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Hydrogen transfer and activation of propane and methane on ZSM5-based catalysts

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Hydrogen exchange between undeuterated and perdeuterated light alkanes (CD_4–C_3H_8, C_3D_8–C_3H_8) occurs on H-ZSM5 and on Ga- and Zn-exchanged H-ZSM5 at 773 K. Alkane conversion to aromatics occurs much more slowly because it is limited by rate of disposal of H-atoms formed in C–H scission steps and not by C–H bond activation. Kinetic coupling of these C–H activation steps with hydrogen transfer to acceptor sites (Ga^{n+}, Zn^{m+}) and ultimately to stoichiometric hydrogen acceptors (H^+, CO_2, O_2, CO) often increases alkane activation rates and the selectivity to unsaturated products. Reactions of $^{13}CH_4/C_3H_8$ mixtures at 773 K lead only to unlabelled alkane, alkene, and aromatic products, even though exchange between CD_4 and C_3H_8 occurs at these reaction conditions. This suggests that the non-oxidative conversion of CH_4 to higher hydrocarbons on solid acids is limited by elementary steps that occur after the initial activation of C–H bonds.

Keywords: Hydrogen transfer; light alkane reactions; deuterium cross-exchange reactions; alkane aromatization

1. Introduction

Recent studies suggest that electrophilic activation of light alkanes occurs on superacid catalysts [1] and on Hg-based organometallic complexes [2] at low temperatures, and on weaker solid acids at higher temperatures [3–9], apparently via heterolytic cleavage of C–H bonds or intermediate partial oxidation of methane to methanol. In contrast, oxidative coupling of light alkanes occurs predominantly on basic metal oxides and involves homolytic processes and gas phase alkyl radicals, in which the activation of C–H bonds limit overall oxidative coupling rates [10–12].

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Recently, we have shown that the rate of propane conversion to aromatics on H-ZSM5 is limited by the removal of H-atoms formed in required dehydrogenation steps [7–9]. The rate and aromatics selectivity increase when metal cations such as Ga^{n+} or Zn^{m+} catalyze the recombination of H-adatoms species to form H_2, a step that reverses heterolytic dissociation steps typical of reducible metal oxide catalysts. Here, we examine the details of the initial C–H activation step and the effect of molecular stoichiometric hydrogen acceptors (CO, CO_2, O_2) on the aromatization of light alkanes (C_3H_8, CH_4) catalyzed by H-ZSM5-based materials.

2. Experimental

Na-ZSM5 (Zeochem, $Si/Al = 14.5$) was converted to its protonic form by ammonium exchange and then impregnated with a gallium nitrate solution, dried at 373 K, and calcined at 623 K for 3 h [6]. This sample (2.0 wt% Ga) was reduced in flowing hydrogen at 823 K for 1 h before catalytic measurements. This treatment reduces Ga^{3+} species to Ga^{1+} and causes the migration of extracrystalline Ga_2O_3 to cation exchange sites within zeolite channels [9]. Zn-H-ZSM5 samples (2.8 wt% Zn) were prepared similarly using a solution of zinc nitrate [8,9]. Zn samples do not require a reductive hydrogen pretreatment because, in contrast with Ga, impregnation steps apparently distribute Zn ions directly onto intracrystalline cation exchange sites [9].

Catalytic measurements were performed in a gradientless recirculating batch reactor [13]. Reactants and products were analyzed by capillary chromatography using thermal conductivity, flame ionization, and mass spectrometric detection. Deuterium and ^{13}C distributions were obtained from electron-impact mass spectrometry by correcting for ion fragmentation, natural ^{13}C abundance and kinetic isotope effects [13,14].

Undeuterated propane (Air Products, 99.5%), perdeuterated propane (MSD Isotopes, 99.5% D) and methane (CD_4, MSD Isotopes, 99.6% D), $^{13}CH_4$ (ICON, 99% ^{13}C), $^{13}CO_2$ (Isotec, 99.995%, 99% ^{13}C), ^{13}CO (ICON, 99% ^{13}C), and O_2 (Matheson, 99.99%) were used as reactants without further purification. He (Arco, 99.99%) was purified using a molecular sieve cooled to liquid N_2 temperatures. Helium was used as a diluent to maintain total pressures near atmospheric values. Deuterium (Air Products, 99.99%) was used without further purification.

Reactant and product concentrations are reported as turnovers based on Al-atoms (mol/g-atom Al) for all catalysts. Turnover rates were obtained from the slope of turnover versus time plots. Selectivities are reported on a carbon basis as the percentage of converted reactants appearing as a given product.

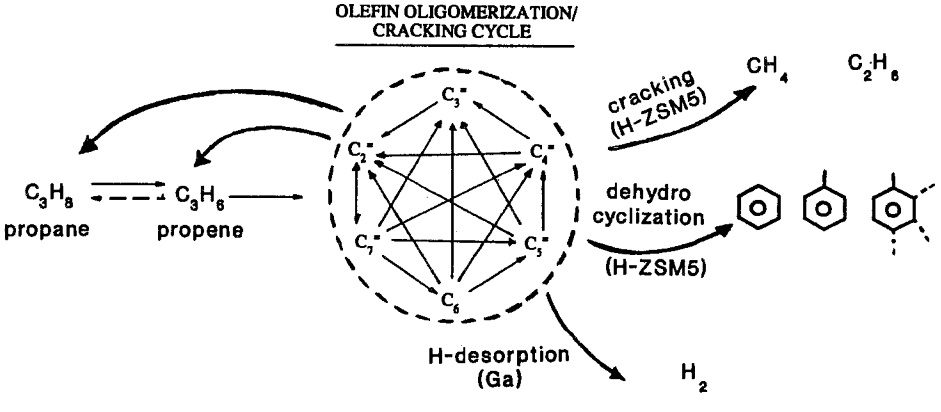
3. Results and discussion

3.1. PROPANE REACTIONS IN THE PRESENCE OF D_2

Deuterium (D_2) exchanges slowly with propane during its conversion to lighter hydrocarbons and C_6–C_8 aromatics on H-ZSM5. The deuterium fraction in unreacted propane increases linearly with contact time but remains below 3% even at 25–30% propane chemical conversion levels. In contrast, ^{13}C tracer studies of propane-2-^{13}C/propylene mixtures suggest that initial dehydrogenation steps in the reaction sequence are reversible. These reversible steps should lead to extensive deuterium incorporation into those propane molecules that have undergone a reversible dehydrogenation–hydrogenation cycle; in contrast, low levels of exchange are observed experimentally.

A study of the deuterium content in the reaction products reveals the underlying cause of this apparent contradiction. Previously, we reported that reactions of propane-2-^{13}C lead to products containing a random number of ^{13}C atoms, showing that every C–C bond is broken and reformed many times in the time required for a catalytic turnover [7–9]. This occurs in rapid oligomerization–cracking cycles involving the alkene products of the initial dehydrogenation steps (scheme 1). This process allows every C–H bond in each product to exchange extensively with the available surface pool of hydrogen adatoms. The deuterium content in the products then becomes a direct measure of the deuterium content in this surface hydrogen pool.

The deuterium fraction is between 0.025 and 0.038 and independent of propane conversion level in all products of propane reactions on H-ZSM5 (fig. 1). The distribution of D-atom isotopomers within each product obeys a binomial distribution, suggesting that multiple exchange events with a common surface hydrogen pool



Scheme 1. Reactions of propane on H-ZSM5-based catalysts [7–9].

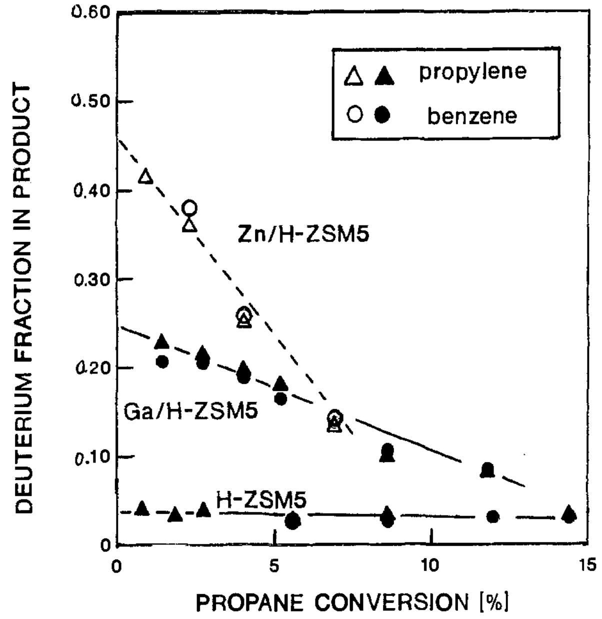


Fig. 1. Deuterium content in benzene product of C_3H_8/D_2 reactant mixtures (773 K, 27.6 kPa propane, 6.7 kPa D_2).

occur as an intrinsic process during one catalytic turnover. On H-ZSM5, this surface hydrogen pool contains 2.5–3.8% D and 96.2–97.5% H-atoms, not the 100% deuterium content expected from full equilibration with the pure D_2 gas phase. Most of the surface is covered by protium atoms formed in dehydrogenation steps; the removal of these protium atoms limits the overall rate of propane conversion to aromatics and prevents equilibration between surface and gas phase hydrogen pools. As a result, propane re-acquires H-atoms instead of D-atoms in most reversible dehydrogenation–hydrogenation steps, leading to slow exchange between C_3H_8 and D_2. On H-ZSM5, the predominant disposal pathway is the attachment of H-adatoms to hydrocarbon fragments, in steps that lower the selectivity to aromatics by forming predominantly methane and ethane, products that do not form readily in carbocation rearrangements because they require formation of primary ions. These hydrogen disposal pathways also maintain the surface free of deactivating deposits, possibly accounting for the unique stability of H-ZSM5 in many alkane conversion reactions.

Ga and Zn cations within zeolite channels can stabilize hydride ions formed in heterolytic dehydrogenation steps and catalyze the recombinative desorption of H-adatoms ($H^+ + H^-$) as H_2 [7–9]. As a result, hydrogen desorption–adsorption steps become increasingly reversible and the deuterium content in the surface pool and in the reaction products increases when such cations are present (fig. 1). For example, the deuterium fraction (extrapolated to zero conversion) in all propane reaction products is about 0.25 on Ga/H-ZSM5 and 0.45 on Zn/H-ZSM5, values much higher than those obtained on H-ZSM5 (0.025–0.038). The deuterium content decreases with increasing conversion because H_2 molecules form during C_3H_8 conversion on Ga- and Zn-containing catalysts and gradually dilute the initially pure D_2 gas phase.

Recombinative hydrogen desorption occurs faster when Ga or Zn cations are present and the overall reaction rate increases, but H-disposal is still rate-limiting, the deuterium fraction in products remains well below one, and the hydrogen pool surface still contains 55–75% protium atoms. Concurrent cracking steps are no longer required to remove most H-adatoms and the selectivity to C_6–C_8 aromatic products consequently increases. The results described below confirm these findings and explore the use of stoichiometric molecular hydrogen acceptors as potential scavengers in hydrogen disposal.

3.2. REACTIONS OF C_3H_8/C_3D_8 MIXTURES

Deuterium exchange studies using D_2 suggest that hydrogen disposal rather than C–H bond activation limits the overall rate of propane conversion. The cross-exchange of hydrogen and deuterium atoms between C_3H_8 and C_3D_8 allows the simultaneous measurement of C–H bond activation and propane conversion rates at reaction conditions.

Cross exchange between C_3H_8 and C_3D_8 occurs readily even at low chemical conversion levels (fig. 2), suggesting that C–H activation occurs much faster than propane conversion. Thus, the rate of C–H activation does not limit the rate of the overall chemical conversion of propane on H-ZSM5. The rate of C–H activation, measured from the rate of incorporation of D-atoms into C_3H_8 and of H-atoms into C_3D_8, is about 40 times higher than propane conversion rates (fig. 3). This value is obtained by extrapolating the data in fig. 3 to zero conversion. Undeuterated propane acquires D-atoms from C_3D_8 more rapidly than from D_2 because hydrogen adsorption–desorption steps required to dissociate D–D bonds on H-ZSM5 are slower than C–D bond activation in C_3D_8. 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 the mostly deuterated propane components of the distribution (fig. 2).

All chemical conversion products of C_3H_8/C_3D_8 mixtures contain similar deuterium fractions (0.436–0.463 D-fraction). These values are only slightly lower than the deuterium content in the reactant mixture (0.464), suggesting a very small H–D kinetic isotope effect in C–H bond activation steps ($k_d/k_h = 0.9$–1.0) at these high reaction temperatures. The deuterium isotopomer concentrations within each product obey binomial distributions (fig. 4) because all reaction products undergo extensive exchange with a common surface hydrogen pool in oligomerization–cracking sequences before desorbing.

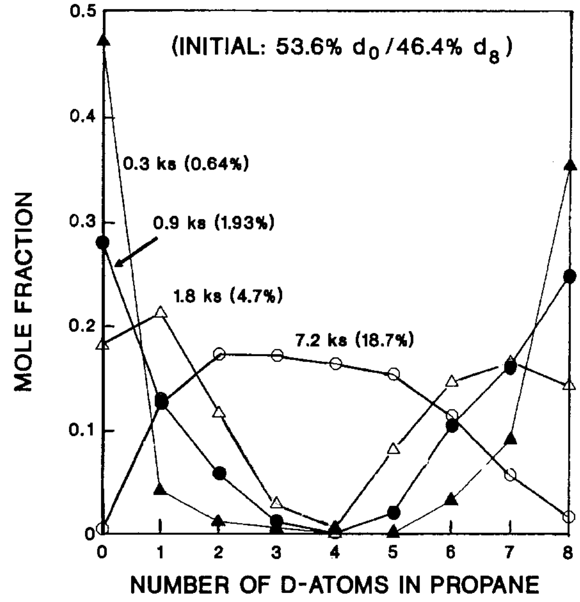


Fig. 2. Cross exchange of C_3H_8/C_3D_8 reactant mixtures on H-ZSM5. Deuterium distributions in unreacted propane (773 K, 3.56 kPa C_3H_8, 3.10 kPa C_3D_8, contact times in ks, % propane conversion within parentheses).

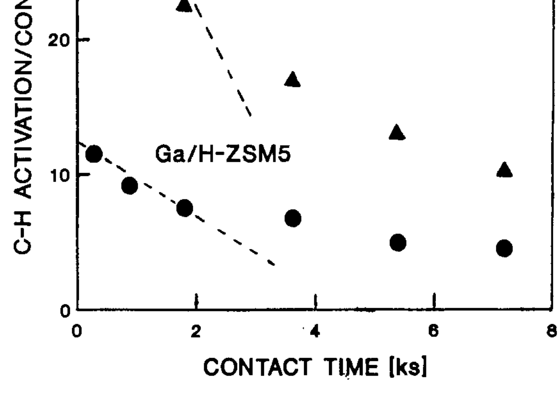


Fig. 3. Ratio of C–H bond activation rate (from cross exchange rates) to propane conversion rate (773 K, 3.56 kPa C_3H_8, 3.10 kPa C_3D_8).

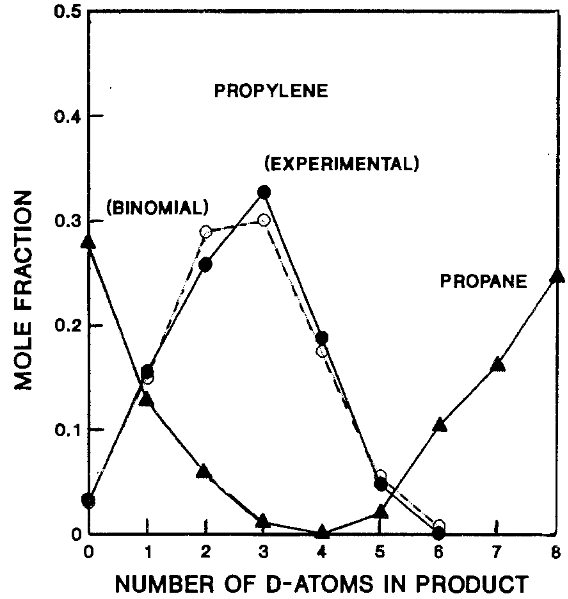


Fig. 4. Cross exchange of C_3H_8/C_3D_8 reactant mixtures on H-ZSM5. Deuterium distributions in unreacted propane and propylene product (773 K, 3.56 kPa C_3H_8, 3.10 kPa C_3D_8, 0.9 ks contact time, 1.9% chemical propane conversion).

The presence of Ga species within zeolite channels leads to much higher propane conversion rates and aromatics selectivity (fig. 5). Turnover rates for overall propane conversion increase by a factor of about three (fig. 5) and the C_6–C_8 aromatics selectivity increases by about a factor of four, leading to a ten-fold increase in the rate of formation of aromatic molecules from propane. Yet, C_3H_8–C_3D_8 exchange data show that C–H bond activation rates on H-ZSM5 are almost identical to those on Ga/H-ZSM5 (fig. 6). Thus, rate of C–H bond cleavage cannot limit the overall reaction rate, because Ga markedly increases the latter without increasing C–H bond activation rates.

The ratio of C–H activation to chemical conversion rates (extrapolated to zero conversion, fig. 3) is much lower on Ga-containing samples (~ 12 on Ga/H-ZSM5; ~ 40 on H-ZSM5). Ga sites catalyze rate-limiting hydrogen disposal steps by providing alternate recombinative desorption pathways unavailable on H-ZSM5; as this step, and the overall conversion rate, become faster, the net rate of other steps in the sequence becomes comparable to that of hydrogen desorption. This is the case for C–H propane bond activation of Ga/H-ZSM5, although C–H activation steps remain much faster than H-atom removal (~ 12 times, fig. 3) and hydrogen disposal is still the rate-limiting step in the overall propane conversion sequence on Ga/H-ZSM5, a conclusion confirmed by deuterium exchange studies using D_2.

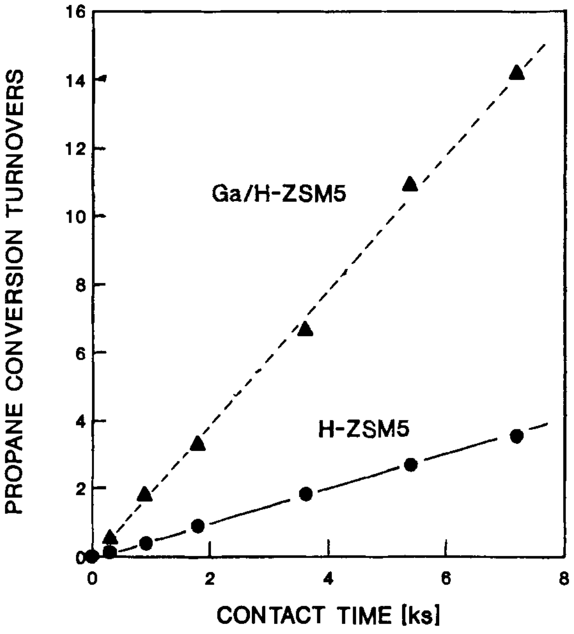


Fig. 5. Propane conversion turnovers versus contact time in recirculating batch reactor (773 K, 3.56 kPa C_3H_8, 3.10 kPa C_3D_8) (turnover rates given by slopes).

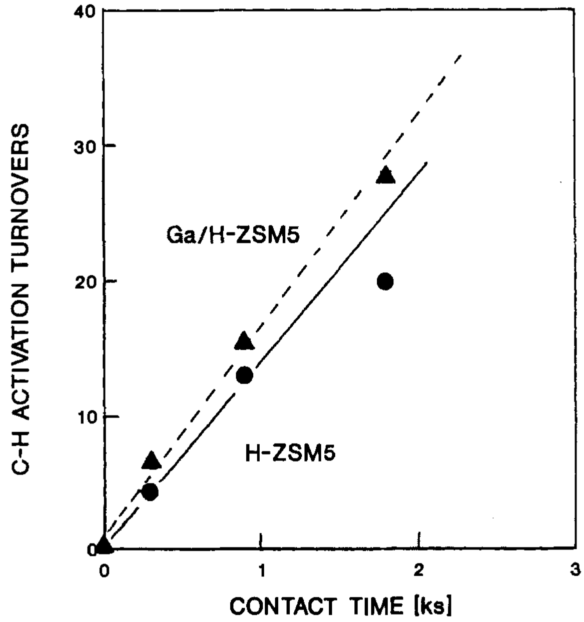


Fig. 6. C–H bond activation turnovers versus contact time in recirculating batch reactor (from cross exchange rates) (773 K, 3.56 kPa C_3H_8, 3.10 kPa C_3D_8) (turnover rates given by slope).

3.3. THE EFFECT OF MOLECULAR HYDROGEN ACCEPTORS ON REACTIONS OF PROPANE

If hydrogen disposal by recombinative desorption or hydrogen transfer to adsorbed hydrocarbons limits propane conversion rates and especially the selectivity to aromatic products, stoichiometric scavengers of such H-adatoms should enhance aromatics selectivity on H-ZSM5. Clearly, these pathways will require the presence of binding sites for such molecular hydrogen sinks. These hydrogen addition reactions would kinetically couple with the sequential dehydrogenation steps required for propane conversion to aromatics and relieve a bottleneck within the catalytic sequence. In some cases, they also could provide an additional thermodynamic incentive for the conversion of alkanes to unsaturated products. Ideally, the required hydrogen transfer processes should also lead to more valuable forms of the hydrogen acceptor, which is used here as a sacrificial reagent.

The presence of O_2, ^{13}CO, or $^{13}CO_2$ increases the selectivity of propane conversion to aromatics on H-ZSM5 (fig. 7). Small amounts of O_2 (1.6 kPa) increase the initial selectivity from near zero to 12–13% (fig. 7); O_2 is not, however, a selective hydrogen scavenger and also reacts with propane to form CO_2. Dioxygen is totally depleted from the reactant stream at 10–15% propane conversion; at higher conversions, propane reacts via non-oxidative pathways and the selectivity to aromatics begins to resemble that obtained using a pure propane feed (fig. 7). Aromatics selec-

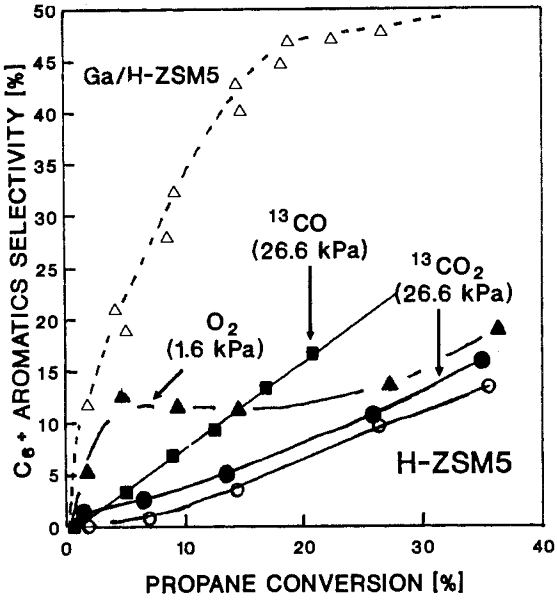


Fig. 7. The effects of ^{13}CO, $^{13}CO_2$, and O_2 on the selectivity to aromatics during propane conversion on H-ZSM5 (773 K, 26.6 kPa propane).

tivity increases with increasing conversion in all cases (fig. 7) because higher concentration of alkene intermediates favor chain growth and formation of the C_{6+} hydrocarbon backbones required for ring closure and aromatization (scheme 1). The propane conversion turnover rate is slightly lower when small amounts of O_2 are present in the alkane feed (fig. 8).

CO_2 increases the aromatics selectivity on H-ZSM5 (fig. 7) without any change in propane conversion turnover rates (fig. 8). Reactions of $^{13}CO_2$–C_3H_8 mixtures lead to the formation of ^{13}CO; hydrocarbon products, however, contained only natural abundance ^{13}C. Thus, the predominant reaction of CO_2 on H-ZSM5 is its hydrogenation using H-adatoms produced in sequential hydrocarbon dehydrogenation steps. Hydrogenation of the resulting low concentrations of CO to methane and higher hydrocarbons does not occur readily on H-ZSM5 at these reaction conditions. Turnover rates for hydrogenation of CO_2 to CO (1.4×10^{-4} s^{-1}) are much smaller than propane conversion turnover rates (4.2×10^{-3} s^{-1}) on H-ZSM5. As a result, the effect of CO_2 on propane conversion selectivity is small, because hydrogen removal by reaction of H-adatoms with oxygen atoms in CO_2 is slow compared with the dehydrogenation reactions that produce such hydrogen adatoms.

CO addition also increases aromatics selectivity during propane conversion on H-ZSM5 (fig. 7). Small amounts of ^{13}CO disappear from $^{13}CO/C_3H_8$ mixtures but the ^{13}C content in reaction products is very low (<0.2% in CH_4; 0.2–0.4% in

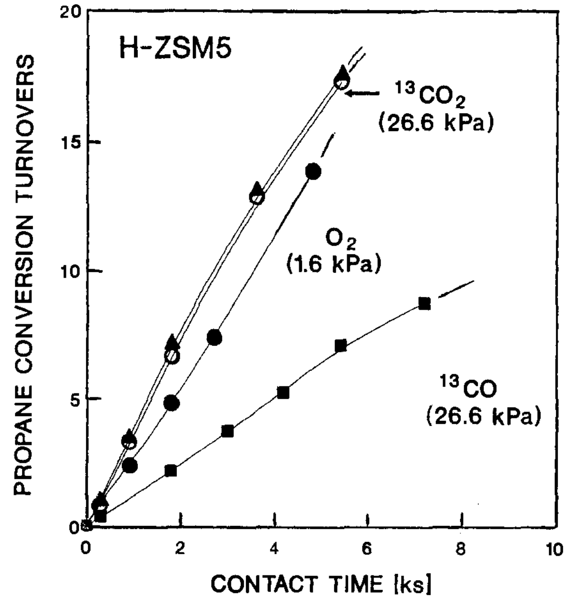


Fig. 8. The effects of ^{13}CO, $^{13}CO_2$, and O_2 on propane conversion turnover rates on H-ZSM5 (773 K, 26.6 kPa propane).

C_2H_4, C_2H_6 and 1-C_4H_8; 0.8–1.3% in benzene; 0.6–0.8% in toluene). Propane conversion turnover rates are lower when CO is present and carbon deposits form more readily than with pure propane feeds. The low activity persists in subsequent runs using pure propane as reactant; it reflects extensive deactivation that occurs during conversion of CO/propane mixtures rather than reversible inhibition of propane reactions by CO. When deactivated catalysts are treated with O_2 after reaction, significant amounts of $^{13}CO_2$ are formed, suggesting that the ^{13}CO component contributes to carbon deposition. These carbon deposits apparently account for the lower activity of H-ZSM materials in reactions of C_3H_8/CO mixtures. Propane carbonylation products form on HF–SbF_5 superacids at much lower temperatures [15] but are not detected on H-ZSM5 at 773 K because these molecules are thermodynamically unstable at these reaction conditions.

The observed low activity and carbon deposits, the low level of ^{13}C enrichment in hydrocarbons ($<1.5\%$ ^{13}C) and CO_2 products, and the promoting effect of CO on aromatics selectivity suggest that oxygen, as atoms or within undissociated CO, scavenges H-atoms formed in dehydrogenation steps, leaving behind carbonaceous deposits,

$$CO_{ads} + H_{ads} \rightarrow C_{ads} + OH_{ads} \xrightarrow{H_{ads}} C_{ads} + H_2O \tag{1}$$

$$CO_{ads} \rightarrow C_{ads}O_{ads} \tag{2}$$

$$O_{ads} + H_{ads} + \ldots H_{ads} \rightarrow H_2O\,, \tag{3}$$

thus increasing the selectivity to unsaturated products. A slight ^{13}C enrichment in the C_6–C_8 aromatic products (0.6–1.5%) suggests that carbon or highly dehydrogenated CH_x species formed from CO can participate in aromatics formation steps. The ^{13}C enrichment in lighter products (C_1–C_5) was much lower ($<0.4\%$) than in the aromatic fraction (0.6–1.3%).

Thus, CO acts as a stoichiometric hydrogen scavenger but without significant formation of gas phase carbon-containing products and without upgrading CO to more valuable products. A more effective pathway for H-atom removal is the hydrogenation of adsorbed CO to CH_4, a process that also improves the thermodynamics of dehydrogenation steps, but which does not occur on H-ZSM5 at our reaction conditions.

None of the molecular hydride acceptors used increased aromatics selectivity to the high values obtained on Ga- or Zn-promoted H-ZSM5 (fig. 7), suggesting that the surface density or reactivity of these adsorbed molecules is lower than that of reducible metal cations. NO also reacts with alkanes and alkenes on H-ZSM5 [16] and on Ga/H-ZSM5 [17] to form N_2 and H_2O; undoubtedly, these NO_x species also act as hydrogen acceptors and increase the rate of propane conversion to unsaturated products.

On H-ZSM5 promoted with Ga or Zn, ^{13}CO or $^{13}CO_2$ added to propane feeds also increased aromatics selectivity (Zn, fig. 9). As on H-ZSM5, $^{13}CO_2$ leads

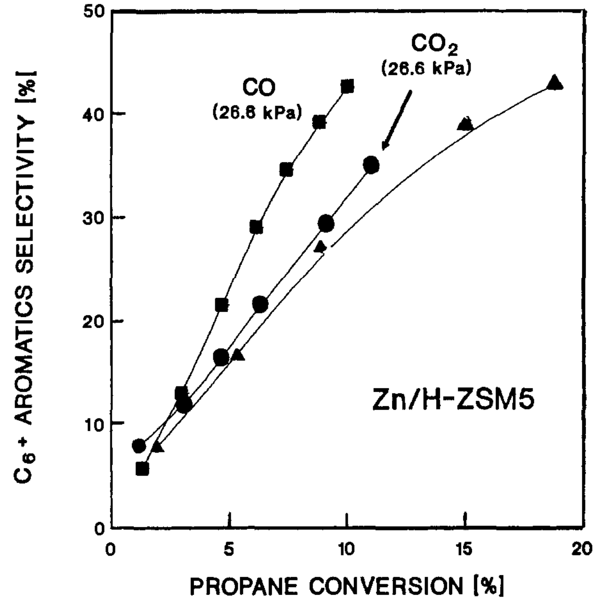


Fig. 9. The effects of ^{13}CO, $^{13}CO_2$, and O_2 on the selectivity to aromatics during propane conversion on 2.8 wt% Zn/H-ZSM5 (773 K, 26.6 kPa propane).

predominantly to ^{13}CO and H_2O, and ^{13}CO to surface carbon deposits and to less than 0.2% ^{13}C enrichment in reaction products. The aromatics selectivity enhancements are less marked than on H-ZSM5, as expected from the presence of Zn or Ga species, which already provide alternate and effective pathways for hydrogen removal as H_2.

Hydrogen acceptor species, whether molecules (CO_2, CO, O_2) or metal cations (Ga^{n+}, Zn^{m+}), increase the ethylene to ethane ratio in the C_2 products formed by concurrent cracking reactions of propane. These hydrogen acceptors also decrease the selectivity to methane during propane conversion. This suggests that the introduction of alternate H-disposal pathways removes the burden of hydrogen removal from H-addition and cracking steps that form light alkanes. The alternate pathways provided by hydride acceptor species lower the effective surface hydrogen pressure during propane reactions on H-ZSM5 and prevent hydrogenation and cracking, reactions that require H-adatom reactants [7,8].

3.4. REACTIONS OF C_3H_8/CD_4 MIXTURES

H-ZSM5 also activates C–H bonds in methane, but much more slowly than the weaker and more reactive C–H bonds in propane. Deuterium appears within the unreacted propane fraction in C_3H_8/CD_4 reactant mixtures (fig. 10). Exchange occurs by stepwise addition of D-atoms from a surface hydrogen pool that contains a mixture of D-atoms from CD_4 and H-atoms from C_3H_8. The D-atom fraction

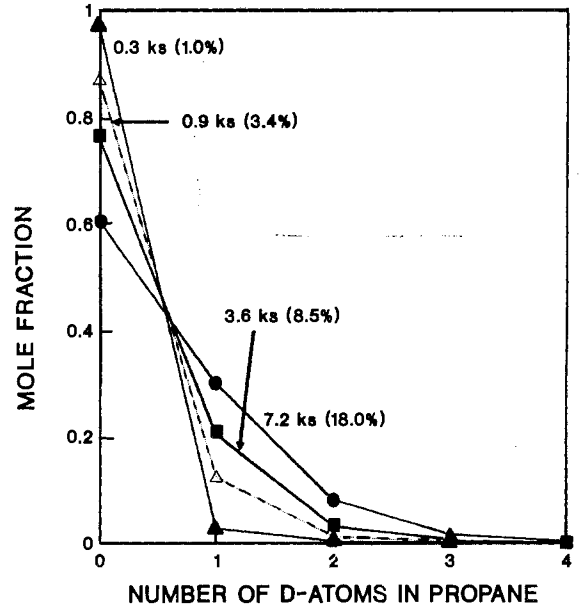


Fig. 10. Cross exchange of C_3H_8/CD_4 reactant mixtures on H-ZSM5. Deuterium distributions in unreacted propane (773 K, 6.66 kPa C_3H_8, 20.0 kPa CD_4, contact times in ks, chemical propane conversion levels in parentheses).

in propane increases linearly with contact time leading to a concurrent increase in the deuterium content of its products (fig. 11) and in the protium content of the methane co-reactant.

The deuterium content in reaction products is, however, higher than in propane (fig. 11). In all products (e.g., ethylene, ethane, propylene, benzene, toluene), the isotopic content is similar and their excess deuterium content (over that in propane) is independent of conversion on H-ZSM5 (fig. 11); also, isotopomer concentrations for each product obey a binomial distribution, suggesting that all products statistically sample the composition of a common surface hydrogen pool before desorption. The deuterium fraction within reaction products at short contact times (low propane conversions), where the propane reactant is totally undeuterated, is about 0.05 on H-ZSM5 (fig. 11), consistent with a surface pool containing about 5% D-atoms (from 20 kPa CD_4) and 95% H-atoms (from 6.66 kPa C_3H_8). Thus, the rate of C–H activation for methane in this reactant mixture is about 20 times slower than that of propane, a result that is unlikely to reflect a H–D kinetic isotope effect, in view of the small isotope effects reported above for C_3D_8–C_3H_8 mixtures. The relative C–H bond reactivity in methane becomes 30 times greater when C–H bond activation rates are normalized using the fraction of the available C–H(D) bonds contained within CH_4 and C_3H_8 molecules in the reactant mixture.

The details of similar studies on Ga/H-ZSM5 will be reported elsewhere. In con-

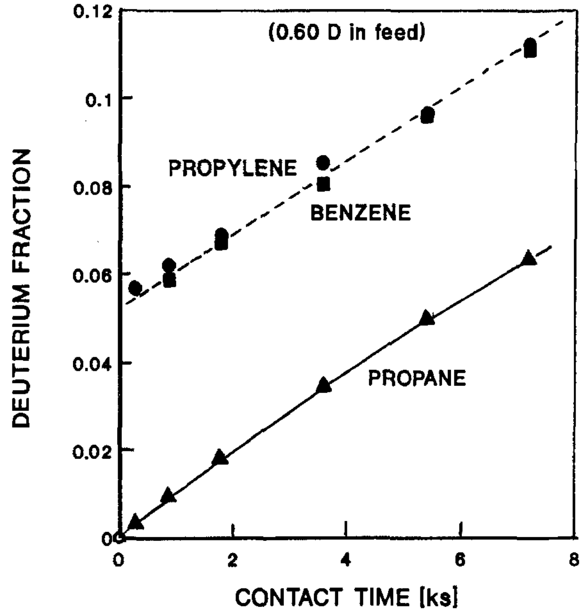


Fig. 11. Cross exchange of C_3H_8/CD_4 reactant mixtures on H-ZSM5. Deuterium content in unreacted propane and in propylene and benzene reaction products (773 K, 6.66 kPa C_3H_8, 20.0 kPa CD_4).

trast with H-ZSM5, the rate of C–H bond activation on Ga/H-ZSM5 is only about 4–5 times slower (~ 7 when normalized to the number of C–H bonds in each reactant) for methane than for propane (fig. 12, 18% D in products). This somewhat surprising result shows that factors other than C–H bond strength must be involved in heterolytic C–H bond dissociation of light alkanes on acidic materials. Clearly, the stability of the carbocation and of its hydridic H-atom counterpart also influences C–H bond activation rates.

The extreme thermodynamic instability of primary carbocations may well require that C–H bond activation in CH_4 proceed via pathways different from those involved in the activation of propane and larger alkanes, which can form more stable secondary and tertiary carbocations. In such alternate homolytic or heterolytic pathways, Ga cations may actually stabilize the neutral or negatively charged carbon-containing fragment of the C–H bond activation step, instead of the H^- species it apparently accommodates in propane conversion reactions. These alternate pathways, unavailable on H-ZSM5 and unnecessary for larger alkanes, may account for the disproportionate increase in the C–H bond reactivity of methane introduced by the presence of Ga cations within H-ZSM5 channels. Ga- and Zn-containing H-ZSM5 zeolites, however, remain unable to provide alkylation and chain growth pathways of the C–H activation products to form higher molecular weight hydrocarbons in non-oxidative reactions of methane.

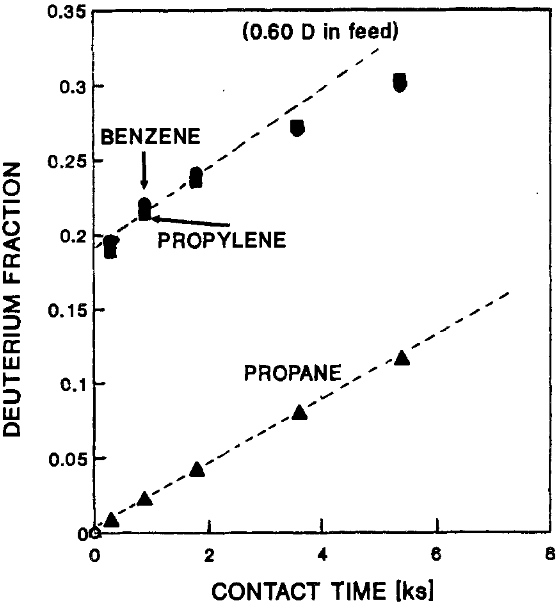


Fig. 12. Cross exchange of C_3H_8/CD_4 reactant mixtures on 2.0 wt% Ga/H-ZSM5. Deuterium content in unreacted propane and in propylene and benzene reaction products (773 K, 6.66 kPa C_3H_8, 20.0 kPa CD_4).

The products of $^{13}CH_4/C_3H_8$ (20.0 kPa, 6.67 kPa, 773 K) reactant mixtures on H-ZSM5, Ga/H-ZSM5, and Zn/H-ZSM5 are not labelled; about 5–10% ^{13}C enrichment should occur if relative conversion rates of the two reactants paralleled their relative C–H bond activation rates on these catalysts. The observed ^{13}C enrichment in reaction products is less than 0.5%. Clearly, the stability of C_1 carbocations precludes their presence at high surface concentrations on thermodynamic grounds. Their stability may increase or their involvement may become unnecessary when alkyl or hydride acceptor species such as Ga^{n+} provide thermodynamic sinks for the hydrogen or carbon fragments of the C–H bond activation step. This may explain why the relative reactivity of C–H bonds in methane compared to propane is higher on Ga/H-ZSM5 than on H-ZSM5.

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