

Reaction Pathways and Rate-Determining Steps in Reactions of Alkanes on H-ZSM5 and Zn/H-ZSM5 Catalysts

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Reactions of ethane and propane on H-ZSM5 lead primarily to undesired products of β -scission reactions. Turnover rates, aromatic site-time yields, and the rate of hydrogen disposal during alkane conversion increase as the density of exchanged Zn cations increases in H-ZSM5. Zn cations decrease β -scission rates and the residence time of alkenes within oligomerization/ β -scission cycles, leading to higher rates and selectivity for the synthesis of C₆–C₈ aromatic products. Reactions of propene/²-¹³C propane mixtures show that initial dehydrogenation steps become increasingly irreversible as Zn cations catalyze the recombinative desorption of H-atoms and H₂. This process depletes the surface hydrogen pool available for the reverse hydrogenation reactions and it increases the overall rate of propene conversion to aromatics. Zn cations promote not only alkane dehydrogenation, but also the subsequent removal of hydrogen as H₂, leading to unsaturated intermediates required in cyclization steps. C₃H₈/C₃D₈ isotopic exchange rates are much higher than propane conversion rates. Exchange rates are similar on H-ZSM5 and Zn/H-ZSM5, but negligible on Na-ZSM5, consistent with the involvement of Bronsted acid sites in isotopic scrambling within alkanes and with a predominant role of Zn in the recombinative desorption of H-atoms. This proposal is consistent with the effects of Zn cations on the rate of H₂/D₂ isotopic equilibration, with the role of added H₂ on alkane reaction rates, and with the rate of incorporation of D-atoms into reaction products formed from C₃H₈/D₂ mixtures. © 1999 Academic Press

Key Words: H-ZSM5; Zn/H-ZSM5; deuterium exchange; alkane reaction mechanisms; ethane reactions; propane reactions; dehydrogenation; aromatization.

1. INTRODUCTION

The conversion of light alkanes to aromatics and H₂ via nonoxidative routes significantly expands the feedstocks available for synthesis of these valuable products. Many studies have focused on the use of medium-pore pentasil zeolites for these reactions. H-ZSM5 catalyzes the conversion of light alkanes to aromatics with low selectivity because of fast β -scission side reactions. The introduction of

Ga (1–23), Zn (24–36), and Pt (37–43) species into H-ZSM5 increases the rate and selectivity of aromatization reactions and inhibits β -scission side reactions that lead to undesirable products.

Aromatization reaction pathways have been discussed extensively. Most studies addressed the effect of catalyst composition on reaction rates and selectivities (1, 4, 10, 24, 26, 38, 40, 44, 45, 47). Recently, direct evidence for the sequence of propane aromatization steps has been obtained using isotopic tracer and exchange methods (48). These methods have established the nature and the rate of individual reaction steps in this reaction sequence.

The catalytic role of metal cations in light alkane aromatization remains the subject of controversy even after significant emphasis and numerous publications. Guisnet *et al.* (3, 4, 10, 18, 40, 46, 49) observed a higher initial rate of propene formation when metal cations (Ga) were added, leading them to suggest that propane dehydrogenation and naphthene dehydrogenation steps occur on the Ga cations. They suggested that all other required steps occurred on Bronsted acid sites within zeolite channels. Mole *et al.* (24) proposed that Zn cations in H-ZSM5 were involved in all dehydrogenation steps required for alkane aromatization, but only by catalyzing the recombinative desorption of H-atoms as H₂, while all other steps occurred on acid sites. Subsequent kinetic and isotopic tracer studies by Inui *et al.* (37, 50), le van Mao *et al.* (5, 7, 30, 51), and Iglesia *et al.* (8, 12, 14, 15, 29, 32) confirmed the involvement of metal cations in rate-determining hydrogen removal steps during propane reactions on Zn- and Ga-promoted H-ZSM5. The latter studies suggested a synergy between acid sites and exchanged cations where alkane activation and initial C–H bond cleavage can occur on acid sites, but hydrogen atoms must be preferentially removed via hydrogen transfer to hydrocarbon species to form C₂H₆ and CH₄, or via recombinative desorption on cation sites to form H₂.

In this study, we present mechanistic evidence for bifunctional pathways in the conversion of ethane and propane to aromatics on H-ZSM5 modified by Zn cations. We also examine the effect of Zn loading on propane conversion and hydrogen removal rates and the nature of hydrogen

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adsorption/desorption steps using deuterium exchange, hydrogen kinetic measurements, and H₂/D₂ isotopic equilibration reactions.

2. EXPERIMENTAL METHODS

2.1. Catalyst Synthesis

Na-ZSM5 (Zeochem, Si/Al = 14.5) was converted to NH₄-ZSM5 by exchange with a 0.67 M solution of NH₄NO₃ (Fisher, Certified ACS, >98.0%) at 353 K for 10 h. The exchange procedure was repeated three times using fresh NH₄NO₃ solutions in order to ensure complete removal of Na⁺ cations. Solids were filtered, washed with deionized water, dried at 373 K for 20 h, and calcined at 773 K for 20 h in order to decompose NH₄⁺ to H⁺ and to form the acidic form of the zeolite (H-ZSM5).

Three Zn/H-ZSM5 catalysts were prepared by ion-exchange of H-ZSM5 with a solution of Zn(NO₃)₂ (0.0050 M, Aldrich, >98.0%) at 343 K for 1, 5.5, or 9 h. Each sample was filtered, washed with deionized water, dried in flowing air at 383 K for 20 h, and then treated in flowing dry air at 773 K for 20 h.

2.2. Elemental Analysis

Si and Al contents in H-ZSM5 were measured by atomic emission spectroscopy (AES). The atomic Si/Al ratio in the ZSM5 material was 14.5. This value remained constant throughout all exchange procedures and thermal treatments. The residual Na content of the H-ZSM5 was less than 0.07 wt%. The Zn content was also measured by AES. Zn contents were 0.62, 1.07, and 1.30 wt%, which correspond to Zn/Al atomic ratios of 0.10, 0.16, and 0.19, respectively. Isotopic exchange of zeolite OH groups with D₂ in H-ZSM5 gave a H/Al ratio of 1.04, suggesting that any extra-framework Al species must be present in very low concentrations (53).

2.3. Catalytic Reaction Studies

Kinetic and isotopic tracer studies were conducted in a gradientless batch reactor consisting of a shallow packed-bed contained within a gas recirculation loop (8). Reactants and products were recirculated at 250 cm³ min⁻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 using liquid nitrogen traps. The chemical and isotopic compositions of the reactants and products were measured by capillary chromatography using flame ionization and electron-impact mass spectrometric detection methods.

Propane (Matheson, instrument purity, >99.5%), perdeuterated propane (Isotec, chemical purity >99.0%, isotopic purity >99.0%), propane-2-¹³C (Cambridge Isotopes,

chemical purity >98.0%, 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. Hydrogen (Matheson, C.P., >99.99%) was purified using an oxygen trap (Matheson) and a 13X molecular sieve trap held at room temperature. Helium (>99.95%) was purified using a 13X molecular sieve trap at room temperature before use as a diluent.

Propane reaction rates are reported as the molar rate of propane conversion per g-atom Al in the catalyst charge. Product concentrations in the batch reactor are given as site-yields (moles of propane converted to a given product per g-atom Al) as a function of contact time; the slope of such plots give site-time yields 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 reported as the percentage of the hydrogen in the propane that appears within each product.

2.4. Isotopic Equilibration of H₂/D₂ Mixtures

Isotopic exchange between H₂ and D₂ was carried out in a flow apparatus consisting of a metered gas manifold connected to a quartz capillary cell. Samples were heated to 773 K in a flowing H₂/Ar mixture (5.0% H₂, Matheson, certified standard, 100 cm³/min), held isothermal for 1 h, and then cooled to 300 K. The flow was then switched to a H₂/D₂/Ar mixture (5.0% H₂, 5.0% D₂, 1.0% N₂, 89.0% Ar, Matheson, certified standard, 100 cm³/min) and the temperature was increased from 300 to 873 K at 10 K/min. The isotopic composition of the effluent from the cell was measured by an on-line mass spectrometer (Leybold-Inficon, Model THP TS200). The kinetic rate constants were determined by analysis methods reported by Boudart (52).

2.5. Deuterium and ¹³C Analysis in Hydrocarbon Mixtures

The deuterium fraction in reactants and products was determined from mass spectral data during propane conversion using C₃H₈/D₂ mixtures. The fraction of the isotopomers for each product was determined from mass spectra after correcting for ion fragmentation (54). Cross exchange products in C₃H₈/C₃D₈ mixtures were measured using a similar technique and the cross exchange rate was determined from the number of deuterium atoms (or hydrogen atoms) in the propane isotopomers multiplied by the moles of "unconverted" propane and reported per g-atom Al in ZSM5 catalysts. ¹³C distributions were measured on the products of C₃H₈-2-¹³C reactants and of C₃H₈-2-¹³C/C₃H₆ mixtures using mass spectral data and analysis methods that account for ion fragmentation and natural ¹³C abundance (54).

3. RESULTS AND DISCUSSION

3.1. The Effect of Metal Cations on Propane and Ethane Conversion Rate and Selectivity

Propane conversion turnover rates and selectivities on H-ZSM5 and Zn/H-ZSM5 are shown in Table 1 at similar propane conversion levels (7.6–8.3%). Propane turnover rates, aromatics site-time yields, propene selectivity, aromatic selectivities, and hydrogen (H₂) selectivity increase with increasing Zn content in H-ZSM5. These results are similar to those reported previously by others (33, 55).

The data in Fig. 1 show that hydrogen desorption site-yields increase with increasing Zn content in H-ZSM5. H-ZSM5 disposes of H-atoms at significantly lower rates and preferentially by hydrogen transfer to adsorbed hydrocarbons followed by desorption of hydrogen-rich CH₄ and C₂H₆ alkanes.

In addition to increasing total propane conversion turnover rates, Zn increases site-yields for the formation of propene from propane (Fig. 2). Initial propene site-time yields increase from $2.4 \times 10^{-4} \text{ s}^{-1}$ to $35.4 \times 10^{-4} \text{ s}^{-1}$ when Zn (1.30 wt%) is ion-exchanged into H-ZSM5. Zn sites increase the rate of dehydrogenation reactions and inhibit the formation of undesired β -scission products such as methane. Methane site-yields are lower on Zn/H-ZSM5 than on H-ZSM5 (Fig. 3), but they increase as Zn loading increases. The change in methane formation rates may result from the introduction of Zn into H-ZSM5 which replaces some of the initially present acid protons.

TABLE 1

Propane Turnover Rates and Product Distribution on H-ZSM5 and Zn/H-ZSM5 [773 K, 26.6 kPa C₃H₈, 74.7 kPa He]

Zn (wt%)	0.00	0.62	1.07	1.30
Zn/Al	0.00	0.10	0.16	0.19
H/Al ^a	1.04	0.84	0.74	0.63
Propane conversion (%)	7.6	7.7	7.6	8.3
Propane turnover rate (per Al, 10 ⁻³ s ⁻¹)	1.7	2.5	4.7	5.1
Aromatization site-time yield (per Al, 10 ⁻³ s ⁻¹)	0.1	0.7	1.6	1.8
<i>Carbon selectivity (%)</i>				
Methane	23.2	11.5	7.0	6.2
Ethene	33.2	23.3	14.9	14.6
Ethane	7.3	3.1	6.2	4.1
Propene	22.4	29.0	33.7	34.7
C ₆ + aromatics	2.4	28.3	33.5	35.4
Benzene	0.8	12.4	15.2	15.4
Toluene	1.5	11.1	13.0	14.0
C ₈ +	0.1	4.8	5.3	6.0
<i>Hydrogen selectivity (%)</i>				
Hydrogen (H ₂)	4.6	25.2	29.0	31.0

^a From D₂ exchange measurements (53).

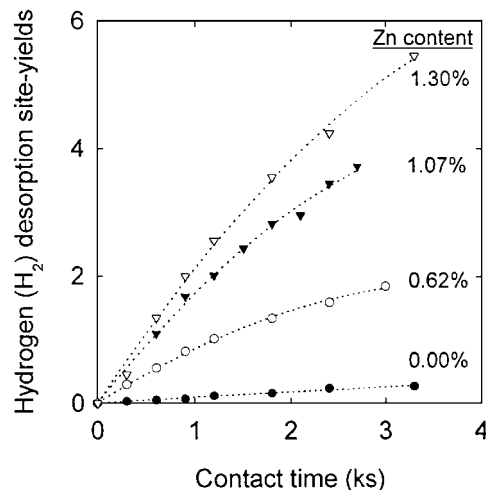


FIG. 1. Hydrogen (H₂) desorption site-yields versus contact time during propane conversion on H-ZSM5 and Zn/H-ZSM5 [773 K, 26.6 kPa C₃H₈, 74.7 kPa He].

Previous structural characterization of the metal and acid density in Zn/H-ZSM5 (Si/Al = 14.5) has suggested that Zn resides at cation exchange sites as O⁻-Zn⁺²-O⁻ species and interacts with two framework aluminum atoms (53). The number of remaining protons after Zn exchange in Zn/H-ZSM5 has been determined from the isotopic titration of remaining surface hydrogen species with deuterium and is reported in Table 1. Thus, methane site-yields calculated based on the number of residual Bronsted acid sites rather than on the total Al sites still give lower values of methane site-time yields on Zn-containing samples than on H-ZSM5 (Fig. 4). The higher methane formation rate as Zn loading increases can be explained using reactions shown in

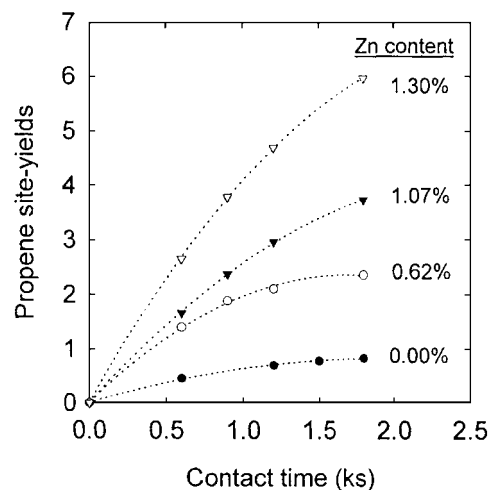


FIG. 2. Propene site-yields versus contact time during propane conversion on H-ZSM5 and Zn/H-ZSM5 [773 K, 26.6 kPa C₃H₈, 74.7 kPa He].

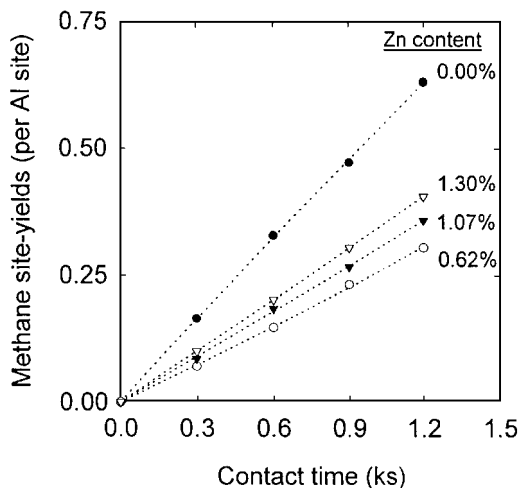


FIG. 3. Methane site-yields (based on Al sites) versus contact time during propane conversion on H-ZSM5 and Zn/H-ZSM5 [773 K, 26.6 kPa C_3H_8 , 74.7 kPa He].

Scheme 1. From this reaction scheme, the rate of β -scission is expressed in Eq. [1]:

$$r_{\beta\text{-scission}} = k_2(C_3^{\ddagger}) = \frac{k_1 k_2 (C_3H_8)}{k_2 + k_3} \quad [1]$$

Zn cations increase the rate of dehydrogenation. When Zn is present, k_3 becomes the dominant term in the denominator and β -scission rates decrease when Zn is added. However, as Zn content increases, k_1 increases proportionately more than k_3 , resulting in higher propane β -scission rates.

The effect of Zn on alkane reactions is also evident for ethane reactants. Ethane conversion rates on H-ZSM5 and Zn/H-ZSM5 at 773 K are shown in Table 2. Ethane con-

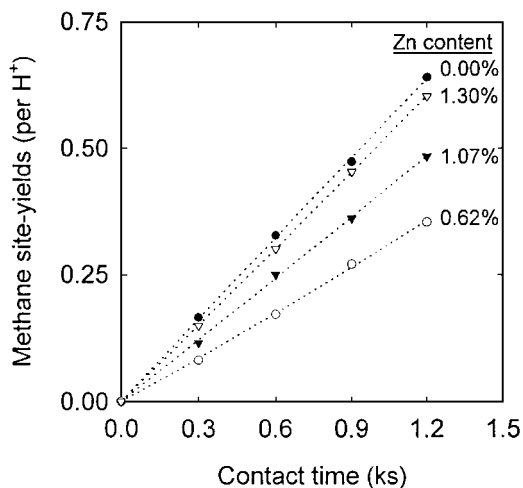
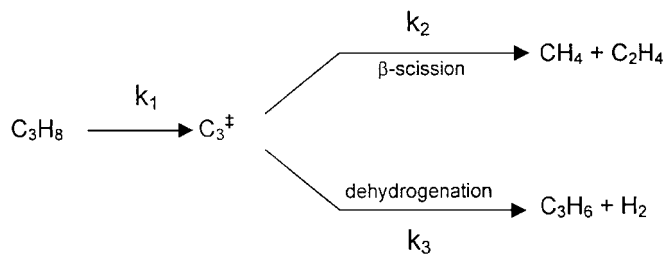


FIG. 4. Methane site-yields (based on H^+ sites) versus contact time during propane conversion on H-ZSM5 and Zn/H-ZSM5 [773 K, 26.6 kPa C_3H_8 , 74.7 kPa He, proton concentrations were determined from deuterium exchange of OH groups (53)].



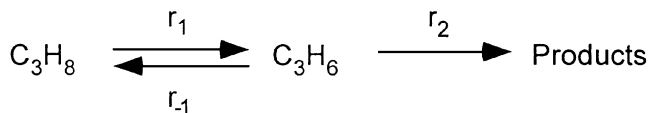
SCHEME 1. Propane reaction mechanism for β -scission and dehydrogenation.

version turnover rates increase when Zn (1.07 wt%) is exchanged into H-ZSM5. As with propane, ethane conversion rates, ethene selectivity, aromatics selectivity, and hydrogen formation rates all increase when Zn is present. Ethane and propane conversions appear to proceed by similar mechanistic routes, leading to methane, aromatics, and the corresponding alkene. Ethane conversion rates are lower than propane conversion rates on all catalysts.

Reaction rates at 773 K on H-ZSM5 and Zn/H-ZSM5 were also measured using propene as the reactant. As with ethane and propane reactants, the addition of Zn species to H-ZSM5 leads to an increase in propene conversion turnover rates, aromatics site-time yields, hydrogen desorption turnovers, aromatics selectivity, and hydrogen selectivity (Table 3). Also, the addition of Zn has a strong effect on the aromatics distribution. On H-ZSM5, toluene is the most abundant product, but benzene becomes the most abundant aromatic product of propene conversion on Zn/H-ZSM5 (Table 3).

3.2. Relative Rates of Propene Hydrogenation (r_{-1}) and Propene Aromatization (r_2)

The reversibility and rate-determining nature of initial propane dehydrogenation steps were investigated using mixtures of propane-2- ^{13}C and unlabeled propene. The results are described using the reactions shown in Scheme 2. Zn species increase the rate of propane dehydrogenation (r_1) (Fig. 2); therefore, they must also catalyze the reverse reaction: propene hydrogenation (r_{-1}). Relative rates of propene hydrogenation (r_{-1}) and conversion to other products (r_2) (Scheme 2) can be measured from the rate of isotopic scrambling between propane-2- ^{13}C and unlabeled propene and from the isotopic content of the other reaction products. From these data, r_2 and r_{-1} values can be obtained as a function of contact time on H-ZSM5 and Zn/H-ZSM5.



SCHEME 2. Propene conversion to propane (r_{-1}) and to aromatics (r_2).

TABLE 2
Ethane and Propane Turnover Rates and Product Distribution on H-ZSM5 and 1.07% Zn/H-ZSM5 [773 K, 26.6 kPa C₃H₈ or 26.6 kPa C₂H₆, 74.7 kPa He]

Catalyst	H-ZSM5	H-ZSM5	Zn/H-ZSM5	Zn/H-ZSM5
Reactant	Ethane	Propane	Ethane	Propane
Alkane conversion (%)	5.5	5.4	5.6	5.7
Alkane turnover rate (per Al, 10 ⁻⁴ s ⁻¹)	0.1	17.1	3.1	53.1
Aromatization site-time yield (per Al, 10 ⁻⁵ s ⁻¹)	0.2	0.4	15.0	165.7
<i>Carbon selectivity (%)</i>				
Methane	58.2	24.9	4.5	6.2
Ethene	5.0	39.4	39.2	14.4
Ethane	—	6.1	—	5.1
Propene	2.0	23.9	3.8	38.9
Propane	1.9	—	2.5	—
C ₆ + aromatics	32.2	2.2	48.4	31.2
Benzene	17.8	0.8	25.1	14.1
Toluene	11.7	1.3	18.5	12.2
C ₈ +	2.7	0.1	4.8	4.9
<i>Hydrogen selectivity (%)</i>				
Hydrogen (H ₂)	4.6	4.8	44.6	29.3

The (r_2/r_{-1}) ratios on these catalysts are almost independent of contact time (and conversion), but they are higher on Zn/H-ZSM5 than on H-ZSM5; these values (after extrapolation to zero conversion) are about 2 on H-ZSM5 and 6 on Zn/H-ZSM5 (Fig. 5). Zn increases the rate of initial propane dehydrogenation steps (r_1) and also the rate of its reverse reaction (r_{-1} , propene hydrogenation). However, Zn increases the rate of subsequent reactions of propene

(r_2) more strongly than it increases r_{-1} , leading to higher (r_2/r_{-1}) ratios. Zn species influence both initial propane dehydrogenation steps and the subsequent dehydrogenation steps required in order to convert propene to aromatics products.

Ono *et al.* (1) have reported that the concentration of alkenes decreases with the addition of metal cations (Ga) during propane conversion. They concluded from these data that metal cations increase only alkene aromatization rates. Our data are not consistent with this proposal and support a different conclusion. Metal cations increase

TABLE 3

Propene Turnover Rates and Product Distribution on H-ZSM5 and 1.07% Zn/H-ZSM5 [773 K, 0.3 kPa C₃H₆, 101.0 kPa He]

	H-ZSM5	Zn/H-ZSM5
Zn/Al	0.00	0.16
H/Al	1.04	0.74
Propene conversion (%)	23.3	20.5
Propene turnover rate (per Al, 10 ⁻⁴ s ⁻¹)	1.7	12.0
Aromatics site-time yield (per Al, 10 ⁻⁴ s ⁻¹)	0.5	6.5
<i>Carbon selectivity (%)</i>		
Methane	0.8	1.2
Ethene	34.2	22.9
Ethane	0.3	0.5
Propane	2.4	10.5
C ₆ + aromatics	27.5	53.8
Benzene	7.5	23.6
Toluene	14.3	22.7
C ₈ +	5.7	7.5
<i>Hydrogen selectivity (%)</i>		
Hydrogen (H ₂)	10.3	18.5

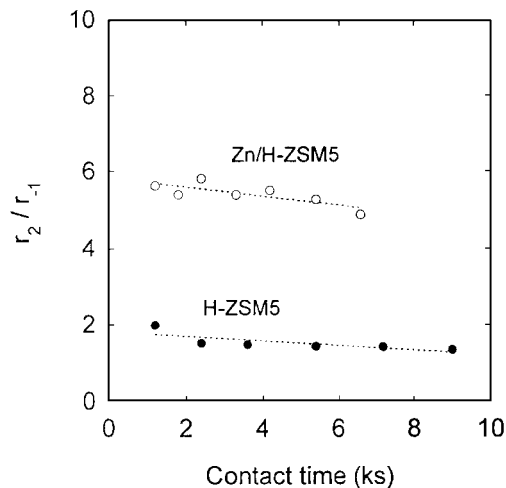


FIG. 5. Measurement of r_2/r_{-1} in propene/propane-2-¹³C mixtures on H-ZSM5 and 1.30% Zn/H-ZSM5 [773 K, 5.6 kPa C₃H₈-2-¹³C, 1.1 kPa C₃H₆, 94.6 kPa He].

propane conversion rates, but increase propene conversion rates even more, thus decreasing the concentration of intermediate alkenes during propane conversion and the (r_{-1}/r_2) ratio.

On both H-ZSM5 and Zn/H-ZSM5, (r_2/r_{-1}) ratios are greater than unity, consistent with a nonequilibrated initial propane dehydrogenation step. In effect, this step becomes even more irreversible (r_2/r_{-1} increases) when Zn is introduced into H-ZSM5 catalysts because required subsequent oligomerization, cyclization, and dehydrogenation reactions become faster and scavenge alkenes before hydrogenation can occur. As propane dehydrogenation steps become increasingly irreversible, propene concentrations decrease and alkenes exit oligomerization/ β -scission cycles more rapidly. The chemical and isotopic compositions of aromatics on Zn/H-ZSM5 should then resemble those expected from direct dimerization and cyclization of propene and the benzene content within C_6 - C_8 aromatics increases (Tables 1 and 3).

Products of propane-2- ^{13}C reactions on Zn/H-ZSM5 suggest that alkenes exit from these oligomerization/ β -scission cycles more rapidly than on H-ZSM5. On H-ZSM5, benzene molecules formed from propane-2- ^{13}C contain a binomial distribution of ^{13}C -atoms even at very low conversions, instead of the expected single isotopomer with two ^{13}C -atoms (Fig. 6). 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 cleaved and re-formed within both C_3 fragments and larger surface chains many times in the time required for an aromatization turnover. Such a turnover requires the formation of a C_6 or larger molecule, a process that involves oligomerization reactions,

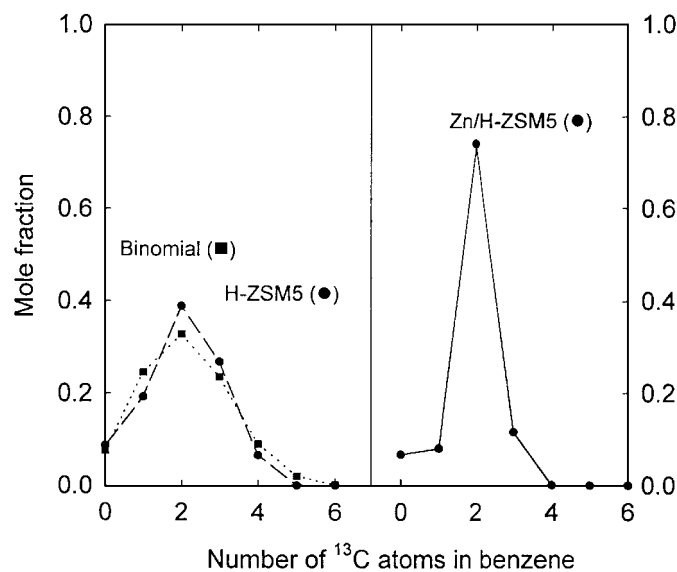


FIG. 6. ^{13}C distribution in benzene formed from propane-2- ^{13}C on H-ZSM5 and 1.30% Zn/H-ZSM5 [773 K, 6.7 kPa C_3H_8 -2- ^{13}C , 94.6 kPa He, <5% conversion].

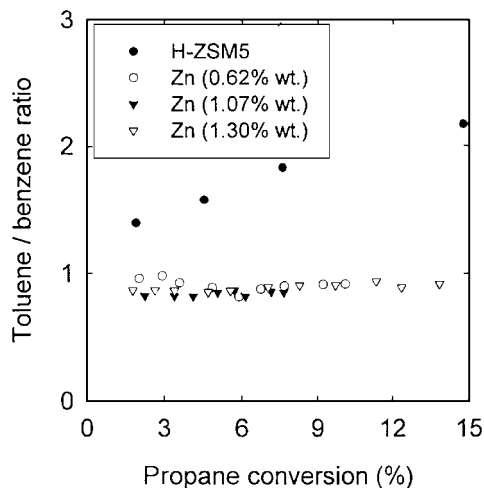


FIG. 7. Toluene/benzene ratio during propane conversion on H-ZSM5 and Zn/H-ZSM5 [773 K, 26.6 kPa C_3H_8 , 74.7 kPa He].

but also a significant number of interspersed β -scission and rapid methyl shift events. Products of propane-2- ^{13}C reactions on Zn/H-ZSM5 contain sharper ^{13}C distributions, with the predominant presence of benzene isotopomers with the expected two ^{13}C atoms (Fig. 6). Therefore, Zn cations increase the rate of removal of alkenes from these oligomerization/ β -scission cycles. This removal must occur by the formation of products, such as aromatics (and H_2) and alkanes, which are less reactive than alkenes in acid-catalyzed reactions. These data confirm that subsequent oligomerization, cyclization, and dehydrogenation reactions are more strongly influenced by exchanged metal cations than the initial propane dehydrogenation step.

Propane-2- ^{13}C /propene mixtures lead to similar ^{13}C contents in benzene and toluene, suggesting that they are formed from a common pool of alkene intermediates (32). Thus, (toluene/benzene) molar ratios become an accurate measure of the average size of the alkenes in this pool. On H-ZSM5, (toluene/benzene) ratios are higher than on Zn-containing catalysts (Fig. 7). If this reduction of the (toluene/benzene) ratio on Zn/H-ZSM5 is due to the decrease in Bronsted acid sites, higher Zn loadings should reduce this ratio even further. However, our data show that (toluene/benzene) ratios are independent of Zn loading (0.62–1.30 wt%) (Fig. 7). Therefore, Zn extracts C_6 alkenes before these alkenes are able to crack and re-oligomerize to form a quasi-equilibrated pool of alkenes.

3.3. Isotopic Equilibration of C_3H_8/C_3D_8 Mixtures and C-H Bond Activation Rates

Initial propane dehydrogenation steps are not quasi-equilibrated during steady-state propane aromatization on H-ZSM5 and Zn/H-ZSM5 (Section 3.2). Thus, aromatization proceeds via a sequence of irreversible dehydrogenation reactions with interspersed fast acid-catalyzed

reactions that lead to chain lengthening/scission with occasional ring closure steps. Consequentially, the overall reaction rate is given accurately by the rate of the initial (irreversible) propane dehydrogenation step. Propane dehydrogenation reactions require elementary steps involving the activation of C-H bonds and the elimination of the H-atoms formed. In this section, we report the relative rates of C_3H_8/C_3D_8 cross exchange and chemical conversion. These rates were measured during steady-state propane reactions on H-ZSM5 and Zn/H-ZSM5 using isotopic exchange and chemical reaction rates for C_3H_8/C_3D_8 reactant mixtures.

Isotopic mixtures can be used to provide information about the identity of elementary processes and intermediates (56–63). Isotopic tracer studies have also been used to determine the reversibility of C-H bond cleavage during alkane conversion (14, 32, 57, 64–66). In our reaction, isotopic cross exchange rates can be used to determine the rate and reversibility of initial C-H bond activation steps. This cross exchange rate is only a true measure of the C-H bond activation rate if all propane reactions (dehydrogenation, β -scission, and cross exchange) proceed through the same surface species (Scheme 3).

The reversibility of C-H activation steps leading to cross exchange, β -scission, and dehydrogenation can be examined by comparing cross exchange rates to those for (irreversible) propane dehydrogenation and β -scission steps. Propane conversion turnover rates were obtained from the total rate of propane conversion (both C_3H_8 and C_3D_8) to products because all products are formed after the same initial propane activation step. Cross-exchange rates can be calculated from the concentration of propane isotopomers (C_3H_8 , $C_3H_7D_1$, $C_3H_6D_2$, ..., C_3D_8) as a function of contact time.

Significant isotopic equilibration occurs between C_3H_8 and C_3D_8 on H-ZSM5, even at low chemical conversions (Fig. 8). C_3H_8/C_3D_8 cross-exchange occurs by stepwise transfer of single D or H atoms, leading to statistical isotopomer distributions within both the mostly undeuterated and mostly deuterated components in “unreacted” propane. The initial reaction products of C_3H_8/C_3D_8 reactant mixtures, propene and ethene, do not contain the two distributions of predominately protium (C_2H_4 , C_3H_6) from C_3H_8 and predominately deuterium (C_2D_4 , C_3D_6) from C_3D_8 , expected of independent reactions of mostly deuter-

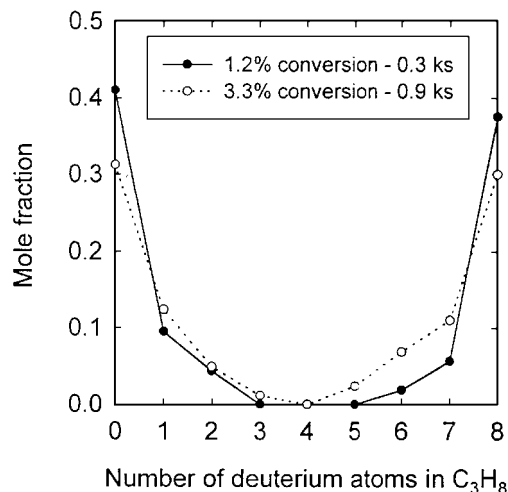
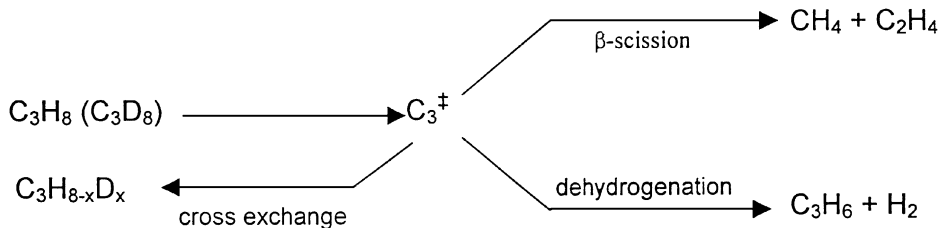


FIG. 8. Cross exchange of C_3H_8/C_3D_8 reactant mixtures on H-ZSM5. Deuterium distributions in “unreacted” propane in a recirculating batch reactor [773 K, 6.6 kPa C_3H_8 , 6.6 kPa C_3D_8 , 87.9 kPa He].

ated and mostly undeuterated propane. Instead, propene and ethene show unimodal binomial deuterium distributions, consistent with statistical scrambling of the H and D atoms contributed by C_3H_8 and C_3D_8 reactants, respectively (Fig. 9). The isotopic compositions of propene and ethene are less than 50% D (Fig. 9) because propane reactions on H-ZSM5 using purely C_3H_8 or C_3D_8 feeds show a ($r_{C_3H_8}/r_{C_3D_8}$) kinetic isotope effect of 1.24, indicating that C_3H_8 reacts preferentially, leading to more protium on the ZSM5 surface after C-H cleavage. These products appear to sample the surface hydrogen–deuterium pool and their isotopic content reflects accurately the isotopic composition of this surface pool because C-H bonds have formed and broken many times in the time required for a propane conversion catalytic turnover.

Comparison of the rates of propane cross exchange and propane chemical conversion on H-ZSM5 show that isotopic exchange occurs much faster than propane conversion (Table 4). Thus, if cross exchange accurately reflects the C-H bond activation step, it appears that this C-H bond activation step does not limit the rate of the overall chemical conversion of propane on H-ZSM5.

Zn cations at H-ZSM5 exchange sites increase propane aromatization rates and selectivities (Table 1). Yet, $C_3H_8/$



SCHEME 3. Propane reactions proceeding through a common surface species.

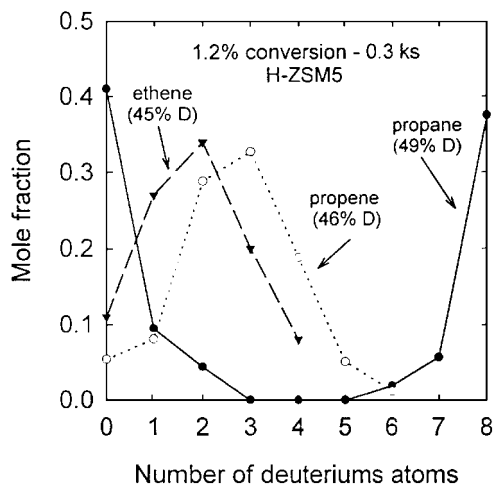


FIG. 9. Deuterium distributions in "unreacted" propane, propene, and ethene from cross exchange of C_3H_8/C_3D_8 reactant mixtures on H-ZSM5 [773 K, 6.6 kPa C_3H_8 , 6.6 kPa C_3D_8 , 87.9 kPa He].

C_3D_8 cross exchange rates are similar (within a factor of 2) on all catalysts, including H-ZSM5 (Table 4). Propane conversion rates, however, vary by more than a factor of 10 among these catalysts. Thus, initial C-H bond cleavage steps cannot limit propane chemical conversion rates, because Zn species increase propane conversion rates much more than they influence faster cross exchange rates.

The requirement of Bronsted acid sites for C_3H_8/C_3D_8 cross-exchange is evident from the data in Table 4. Cross exchange rates are much lower on Na-ZSM5 than on H-ZSM5, suggesting that Na-ZSM5, which lacks protonic sites, activates C-H bonds much more slowly than H-ZSM5. The rate of C-H bond activation, obtained from C_3H_8/C_3D_8 cross-exchange rates, increases by about a factor of 2 when Zn cations are introduced (Table 4), suggesting that Zn may interact directly with propane molecules or that remaining acid sites become more active for C-H bond activation when Zn cations reside nearby. Bronsted acid site requirements in C-H bond activation were also examined by Ono and co-workers (25) on weakly acidic Zn exchanged-borosilicates

TABLE 4

Propane Conversion Turnover and Cross Exchange Rates on H-ZSM5, Zn/H-ZSM5, and Na-ZSM5 (from cross exchange rates of C_3H_8/C_3D_8 mixtures) [773 K, 6.6 kPa C_3H_8 , 6.6 kPa C_3D_8 , 87.9 kPa He]

	Propane conversion turnover rate per Al site ($10^{-2} s^{-1}$)	Cross exchange turnover rate per Al site ($10^{-2} s^{-1}$)
H-ZSM5	0.03	3.0
1.07% Zn/H-ZSM5	0.28	5.5
1.30% Zn/H-ZSM5	0.42	6.7
Na-ZSM5	<0.01	0.1

with pentasil structures. Zn-exchanged borosilicates did not catalyze propane aromatization, but they converted propene to aromatics at significant rates. These data suggest that neither Zn cations nor weak Bronsted acid sites in borosilicates can activate C-H bonds in propane by themselves. These weak acid sites, however, catalyze C-H activation in propene. Zn cations are unable to carry out propane dehydrogenation steps without the concurrent presence of strong Bronsted acid sites, which appear to be involved in the initial activation of C-H bonds in alkanes.

3.4. Reversibility of Hydrogen Adsorption/Desorption Steps

The rate of hydrogen recombinative desorption steps during propane conversion can be measured from the deuterium content in reaction products and in "unreacted" propane using C_3H_8/D_2 mixtures as reactants. Quasi-equilibrated desorption steps would lead to complete mixing of D-atoms from D_2 with H-atoms from propane in all reaction products, because aromatics formed from quasi-equilibrated alkene mixtures would sample statistically a surface hydrogen pool in chemical and isotopic equilibrium with the gas phase hydrogen (deuterium) pool. In contrast, irreversible (rate-determining) recombinative desorption steps would lead to the predominant appearance of H-atoms in reaction products, because of slow communication between gas phase (D_2) and surface pools (H-atoms from reacting C_3H_8) of hydrogen isotopes.

On H-ZSM5, the initial deuterium content in all products of C_3H_8/D_2 reactions is very low (3% D) and independent of conversion (e.g. toluene, propene; see Fig. 10), suggesting that hydrogen adsorption-desorption steps are irreversible. The distribution of D-atom isotopomers within each product formed on H-ZSM5 obeys a binomial distribution,

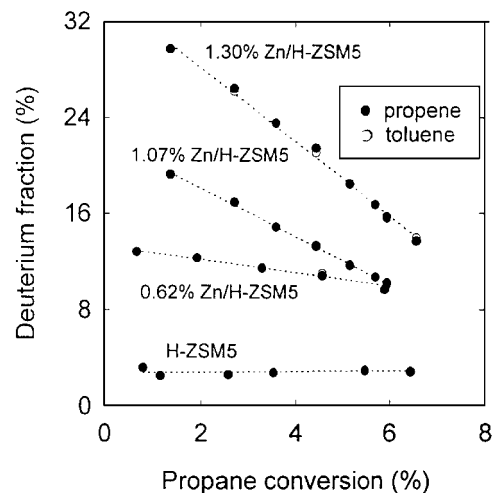


FIG. 10. Deuterium fraction in toluene and propene products of C_3H_8/D_2 mixtures on H-ZSM5 and Zn/H-ZSM5 [773 K, 26.6 kPa C_3H_8 , 6.7 kPa D_2 , 68.0 kPa He].

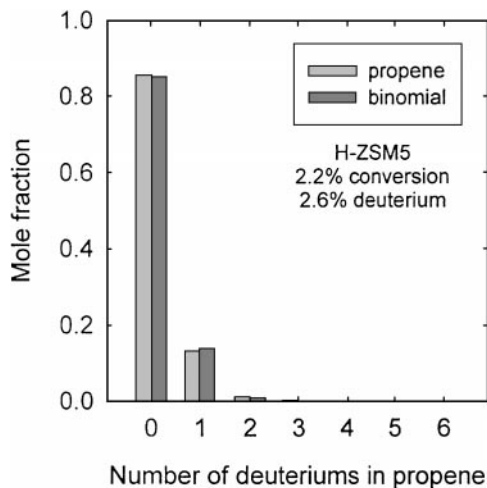


FIG. 11. Deuterium distribution in propene product of propane/deuterium mixtures on H-ZSM5 [773 K, 26.6 kPa C_3H_8 , 6.7 kPa D_2 , 68.0 kPa He, 2.2% propane conversion].

suggesting that multiple exchange events with a common surface hydrogen/deuterium pool occur during the formation of each reaction product (e.g. propene; see Fig. 11). Therefore, the deuterium content (3% D) in products reflects the composition of a surface hydrogen/deuterium pool containing about 3% D and 97% H, instead of the predominant deuterium coverage expected from equilibration with the (initially) pure D_2 gas phase (Table 5). The surface hydrogen pool in H-ZSM5 contains mostly H atoms formed in C-H bond activation steps, the removal of which limits the rate of propane dehydrogenation reactions.

Deuterium contents are also very similar within all products of C_3H_8/D_2 reactants formed on a given Zn/H-ZSM5 catalyst (Fig. 10). Deuterium distributions are binomial in all products, even though aromatics form after shorter residence times within oligomerization/ β -scission cycles on Zn/H-ZSM5 than on H-ZSM5. Deuterium contents decrease with increasing contact time (or conversion), because of the faster rate of formation of H_2 on Zn-containing samples, which dilutes the initially pure D_2 gas phase. Gas

TABLE 5

Initial Isotopic Composition in Toluene Product of Propane/Deuterium Mixtures on H-ZSM5 and Zn/H-ZSM5 [773 K, 26.6 kPa C_3H_8 , 6.7 kPa D_2 , 68.0 kPa He]

	Deuterium fraction	
	Experimental	Expected ^a
H-ZSM5	0.03	0.96
0.62% Zn/H-ZSM5	0.13	0.98
1.07% Zn/H-ZSM5	0.22	0.99
1.30% Zn/H-ZSM5	0.33	0.99

^a Expected deuterium fraction is calculated from the initial moles of D_2 in the gas phase and protium initially on the catalyst.

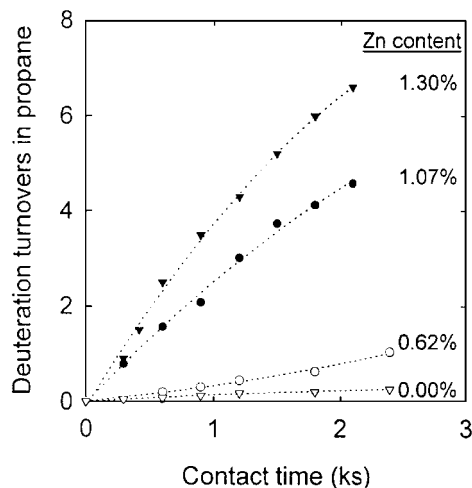


FIG. 12. Deuterium incorporation turnovers into propane molecules versus contact time from propane/deuterium mixtures on H-ZSM5 and Zn/H-ZSM5 in a recirculating batch reactor [773 K, 26.6 kPa C_3H_8 , 6.7 kPa D_2 , 68.0 kPa He].

phase H_2 and HD are much more abundant and communicate more effectively with reaction products when Zn is present in H-ZSM5 catalysts. The deuterium fraction within all products is much higher on Zn/H-ZSM5 catalysts than on H-ZSM5 (e.g. toluene and propene; see Fig. 10 and Table 5) and it increases with increasing Zn content.

The addition of Zn cations also increases the deuterium content in “unreacted” propane (Fig. 12), a result that seems surprising in view of the decrease in the reversibility of propane dehydrogenation steps as Zn content increases (Fig. 5). The rate of incorporation of D atoms into “unreacted” propane provides an independent measure of the D content in the surface pool. Deuteration turnovers, calculated from the number of propane molecules that contain one or more deuterium atoms, increase upon the addition of Zn. These turnovers reflect the rate of the propane hydrogenation 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 deuterium atom.

3.5. Isotopic Equilibration of H_2/D_2 Mixtures

The increase in the hydrogen (H_2) desorption rate during propane conversion on Zn/H-ZSM5 suggests that Zn cations catalyze the recombinative desorption of H atoms. This was confirmed by the higher D contents in the products of C_3H_8/D_2 mixtures on Zn-containing catalysts. Thus, Zn cations must also increase the rate of dissociative chemisorption of dihydrogen. Isotopic equilibration measurements using H_2/D_2 mixtures were conducted on Na-ZSM5, H-ZSM5, 1.07% Zn/H-ZSM5, and 1.30% Zn/H-ZSM5 in order to examine the role of Zn cations in the equilibration of hydrogen isotopes. H_2/D_2 exchange reactions directly probe the rates of H_2 (and D_2) dissociative

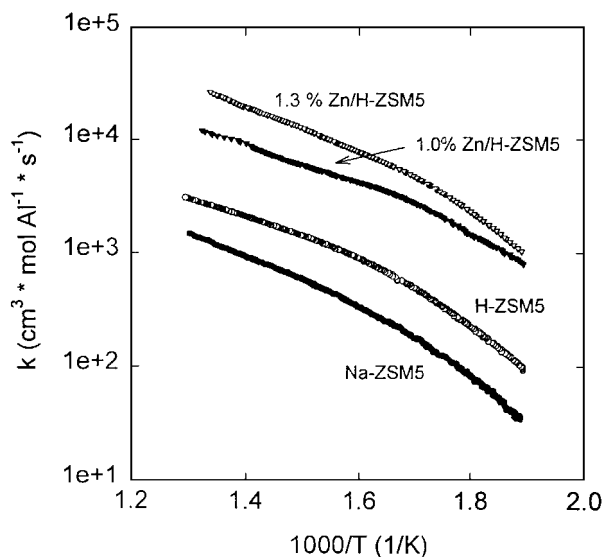


FIG. 13. Isotopic equilibration of H_2/D_2 mixtures on Na-ZSM5, H-ZSM5, and Zn/H-ZSM5 [5% H_2 , 5% D_2 , 1% N_2 , 89% Ar. 100 cm^3/min , 10 K/min].

adsorption, which must occur as the initial step in equilibration reactions.

The rate of HD formation from H_2/D_2 reactants is very low on Na-ZSM5 (Fig. 13). Heylen *et al.* (67) examined the rate of H_2/D_2 equilibration on Na-Y and $\text{NH}_4\text{-Y}$ and reported similar HD formation rates, which they attributed to catalytic impurities. The HD formation rate on our samples increases, however, when Na cations are replaced with protons in ZSM5. It appears that Na titrates sites responsible for H_2 dissociation whether these sites consist of defects, impurities, or protons.

Isotopic equilibration rates increase when Zn cations are introduced into H-ZSM5 (Fig. 13). The temperature required to reach equilibration rates (per Al) of $2.5 \times 10^{-2} \text{ s}^{-1}$ (the isokinetic temperature) is 750 K on Na-ZSM5 and 650 K on H-ZSM5. This isokinetic temperature decreases to 554 K and 537 K on 1.07% and 1.30% Zn/H-ZSM5, respectively. These results show that dissociative chemisorption of dihydrogen and recombinative desorption of H atoms occur slowly on H-ZSM5, consistent with the lack of deuterium incorporation in products of $\text{C}_3\text{H}_8/\text{D}_2$ mixtures.

3.6. Hydrogenation and Hydrogen Transfer Properties of ZSM5

The presence of Zn increases the rate of H_2/D_2 isotopic equilibration and the rate of deuterium incorporation into the products of $\text{C}_3\text{H}_8/\text{D}_2$ reactions. These data suggest that Zn increases the rate of communication between gas phase and surface hydrogen pools. In view of this, we have examined the effect of H_2 concentration on propane conversion turnover rates and selectivities on H-ZSM5 and Zn/H-ZSM5.

Propane aromatization rates and selectivities are independent of H_2 pressure (0–26.6 kPa H_2) on H-ZSM5, as also reported by others (24, 31, 42, 46, 52). The isotopic content in reaction products of $\text{C}_3\text{H}_8/\text{D}_2$ mixtures also shows that neither hydrogen (deuterium) dissociative adsorption nor recombinative desorption occurs readily on H-ZSM5. Hydrogen desorption steps are irreversible on H-ZSM5 and the surface is covered with protium (97%) from propane activation steps rather than deuterium atoms from the contacting gas phase. As a result, gas phase hydrogen species compete ineffectively for available surface sites with H species formed locally in C-H activation steps; the local surface concentration of hydrogen is high because of a recombinative desorption bottleneck.

On Zn/H-ZSM5, propane conversion turnover rates and aromatic selectivities decrease as H_2 pressure increases (0–26.6 kPa H_2), because adsorption–desorption sites provided by Zn cations allow gas phase hydrogen pressures to influence surface hydrogen concentrations and the rate of hydrogenation–dehydrogenation steps (Table 6). The presence of Zn species allows gas phase hydrogen to dissociatively adsorb and to effectively compete for surface sites, thus decreasing aromatics selectivity. Similar results were reported by Mole *et al.* (24) and Hagen *et al.* (31) on Zn/H-ZSM5, by Meitzner *et al.* (12) on Ga/H-ZSM5, and by Roessner *et al.* (41–42) on Pt/H-ZSM5, suggesting that all these metal cations play similar roles during propane conversion. As Zn cations increase the rate (and reversibility) of adsorption–desorption steps, surface hydrogen concentrations and the extent of dehydrogenation of adsorbed intermediates begin to reflect not only the rate at which hydrogen forms in C-H bond activation steps, but also the rate at which it is introduced into the surface via dissociative chemisorption steps involving H_2 in the gas phase.

TABLE 6

Propane Turnover Rates and Product Distribution on 1.07% Zn/H-ZSM5 [773 K, 26.6 kPa C_3H_8 , 0–26.6 kPa H_2 , balance He]

Gas phase hydrogen (H_2) (kPa)	0.0	16.6	26.6
Propane conversion (%)	5.7	5.7	5.7
Propane turnover rate (per Al, 10^{-3} s^{-1})	5.3	4.6	4.0
Aromatization site-time yield (per Al, 10^{-3} s^{-1})	1.6	1.2	0.7
<i>Carbon selectivity (%)</i>			
Methane	6.2	11.4	14.3
Ethene	14.4	13.7	10.3
Ethane	5.1	13.0	20.4
Propene	38.9	32.5	30.0
C_6+ aromatics	29.4	26.7	17.3
Benzene	14.1	12.9	9.3
Toluene	11.3	9.7	6.0
C_8+	4.0	4.1	2.0
<i>Hydrogen selectivity (%)</i>			
Hydrogen (H_2)	28.2	20.2	11.9

TABLE 7

Virtual Surface Pressures Calculated for H-ZSM5 and Zn/H-ZSM5 Determined from C₃H₈/D₂ Mixtures [773 K, 26.6 kPa C₃H₈, 6.7 kPa D₂, 68.0 kPa He, selectivities are at 7.6–8.3% propane conversion]

	Initial D% in products from C ₃ H ₈ /D ₂ data	Virtual surface from C ₃ H ₈ data	H ₂ selectivity from C ₃ H ₈ data	β -scission selectivity
H-ZSM5	0.03	220	4.6	63.7
0.62% Zn/H-ZSM5	0.13	50	25.2	37.9
1.07% Zn/H-ZSM5	0.22	30	29.0	28.1
1.30% Zn/H-ZSM5	0.33	20	31.0	24.9

Zn species act as “portholes” (68) for the desorption of H-atoms; as a result, they also increase the reverse reaction, the dissociative chemisorption of dihydrogen, as shown by the introduction of D atoms in the products of C₃H₈/D₂ mixtures. The presence of H₂ in the gas phase and of Zn sites to dissociate it causes Zn/H-ZSM5 to resemble H-ZSM5 catalytically as H₂ gas-phase pressures increase. In effect, H-ZSM5 has a high “virtual” hydrogen surface concentration (69, 70), imposed by its inability to remove the hydrogen formed in fast C-H bond activation elementary steps. As a result, products tend to be mostly saturated hydrocarbons on H-ZSM5. Ambient gas phase H₂ pressures are much lower than those that would be in equilibrium with this virtual surface concentration on H-ZSM5. As H₂ ambient pressures increase, the surface of Zn/H-ZSM5 also becomes hydrogen-rich and surface intermediates and gas phase products become increasingly saturated; they resemble those formed on hydrogen-rich H-ZSM5 surfaces. This virtual surface concentration of hydrogen can be calculated from C₃H₈/D₂ data (8). These data show that the hydrogen concentration on the surface of H-ZSM5 corresponds

to that in equilibrium with a H₂ pressure (220 kPa), much higher than that in the gas phase (6.6 kPa) (Table 7). When Zn is added, the virtual surface pressure decreases and gas phase and surface pools communicate more effectively, but they are still not equilibrated even on 1.30% Zn/H-ZSM5. This virtual surface concentration is inversely related to the hydrogen selectivity and aromatic selectivities during propane reactions (Fig. 14). The H-ZSM5 surface does not react with the gas phase hydrogen because it has such a high local concentration due to hydrogen desorption bottlenecks. As the gas phase H₂ concentration becomes similar in magnitude to this surface pressure, the effect of gas phase H₂ pressure begins to reduce propane conversion rates and aromatic selectivities.

4. CONCLUSIONS

Modifications of pentasil zeolites with exchanged Zn cations increase turnover rates, aromatic site-time yields, and the rate of hydrogen disposal during ethane, propane, and propene aromatization. The ratio of propene aromatization (r_2) to propene hydrogenation (r_{-1}) rates is higher on Zn-containing samples than on H-ZSM5, even though Zn cations increase the rate of dehydrogenation-hydrogenation steps (r_1 , r_{-1}). Zn cations not only catalyze alkane dehydrogenation (r_1), but also alkene conversion rates. This is not surprising because aromatization of alkenes (r_2) also requires dehydrogenation steps and forms H atoms that are removed by Zn cations.

These Zn cations increase the rates of alkane aromatization by increasing the rate of recombinative desorption of the hydrogen atoms formed in C-H activation steps. In effect, C-H bond activation steps that can occur reversibly, but unproductively, on acid site because of unfavorable reaction affinities become coupled with recombinative desorption on a separate site. These sites communicate with acid sites via rapid migration of H atoms from momentary adsorption sites in the vicinity of Bronsted acid sites to Lewis acids sites provided by the exchanged Zn cations. Hydrogen adsorption-desorption steps, however, remain irreversible (rate-determining) even on Zn/H-ZSM5 catalysts. This proposal is consistent with the rate of H₂/D₂ isotopic equilibration and with the predominant presence of

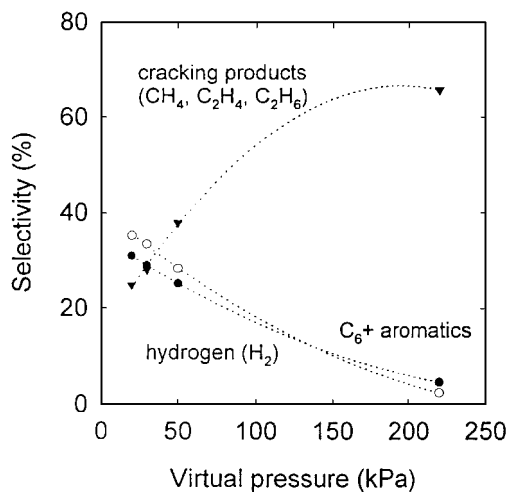


FIG. 14. Hydrogen, aromatics, and β -scission selectivities versus virtual pressure calculated for H-ZSM5 and Zn/H-ZSM5 [773 K, 26.6 kPa C₃H₈, 6.7 kPa D₂, 68.0 kPa He, selectivities are at 7.6–8.3% propane conversion].

protium among adsorbed species and reaction products of C_3H_8/D_2 mixtures on all catalysts.

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