21. Propene conversion turnovers to aromatic products versus contact time in recirculating batch reactor on H-ZSM5 and 2.1% Ga/H-ZSM5 [773 K, 0.67 kPa C_3H_6 , balance He, turnover rates given by slope].

factor of 7, while the rate of propene conversion (to all products) (Fig. 21) increases by a factor of 4 when Ga is added to H-ZSM5. These results are consistent with a hydrogen desorption function provided by Ga species and do not require the proposal of a Ga-catalyzed cyclization reaction. In effect, the conversion of propene to aromatics also requires a sequence of several additional dehydrogenation steps that are limited by the disposal of H-atoms in recombinative desorption or hydrogen transfer reactions.

Additional evidence for Ga and Zn playing a role in propene dehydrocyclodimerization is obtained by concurrent measurements of the rate of propene hydrogenation (r_{-1}) and conversion to products (r_2) (Eq. (4)) during reactions of propene/propane-2- ^{13}C mixtures. These data show that r_{-1}/r_2 is much lower on Ga/H-

ZSM5 and Zn/H-ZSM5 than on H-ZSM5 (Fig. 7). Thus, the introduction of Ga and Zn in zeolite channels increase r_2 proportionally more than it increases r_{-1} . The catalytic effect of Ga and Zn is stronger on propene conversion reactions than on propene formation from propane, consistent with the expected requirement for several additional hydrogen desorption in order to complete a propene aromatization turnover.

Meriaudeau et al. [25] and Guisnet et al. [17,18,24,46] have suggested that Ga species provide only a propane and naphthene dehydrogenation function, while all subsequent reactions of propene proceed exclusively and rapidly on protonic acid sites via conventional acid catalysis. Guisnet et al. [17] state that Ga_2O_3 shows 'great activity' for propane dehydrogenation to propene. Meriaudeau and Naccache [70] and Buckles and Hutchings [36] have also ex-

Table 6
Propane dehydrogenation reaction rates on Ga-based catalysts

Catalyst [Ref.]	<i>T</i> (K)	Ga-based ^a turnover rate ($10^{-3} s^{-1}$)	Dehydrogenation selectivity (%)
Ga_2O_3 [17]	803	2.8	65
Ga_2O_3 [70]	773	2.0	91
Ga_2O_3 [36]	873	3.9	74
		9.8 ^b	73 ^b
Ga/H-ZSM5 (this work)	773	25.4	70 ^c

^a Ga_2O_3 rate based on 10^{19} Ga sites/ m^2 and reported surface areas. Ga/H-ZSM5 rate based on Ga/Al = 0.29 and assumes all Ga atoms are available for reaction.

^b With H_2 co-feed.

^c Dehydrogenation selectivity = $100 - (C_1 + C_2 \text{ selectivities})$ at 9% propane conversion.

amined the dehydrogenation activity of Ga_2O_3 . Dehydrogenation turnover rates on Ga_2O_3 and on Ga/H-ZSM5 were calculated from the reported literature. Ga_2O_3 catalyzes propane dehydrogenation, but the dehydrogenation turnover rate on Ga/H-ZSM5 is more than 10 times greater than the observed reactions rates on Ga_2O_3 (Table 6). The low dehydrogenation rates on Ga_2O_3 catalyst suggest that propane activation does not occur solely on monofunctional Ga sites at typical propane dehydrocyclodimerization conditions.

Clearly, the function of Ga sites cannot be limited to the initial dehydrogenation of propane because the rate of propene conversion to aromatics also increases when Ga is introduced into H-ZSM5. Moreover, Ga sites do not increase the rate of C–H bond activation in propane and participate predominantly in hydrogen desorption elementary steps required for dehydrogenation reactions. It is possible that Ga sites in Ga_2O_3 catalyze only the recombination of hydrogen atoms formed in this case by thermal activation of C–H bonds in propane at high temperatures (> 773 K). These thermal reactions are much slower than C–H bond activation reactions on Brønsted acid sites in H-ZSM5.

Iglesia et al. [22,26,28,29,42], Inui et al. [43,50], and Le Van Mao et al. [19,21,41] have provided supporting evidence for the earlier suggestion by Mole et al. [37] that extra-framework reducible cations catalyze the recombinative desorption of H-atoms as H_2 . Specifically, the rate of cross-exchange during dehydrocyclodimerization of $\text{C}_3\text{H}_8/\text{C}_3\text{D}_8$ mixtures on H-ZSM5, Ga/H-ZSM5, and Zn/H-ZSM5 allows the concurrent measurement of chemical conversion and C–H bond activation rates [28,42]. The data in Table 3 show that C–H activation turnover rates are much greater than chemical conversion rates on all catalysts. Therefore, propane conversion to aromatics is not limited by the C–H activation elementary steps in sequential irreversible dehydrogenation steps required for aromatics formation. Moreover, propane chemical conversion rates in-

crease when Ga or Zn are present, but the C–H activation rate is not affected as strongly by these cations. Ga and Zn introduce sites that increase the rate of other elementary steps in dehydrogenation reactions; these steps are associated with the disposal of H-atoms formed in C–H activation steps.

The requirement for acid sites in order to activate C–H bonds is evident from these studies of the reactions of $\text{C}_3\text{H}_8/\text{C}_3\text{D}_8$ mixtures. No cross exchange of deuterium atoms into C_3H_8 or hydrogen atoms into C_3D_8 was found on Na-ZSM5, because without protonic sites, it cannot activate C–H bonds in propane (Fig. 11). The requirement for Brønsted acid sites in C–H bond activation is consistent with studies by Ono and co-workers [38] on weakly acidic borosilicates with ZSM5 structure [71–73]. Zn-exchanged borosilicates did not catalyze propane dehydrocyclodimerization, but these samples were able to convert propene to aromatics at significant rates. Weak acid sites within borosilicate channels catalyze C–H activation in propene, but cannot activate C–H bonds in propane, a step required for the Zn-catalyzed removal of H-atoms and for the completion of a propane dehydrogenation turnover. Thus, Zn species, by themselves, cannot catalyze the required initial dehydrogenation of propane without the additional presence of strong Brønsted acid sites involved in the initial activation of C–H bonds in propane.

3.12. Hydrogenation and hydrogen transfer properties of modified pentasil zeolites

Propane dehydrocyclodimerization rates and selectivities are independent of dihydrogen pressure (0–25 kPa) on H-ZSM5 (Figs. 22 and 23). The isotopic content in reaction products of $\text{C}_3\text{H}_8/\text{D}_2$ mixtures also shows neither dissociative adsorption or recombinative desorption occur readily on H-ZSM5. Hydrogen desorption steps are irreversible over H-ZSM5 and the surface is covered with protium (96–98%) from

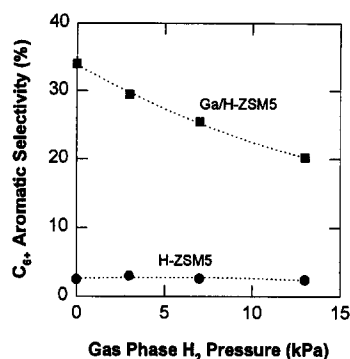


Fig. 22. The effect of dihydrogen pressure on the C₆₊ aromatics selectivity during propane dehydrocyclodimerization on H-ZSM5 and 2.1% Ga/H-ZSM5 [773 K, 26.6 kPa C₃H₈, 0–25 kPa H₂, balance He, 10–15% propane conversion].

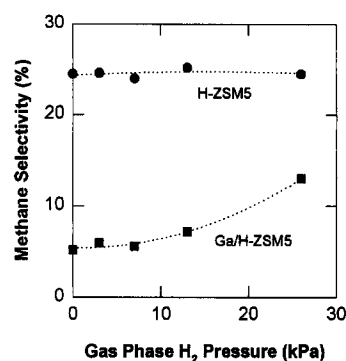


Fig. 23. The effect of dihydrogen pressure on the methane selectivity during propane dehydrocyclodimerization on H-ZSM5 and 2.1% Ga/H-ZSM5 [773 K, 26.6 kPa C₃H₈, 0–25 kPa H₂, balance He, 10–15% propane conversion].

C–H bond activation steps rather than deuterium atoms from the contacting gas phase.

On Ga/H-ZSM5, both turnover rates and aromatics selectivity depend on H₂ pressure; they decrease as H₂ pressure increases (0–25 kPa) because hydrogen adsorption/desorption sites allow gas phase hydrogen pressures to influence surface hydrogen concentrations and surface hydrogenation–dehydrogenation reactions (Figs. 22 and 23). The presence of Ga species allows gas phase hydrogen to dissociatively adsorb and to effectively compete for surface sites, thus decreasing aromatic selectivity. Similar results were reported by Mole on Zn/H-ZSM5 [37].

Ga species act as ‘portholes’ for the desorption of H-atoms, but also increase the reverse reaction, the dissociative chemisorption of dihydrogen, as shown by the introduction of D-atoms in the products of propane/deuterium mixtures. The addition of H₂ to C₃H₈/He mixtures causes the Ga/H-ZSM5 to resemble H-ZSM5 catalytically because the H-ZSM5 already has an ‘autogenous’ high hydrogen concentration caused by the bottleneck hydrogen desorption step. Higher H₂ pressures lower aromatic selectivity and cause Ga/H-ZSM5 to form a product distribution more closely resembling the undesired H-ZSM5 product distribution.

The introduction of Ga and Zn cations into H-ZSM5 channels may introduce momentary

hydrogen acceptors that allow the recombinative desorption of H-atoms as H₂. Permanent stoichiometric hydrogen acceptors also remove H-atoms formed on H-ZSM5 during propane dehydrocyclodimerization [28]. Iglesia and Baumgarter [28] have shown that the kinetic coupling of the C–H bond activation steps during propane dehydrocyclodimerization with hydrogen transfer of H-atoms to stoichiometric hydrogen acceptors (¹³CO, ¹³CO₂, and O₂) also increases aromatic turnover rates and selectivities to unsaturated products (Fig. 24).

¹³CO acts as a stoichiometric scavenger and increases aromatics selectivity during propane conversion on H-ZSM5, but only small amounts of ¹³C (< 1%) appear in reaction products. Instead of the desired conversion of ¹³CO and

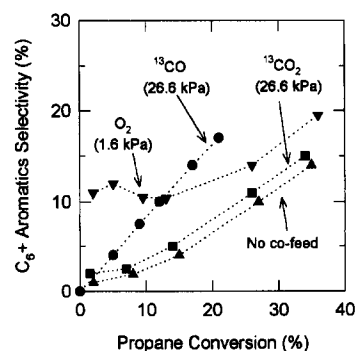
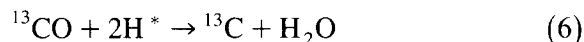
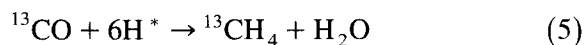


Fig. 24. The effect of ¹³CO, ¹³CO₂, and O₂ on aromatics selectivity during propane dehydrocyclodimerization on H-ZSM5 [773 K, 26.6 kPa C₃H₈, balance He].

H-atoms to form CH₄ and H₂O (Eq. 5), ¹³CO reacts with H-atoms to form H₂O and ¹³C (Eq. 6), in a process that rapidly deactivates H-ZSM5 and reduces propane turnover rates.



The presence of small amounts of O₂ in C₃H₈/He increases aromatics selectivity on H-ZSM5 (Fig. 24). O₂ is not, however, a selective hydrogen scavenger and also reacts with propane to form CO₂. At higher conversions, oxygen is depleted and propane reacts via purely non-oxidative pathways and the selectivity to aromatics begins to resemble that obtained using pure propane [28].

The addition of ¹³CO₂ also increases the aromatics selectivity on H-ZSM5 (Fig. 24). However, reaction products of ¹³CO₂/C₃H₈ mixtures on H-ZSM5 contain minimal amounts (< 1%) of ¹³C. The effect of CO₂ addition is minimal because the hydrogenation of CO₂ is not thermodynamically favored at these reaction temperatures (773 K).

The introduction of alternate H-disposal pathways, whether by using stoichiometric acceptors (CO, CO₂, or O₂) or metal cations (Ga or Zn), removes the burden of hydrogen removal from other steps that form light alkanes and reduce aromatics selectivity. These alternate pathways dispose of H-atoms during propane dehydrocyclodimerization on H-ZSM5 and prevent hydrogenation and cracking reactions that provide an alternate disposal route for H-atoms.

4. Conclusions

Reactions of propane on H-ZSM5 require the activation of C–H bonds and the disposal of the hydrogen atoms produced in these reactions. Hydrogen disposal can take place by transfer to adsorbed hydrocarbon fragments on the surface or by the recombinative desorption to form dihydrogen (H₂). The sequential release of sev-

eral H-atoms during a propane aromatization turnover limits the rate and selectivity of this reaction on H-ZSM5.

Isotopic exchange experiments suggest that propane aromatization occurs on H-ZSM5 by a complex reaction sequence involving dehydrogenation to propene, rapid oligomerization–cracking of alkene intermediates, and the cyclization and aromatization of these alkenes into stable C₆ + aromatics. These reactions proceed in parallel with acid-catalyzed and thermal cracking reactions to form methane and ethane. Hydrogen is also formed as a result of the recombinative desorption of hydrogen adsorbed on the zeolite surface.

Modifications of such pentasil zeolites with exchanged Ga and Zn cations increase the rate of hydrogen disposal, the propane turnover rate, and aromatic selectivity. Isotopic studies show that C–H bond activation appears to occur at similar rates on H-ZSM5, Ga/H-ZSM5, and Zn/H-ZSM5, but that exchanged Ga and Zn cations increase the rates of chemical propane conversion, of recombinative hydrogen desorption, and of incorporation of D-atoms from D₂ into reaction products.

The initial rate of propene formation is much higher on Ga/H-ZSM5 and Zn/H-ZSM5 compared to H-ZSM5, but isotopic evidence from C₃H₈/C₃D₈ mixtures show that C–H bond activation rate depends weakly on the presence of Ga and Zn. Reactions over Na-ZSM5 confirm that C–H bond activation occurs predominantly on Brønsted acid sites. Ga and Zn sites increase the rate of propene formation by removing H-atoms from acid sites that activate C–H bonds, allowing acid sites to turnover without the formation of cracking products. Ga and Zn act as ‘portholes’ and catalyze the recombinative desorption of H-atoms, formed from acid-catalyzed C–H bond cleavage, as dihydrogen (H₂). This removal of H-atoms by the recombinative desorption is highly desired in order to minimize unwanted by-products such as methane and ethane and to extract valuable H₂ with a high selectivity from light alkanes.

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References

- [1] S.M. Csicsery, *J. Catal.*, 17 (1970) 207.
- [2] S.M. Csicsery, *J. Catal.*, 17 (1970) 216.
- [3] S.M. Csicsery, *J. Catal.*, 17 (1970) 315.
- [4] S.M. Csicsery, *J. Catal.*, 17 (1970) 323.
- [5] S.M. Csicsery, *J. Catal.*, 18 (1970) 30.
- [6] R. Gregory and A.J. Kolombos, US Patent 4 056 575 (1977).
- [7] S.N. Bulford and E.E. Davies, US Patent 4 157 356 (1979).
- [8] J.R. Anderson, K. Foger, T. Mole, R.A. Rajadhyaksha and J.V. Sanders, *J. Catal.*, 58 (1979) 114.
- [9] D.V. Dass and A.L. Odell, *J. Catal.*, 113 (1988) 259.
- [10] R. Shigeishi, A. Garforth, I. Harris and J. Dwyer, *J. Catal.*, 130 (1991) 423.
- [11] Y. Ono and K. Kanae, *J. Chem. Soc., Faraday Trans.*, 87 (1991) 663.
- [12] M. Guisnet, N.S. Gnep, D. Aittaleb and Y.J. Doyemet, *Appl. Catal.*, 87 (1992) 255.
- [13] N.Y. Chen and T.Y. Yan, *Ind. Eng. Proc. Des. Dev.*, 25 (1986) 151.
- [14] N.Y. Chen, W.E. Garwood and R.H. Heck, *Ind. Eng. Chem. Res.*, 26 (1987) 706.
- [15] H. Kitagawa, Y. Sendoda and Y. Ono, *J. Catal.*, 101 (1986) 12.
- [16] T. Yashima, T. Sasaki, K. Takahashi, S. Watanabe and S. Namba, *Sekiyu Gakkaishi*, 31 (1988) 154.
- [17] N.S. Gnep, J.Y. Doyemet and M. Guisnet, *J. Mol. Catal.*, 45 (1988) 281.
- [18] N.S. Gnep, J.Y. Doyemet, A.M. Seco, F.R. Ribeiro and M. Guisnet, *Appl. Catal.*, 43 (1988) 155.
- [19] J. Yao, R. Le Van Mao and L. Dufresne, *Appl. Catal.*, 65 (1990) 175.
- [20] G.L. Price and V. Kanazirev, *J. Catal.*, 126 (1990) 267.
- [21] R. Le Van Mao, R. Carli, J. Yao and V. Ragaini, *Catal. Lett.*, 16 (1992) 43.
- [22] E. Iglesia, J.E. Baumgartner and G.L. Price, *J. Catal.*, 134 (1992) 549.
- [23] K.M. Dooley, C. Chang and G.L. Price, *Appl. Catal.*, 84 (1992) 17.
- [24] M. Guisnet, N.S. Gnep and F. Alario, *Appl. Catal.*, 89 (1992) 1.
- [25] P. Meriaudeau, S.B. Abdul Hamid and C. Naccache, *J. Catal.*, 139 (1993) 683.
- [26] G.D. Meitzner, E. Iglesia, J.E. Baumgartner and E.S. Huang, *J. Catal.*, 140 (1993) 209.
- [27] B.S. Kwak and W.H.M. Sachtler, *J. Catal.*, 141 (1993) 729.
- [28] E. Iglesia and J.E. Baumgartner, *Catal. Lett.*, 21 (1993) 55.
- [29] E. Iglesia, J.E. Baumgartner and G.D. Meitzner, in L. Guzzi, F. Solymosi and P. Tetenyi (Eds.), *Proc. 10th Int. Congr. Catalysis*, Budapest 1992, Elsevier, Amsterdam.
- [30] G. Giannetto, R. Monque and R. Galiasso, *Cat. Rev. Sci. Eng.*, 36 (1994) 271.
- [31] B.S. Kwak and W.H.M. Sachtler, *J. Catal.*, 145 (1994) 456.
- [32] M. Barre, N.S. Gnep, P. Magnoux, S. Sansare, V.R. Choudhary and M. Guisnet, *Catal. Lett.*, 21 (1993) 275.
- [33] I.I. Ivanova, N. Blom, S.B. Abdul Hamid and E.G. Derouane, *Recl. Trav. Chim. Pays-Bas.*, 113 (1994) 454.
- [34] P. Meriaudeau, G. Sapaly, G. Wicker and C. Naccache, *Catal. Lett.*, 27 (1994) 143.
- [35] E.G. Derouane, S.B. Abdul Hamid, I.I. Ivanova, N. Blom and P.E. Hojlund-Nielsen, *J. Mol. Catal.*, 86 (1994) 371.
- [36] G. Buckles and G.J. Hutchings, *Catal. Lett.*, 27 (1994) 361.
- [37] T. Mole, J.R. Anderson and G. Creer, *Appl. Catal.*, 17 (1985) 141.
- [38] M. Shibata, H. Kitagawa, Y. Sendoda and Y. Ono, *Proc. 7th Int. Zeolite Conf.*, 1986, p. 717.
- [39] M.S. Scurrell, *Appl. Catal.*, 41 (1988) 89.
- [40] Y. Ono and K. Kanae, *J. Chem. Soc., Faraday Trans.*, 87 (1991) 669.
- [41] L.A. Dufresne and R. Le Van Mao, *Catal. Lett.*, 25 (1994) 371.
- [42] J.A. Biscardi, G.D. Meitzner and E. Iglesia, *J. Catal.*, submitted.
- [43] T. Inui and F. Okazumi, *J. Catal.*, 90 (1984) 366.
- [44] C.W.R. Engelen, J.P. Wolthuizen and J.H.C. van Hooff, *Appl. Catal.*, 19 (1985) 153.
- [45] C.W.R. Engelen, J.P. Wolthuizen, J.H.C. van Hooff and H.W. Zandbergen, *Stud. Surf. Sci. Catal.*, 28 (1986) 709.
- [46] N.S. Gnep, J.Y. Doyemet, A.M. Seco, F.R. Ribeiro and M. Guisnet, *Appl. Catal.*, 35 (1987) 93.
- [47] B.S. Kwak, W.M.H. Sachtler and W.O. Haag, *J. Catal.*, 149 (1994) 465.
- [48] J.A. Johnson and G.K. Hilder, *NPRA Annual Meeting*, Dallas, AM-84-45, 1984.
- [49] J.R. Mowry, R.F. Anderson and J.A. Johnson, *Oil Gas J.*, 83 (1985) 128.
- [50] T. Inui, Y. Ishihara, K. Kamachi and H. Matsuda, *Zeolites: Facts, Figures, Future*, (1989) 1183.
- [51] G.D. Meitzner and E.S. Huang, *Fresenius' J. Anal. Chem.*, 342 (1992) 61.
- [52] F.W. Lytle, P.S. Wei, R.B. Gregor, G.H. Via and J.H. Sinfelt, *J. Chem. Phys.*, 70 (1979) 4849.
- [53] S.P. Cramer, T.K. Eccles, F.W. Kutzler, K.O. Hodgson and L.E. Mortenson, *J. Am. Chem. Soc.*, 98 (1976) 1287.
- [54] G.L. Price and E. Iglesia, *Ind. Eng. Chem. Res.*, 28 (1989) 839.
- [55] E. Iglesia, J.E. Baumgartner, G.L. Price, J.L. Robbins and K.D. Rose, *J. Catal.*, 125 (1990) 95.
- [56] C.R. Bayense, A.J.H.P. van der Pol and J.H.C. van Hooff, *Appl. Catal.*, 72 (1991) 81.
- [57] J. Bandiera and Y. Taarit, *Appl. Catal.*, 76 (1991) 199.

- [58] G. Giannetto, A. Montes, N.S. Gnep, A. Florentino, P. Cartraud and M. Guisnet, *J. Catal.*, 145 (1993) 86.
- [59] S. Kaliaguine, G. Lemay, A. Adnot, S. Burelle, R. Audet, G. Jean and J.A. Sawicki, *Zeolites*, 10 (1990) 559.
- [60] S.A. Tabak, F.J. Krambeck and W.E. Garwood, *AIChE J.*, 32 (1986) 1526.
- [61] R.J. Quann, L.A. Green, S.A. Tabak and F.J. Krambeck, *Ind. Eng. Chem. Rev.*, 27 (1988) 565.
- [62] H. Pines, *The Chemistry of Catalytic Hydrocarbon Conversions*, Academic Press, New York, 1981.
- [63] W.O. Haag and R.M. Dessau, *Proc. 8th Int. Congr. Catal.*, Berlin, Vol. 2, 1984, p. 305.
- [64] B.H. Davis and P.B. Venuto, *J. Org. Chem.*, 36 (1971) 337.
- [65] G.L. Price and G.R. Egedy, *J. Catal.*, 84 (1983) 461.
- [66] E. Iglesia and J.E. Baumgartner, unpublished results.
- [67] H.S. Taylor, *Annu. Rev. Phys. Chem.*, 12 (1961) 127.
- [68] A.L. Dent and R.J. Kokes, *J. Phys. Chem.*, 73 (1969) 3372.
- [69] P. Meriaudeau and C. Naccache, *Appl. Catal.*, 73 (1991) L13.
- [70] P. Meriaudeau and C. Naccache, *J. Mol. Catal.*, 50 (1989) L7.
- [71] K. Acholle, W. Kentgens, W. Veeman, P. Frenken and G. Valdin, *J. Phys. Chem.*, 88 (1984) 5.
- [72] C.T. Chu and C.D. Chang, *J. Phys. Chem.*, 89 (1985) 1569.
- [73] C.T. Chu, R.M. Kuehl, R.M. Lago and C.D. Chang, *J. Catal.*, 93 (1985) 451.