Isotopic Tracer Studies of Thiophene Desulfurization Reactions Using Hydrogen from Alkanes on H-ZSM5 and Co/H-ZSM5

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Reaction pathways for the desulfurization of thiophene using alkanes as hydrogen sources were probed by measuring the chemical and isotopic composition of products formed from ^{13}C-labeled C_3H_8 and unlabeled C_4H_4S mixtures on H-ZSM5 and Co/H-ZSM5. Aliphatic hydrocarbons formed only from propane carbon atoms while aromatic molecules contained carbon atoms from both propane and thiophene. Hydrogen-deficient thiophene and thiophene-derived species react with surface hydrogen and alkenes formed from propane and desorb as unreactive aromatics, in steps that lead to the irreversible exit of alkenes from oligomerization-cracking cycles. These steps remove kinetic bottlenecks in thiophene desulfurization resulting from the irreversible formation of strongly adsorbed unsaturated species, which cannot desorb without reactions with hydrogen or hydrogen-rich surface species. This kinetic coupling between alkane and thiophene reactions leads to the observed concurrent increase in the rates of both propane aromatization and thiophene desulfurization compared with those achieved with each pure reactant. The scavenging of unsaturated intermediates formed via thiophene decomposition using hydrogen or hydrogen-rich intermediates formed from propane decreases the rate of bimolecular Diels–Alder reactions, which lead to larger organosulfur compounds and to low H_2S selectivity. As a result, H_2S selectivities are higher and deactivation rates are lower when propane is present as a co-reactant during reactions of thiophene. © 2001 Academic Press

Key Words: thiophene desulfurization; propane dehydrogenation; reaction pathways; H-ZSM5; Co/H-ZSM5.

INTRODUCTION

Recently, we showed that thiophene desulfurization rates increase significantly when coupled with propane dehydrogenation reactions on cation-modified H-ZSM5 (1, 2). Thiophene desulfurization occurs via reactions with alkenes and surface hydrogen species formed during propane dehydrogenation and not by reactions with the gas phase H_2 also formed during these reactions. The coupling of thiophene desulfurization and propane dehydrogenation reactions leads to the formation of sulfur-free hydrocarbons and H_2S.

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In the present study, we explore the reaction pathways involved in the coupling of propane and thiophene reactions by monitoring the chemical and isotopic composition of the products formed in reactions of ^{13}C-labeled propane ($2–^{13}C–C_3H_8$) and unlabeled thiophene on H-ZSM5 and Co/H-ZSM5. Isotopic tracer studies using ^{13}C-labeled and D-labeled reactants were previously used to establish the rate-determining steps in alkane dehydrogenation reactions on cation-modified H-ZSM5 (3, 4). Here, we probe the origin and the formation routes of the products of propane–thiophene mixtures and the effects of the thiophene co-reactant on propane dehydrogenation rates and selectivities. The ^{13}C-labeled propane and unlabeled thiophene used as reactants allow the identification of the carbon source used to form each product. Also, the ^{13}C isotopomer distribution in each product can be used to probe the formation routes and lifetimes of the adsorbed precursors used to form a specific product molecule. For example, the extent of intermolecular ^{13}C scrambling in products can be used to estimate the extent to which C–C bonds are made and broken while forming a given product, as well as the average residence time of alkene intermediates within oligomerization-cracking cycles occurring during propane dehydrocyclodimerization (4, 5). Finally, the effects of thiophene on the rate and selectivity for the formation of propene and aromatics can be used to establish any inhibition or promotion effects of thiophene on propane conversion reactions.

EXPERIMENTAL

Co/H-ZSM5 samples were prepared by aqueous exchange of H-ZSM5 (from exchange of Na-ZSM5; Zeochem, Si/Al = 14.5, with NH_4NO_3) using an aqueous solution of cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, Aldrich, 99%) at 353 K. The synthesis and characterization details of the H-ZSM5 and Co/H-ZSM5 samples were reported previously (6). The Co content (0.91% wt, Co/Al = 0.17) was measured by atomic absorption methods (Galbraith Laboratories, Inc.).

Catalytic reaction measurements were carried out in a glass recirculating batch reactor at 773 K. Recirculation

rates were greater than $4 \, cm^3 \, s^{-1}$ to ensure low propane conversions per pass ($<1\%$). Catalyst samples (~ 0.05 g) were treated in flowing air (Airgas, Grade Dry, $1.67 \, cm^3 \, s^{-1}$) for 1 h at 773 K before reaction at 773 K. C_4H_4S (Aldrich, 99%) and $2-^{13}C-C_3H_8$ (Isotec, 99.5%, 99% ^{13}C) partial pressures were 1 kPa and 20 kPa, respectively; helium was used as a diluent. Reactant and product concentrations were measured as a function of contact time by injecting a gas sample ($0.2 \, cm^3$) into a gas chromatograph (Hewlett–Packard 5890) equipped with a capillary column (Hewlett–Packard, HP-1 methyl–silicone column, 50 m, 0.32-mm diameter, 1.05-μm film thickness) and a flame ionization detector. The isotopic composition of reactants and products was measured by injecting a gas sample ($0.3 \, cm^3$) into a gas chromatograph (Hewlett–Packard 5890) equipped with a capillary column (same as above) and an electron-impact mass selective detector (Hewlett–Packard 5971).

The ^{13}C contents and the isotopomer distributions were determined for each product and for the unconverted reactants using mass spectrometric data and matrix deconvolution methods (7) that correct for fragmentation and ^{13}C natural abundance. Carbon selectivities of products formed from either propane or thiophene are reported as the percentage of the converted reactants (propane or thiophene) appearing as a given product. The fraction of the carbon in each product contributed by propane was calculated by dividing its ^{13}C fraction by that in propane (0.33). The carbon selectivities of the products (from propane and thiophene) were multiplied by the fraction of the carbon in each product contributed by propane and renormalized to obtain the carbon selectivities from propane. Batch reactor rate data are reported as turnovers (moles of propane or thiophene converted per g-atom Al) or site-yields (moles of propane appearing as a given product per g-atom Al) as a function of contact time. The site-yield for the formation of a given product from propane is calculated from the total site-yield for the formation of this product multiplied by the fraction of this product formed using carbon atoms from propane.

RESULTS AND DISCUSSION

^{13}C Content and Isotopomer Distribution of Reaction Products on H-ZSM5

Figure 1 shows the ^{13}C content in propene, ethene, and ethane molecules formed from $2-^{13}C-C_3H_8$/unlabeled C_4H_4S mixtures on H-ZSM5 at 773 K as a function of contact time. The ^{13}C fraction in propene remains at the value (0.33) of the propane reactant throughout. Thus, propene forms exclusively from propane at all contact times. It does not contain any carbon atoms from the thiophene co-reactant.

The isotopomer distribution in propene can identify possible routes for its formation. Direct dehydrogenation of propane ($2-^{13}C$–propane) would yield propene with

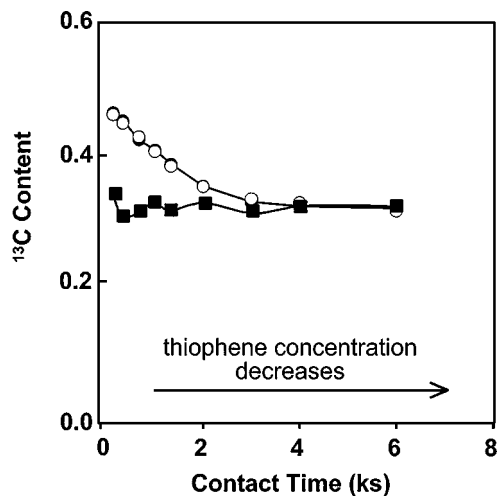**FIG. 1.** ^{13}C contents in propene (solid squares), ethene (solid circles), and ethane (open circles) versus contact time on H-ZSM5 (Si/Al = 14.5; 773 K; 20 kPa C_3H_8, 1 kPa C_4H_4S, balance He).

one ^{13}C atom at the methylene position. Propene molecules formed from alkene oligomerization-cracking cycles (Scheme 1) ultimately reach binomial isotopomer distributions, because rapid C–C bond breaking and making reactions within these cycles lead to intermolecular isotopic mixing. Propene molecules initially contain mostly one ^{13}C atom because they form directly via dehydrogenation of propane (Fig. 2a). As contact time increases, however, all propene isotopomers approach their binomial concentrations, as in the case of reactions of pure $2-^{13}C$–propane, indicating that they form in oligomerization-cracking cycles leading to intermolecular scrambling. Since propene forms after significant isotopic mixing in oligomerization-cracking cycles but contains no carbon atoms from thiophene, we conclude that alkenes within the cycle do not exit as alkenes after any reactions with thiophene. Instead, thiophene reactions with any alkenes formed from propane leads to their immediate and irreversible removal from this cycle as unreactive aromatic molecules (Scheme 1).

We define the approach to binomial as an isotopic fractional conversion, which evolves with contact time from the
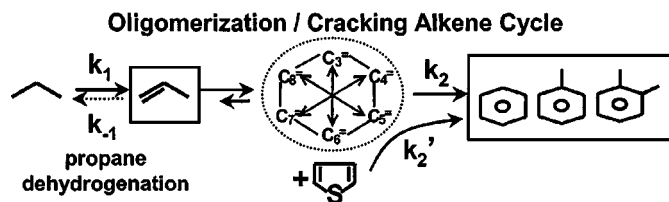
SCHEME 1. Schematic of propane–thiopene coupling reaction. Here k_1, k_2, and k_2' are rate constants of propane dehydrogenation to form propene, aromatics formation from alkene oligomerization-cracking cycles, and aromatics formation from thiopene-derived species, respectively.
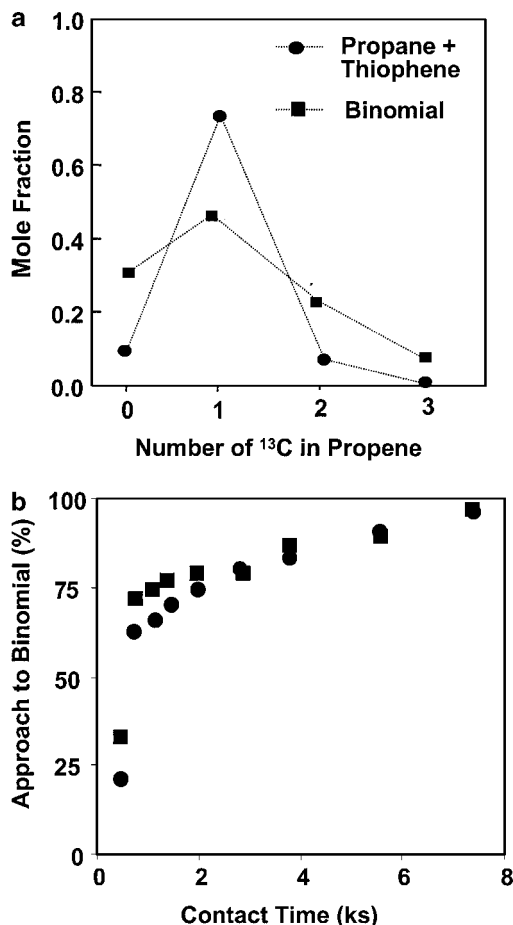
FIG. 2. (a) ^{13}C isotopomer distribution in propene on H-ZSM5 (contact time: 0.6 ks, propane conversion: 4.9%, thiophene conversion: 40.4%) in comparison with binomial distribution. (b) Approach to binomial distribution versus contact time during reactions of propane only (squares) and propane–thiophene (circles) (H-ZSM5; Si/Al = 14.5; 773 K; 20 kPa C_3H_8, 1 kPa C_4H_4S, balance He).

product expected from singly labeled 2–^{13}C–propane (0%) to one with a binomial distribution (100%):

$$X\% = \left[1 - \frac{\sum_i \left(a_i - a_i^b \right)^2}{\sum_i \left(a_i^0 - a_i^b \right)^2} \right] \times 100. \qquad [1]$$

Here, a_i^0, a_i, and a_i^b ($i = 0, 1, \ldots n$; n = total number of carbon atoms in the molecule) represent the mole fractions of isotopomers with i ^{13}C-atoms expected from unscrambled feed, measured during reaction, or calculated based on a binomial distribution, respectively. This isotopic conversion provides a measure of the reactive residence time of alkenes in the oligomerization-cracking cycle. A higher isotopic conversion indicates that alkenes reside longer or that reactions are faster within the cycle, leading to more extensive scrambling before forming stable aromatics.

For propene, the isotopic conversion increases and ultimately reaches 100% with increasing contact time (Fig. 2b),

as propene molecules increasingly form by the cracking of larger alkenes within the cycle instead of via direct dehydrogenation of propane. The isotopic conversion increases more slowly with contact time with propane–thiophene reactants than with pure propane. The intermolecular isotopic scrambling requires that propene molecules be formed in oligomerization-cracking cycles and return from such cycles as alkenes before irreversible aromatization steps. The less extensive isotopic scrambling observed in the presence of thiophene suggests that propene formation from oligomerization-cracking cycles is inhibited by the thiophene co-reactant, apparently because thiophene or thiophene-derived species react with alkenes or alkene-derived intermediates to form aromatics. As discussed below, carbon atoms are indeed present in the aromatic molecules formed from thiophene–propane mixtures, as expected from such reactions.

The ^{13}C fraction in ethene is ~0.5 at short contact times, because it initially forms only via primary cracking of 2–^{13}C–C_3H_8 isotopomers of propane. This ^{13}C fraction decreased to the value in the propane reactant (~0.33), with increasing contact time (Fig. 1). There are two possible routes to form ethene with 0.33 ^{13}C: cracking of scrambled propane molecules or formation of ethene via alkene oligomerization-cracking cycles. The first reaction requires propane molecules that have undergone at least intramolecular scrambling; the expected propane isotopomers were not detected at any contact time. The isotopic content of the C_2 mass fragments in unreacted propane is identical to that in the 2–^{13}C–C_3H_8 reactant, as discussed herein. Thus, it appears that ethene initially forms via cracking of propane and then enters oligomerization-cracking cycles as its concentration increases with increasing contact time. Often, it is converted to aromatics, but occasionally returns as ethene or larger alkenes via cracking of larger isotopically scrambled alkenes. As expected from this mechanism, the ethene formed at short contact times contains predominantly one ^{13}C atom, but the distribution approaches binomial at longer contact times. This also shows that, as in the case of propene, ethene molecules do not contain carbon atoms from thiophene.

The ^{13}C fraction and the isotopomer distribution in ethane resemble those in ethene at all contact times (Fig. 1). Thus, ethane appears to form only via secondary hydrogenation of ethene, using surface hydrogen species formed in C–H bond activation and alkene aromatization steps. Methane is essentially unlabeled at all contact times, as expected from its formation via cracking of propane molecules retaining their initial isotopic identity. Oligomerization-cracking reactions of alkenes do not produce CH_4, since such reactions would lead to a ^{13}C fraction of ~0.33 in CH_4.

All butenes show ^{13}C fractions (~0.33) (Fig. 3) similar to those in the 2–^{13}C–C_3H_8 reactant, suggesting that
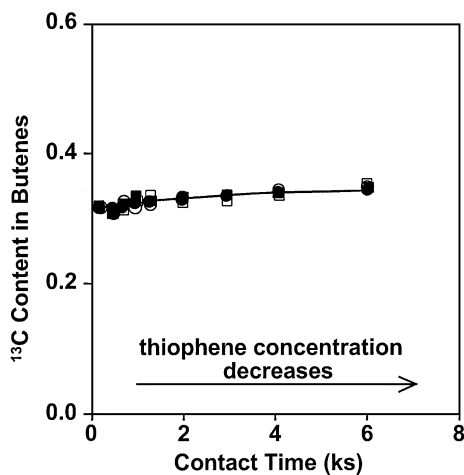
FIG. 3. ^{13}C contents in isobutene and 1-butene (triangles), *cis*-2-butene (circles), and *trans*-2-butene (squares) on H-ZSM5 versus contact time (Si/Al = 14.5; 773 K; 20 kPa C_3H_8, 1 kPa C_4H_4S, balance He).

butenes form only from propane-derived intermediates, without detectable contributions from carbon atoms in thiophene. The butene isotopomer distributions are binomial at all contact times for all butene isomers. Thus, butene isomers form after many oligomerization-cracking events, but without contribution from thiophene fragments, confirming that thiophene-derived intermediates do not participate in oligomerization-cracking reactions. Instead, such intermediates appear to scavenge the alkenes or alkene-derived intermediates and remove them from such cycles via irreversible reactions leading to stable aromatics.

These scavenging reactions of thiophene appear to require intermediates also involved in thiophene decomposition reactions on H-ZSM5 and not independent pathways occurring in parallel with the decomposition reaction. This is confirmed by the faster deactivation observed during thiophene decomposition (in the absence of a hydrogen source) than during propane–thiophene reactions on both H-ZSM5 and Co/H-ZSM5 (Table 1). If reaction, and deactivation, pathways during thiophene decomposition remained unaffected by propane, they would form the deactivating species at rates also unaffected by the propane

TABLE 1

Thiophene Desulfurization Deactivation Rate Constants (h^{-1}) during Reactions of Pure Thiophene and of Propane–Thiophene Mixtures on H-ZSM5 and Co/H-ZSM5

H-ZSM5		Co/H-ZSM5	
C_4H_4S	C_3H_8–C_4H_4S	C_4H_4S	C_3H_8–C_4H_4S
0.18	0.03	0.49	0.02

Note. Si/Al = 14.5; Co/Al = 0.17; 773 K; 0 or 20 kPa C_3H_8; 1 kPa C_4H_4S, balance He.

TABLE 2

Benzothiophene Formation Rates (per Al, 10^{-3}, s^{-1}) during Reactions of Thiophene Only and Propane–Thiophene Mixtures on Co/H-ZSM5

Benzothiophene formation rates (per Al, 10^{-3}, s^{-1})	
C_4H_4S	C_3H_8–C_4H_4S
0.15	0.045
(15.3%)	(27.9%)

Note. Si/Al = 14.5, Co/Al = 0.17; 773 K; 0 or 20 kPa C_3H_8, 1 kPa C_4H_4S, balance He. Thiophene conversion is reported in parentheses.

co-reactant. It appears that alkenes and adsorbed hydrogen species formed from propane scavenge the hydrogen-deficient products formed via thiophene decomposition by providing enough hydrogen to allow them to desorb as stable aromatic hydrocarbons. Also, benzothiophene, a product of bimolecular Diels–Alder-type reactions of thiophene, forms at much lower rates when propane is present as a co-reactant (Table 2), because these reactions also appear to involve dehydrogenated intermediates formed by thiophene decomposition and are more abundant in the absence of a hydrogen source.

On H-ZSM5, desulfurized thiophene fragments are expected to be highly unsaturated and unable to desorb as stable gas phase molecules without a source of hydrogen. This hydrogen can be provided directly by surface hydrogen species formed during dehydrogenation of propane. Alkenes can also act as hydrogen transfer agents, because they contain a sufficient number of hydrogen atoms to convert thiophene-derived fragments (e.g., di-alkynes C_4H_2) into aromatics. No butene products are formed during reactions of thiophene–He or thiophene–H_2 mixtures on H-ZSM5, which form predominantly aromatics and organosulfur compounds (e.g., methylthiophene, benzothiophene). Hydrogenation of desulfurized C_4 thiophene fragments would be expected to form C_4 molecules, but these fragments appear to react instead with other thiophene molecules or with thiophene-derived intermediates to form aromatics and larger organosulfur compounds on H-ZSM5.

The ^{13}C fraction is similar in all C_6–C_8 aromatic products (benzene, toluene, and xylenes) and significantly lower than in the propane reactant, especially at short contact times (Fig. 4). Thus, C_6–C_8 aromatic molecules contain carbon atoms from both propane and thiophene at all contact times. Their ^{13}C fractions increase with increasing contact time and they approach 0.33 as thiophene co-reactants are depleted more rapidly than propane with increasing contact time. The similar ^{13}C content in all the aromatics (Fig. 4) suggests that all aromatics form via similar pathways from a common pool of adsorbed intermediates.
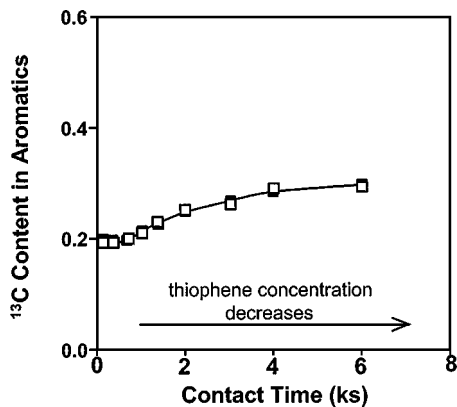
FIG. 4. ^{13}C contents in benzene (open squares) and toluene (solid squares) during propane–thiophene reactions on H-ZSM5 versus contact time (Si/Al = 14.5; 773 K; 20 kPa C_3H_8, 1 kPa C_4H_4S, balance He).

During reactions of pure propane, C_{6+} aromatics form via cyclization and dehydrogenation of C_{6+} alkenes. These steps extract alkenes irreversibly from oligomerization-cracking cycles (4, 5, 8–10). The approach to binomial for aromatic isotopomers, defined earlier as the isotopic conversion (Eq. [1]), increases as the residence time of reactive alkenes within this oligomerization-cracking cycle increases (8). Thus, the role of thiophene-derived alkene scavengers can be assessed by comparing the isotopic conversion of aromatic molecules formed from propane with those formed from propane–thiophene mixtures. On H-ZSM5, pure propane reactants produce binomial ^{13}C distributions in all aromatics as a result of the slow exit of alkenes from the cycle (8). During propane–thiophene reactions, C_{6+} aromatics (benzene, toluene, and xylenes) isotopomers with one ^{13}C exceed their expected binomial concentration. The toluene isotopomer distribution is shown in Fig. 5a. This initial excess of singly labeled toluene molecules reflects the reactions of thiophene-derived fragments with alkenes, before alkenes mix isotopically within oligomerization-cracking cycles. With increasing contact time, toluene isotopomers approach a binomial distribution as the alkene pool reaches a binomial isotopomer distribution and as thiophene is depleted and its alkene scavenging reactions slow down (Fig. 5b). The approach to binomial is slower (isotopic conversion is lower) for propane–thiophene mixtures than for pure propane (Fig. 5b), as expected if thiophene-derived species scavenged alkene or alkene-derived intermediates before significant intermolecular isotopic scrambling.

Therefore, it appears that thiophene increases the exit rate of alkenes from the cycle relative to their entry step via propane dehydrogenation (k_2 and k_2' in Scheme 1) by scavenging hydrogen and alkenes formed from propane. In this manner, thiophene decreases the average residence time of alkenes in the cycle. The decrease in alkene residence times caused by the thiophene co-reactant resembles that

observed when H-ZSM5 is modified by cations (Fig. 5b). Cations also increase the exit rate of alkenes from the cycle by desorbing surface hydrogens as H_2 and increasing in this manner the rate of alkene conversion to stable aromatic products (4).

Thus, the nature of propane conversion steps appears to be unaffected by the presence of thiophene, but alkenes leave the oligomerization-cracking cycle more rapidly when thiophene is present as a co-reactant. It would then be expected that the formation rate of alkenes from propane would be lower and the aromatics formation rates from propane would be higher with thiophene co-reactants. Such trends are indeed observed and will be described below (Table 3).

The ^{13}C distribution in the "unreacted" propane during propane–thiophene reactions indicates that propane remains mostly as $2-^{13}C-C_3H_8$. This was established by analyzing the ^{13}C content in the C_2 mass fragments from propane, which remains almost identical to that in the reactant. These C_2 fragments contained one ^{13}C, instead of
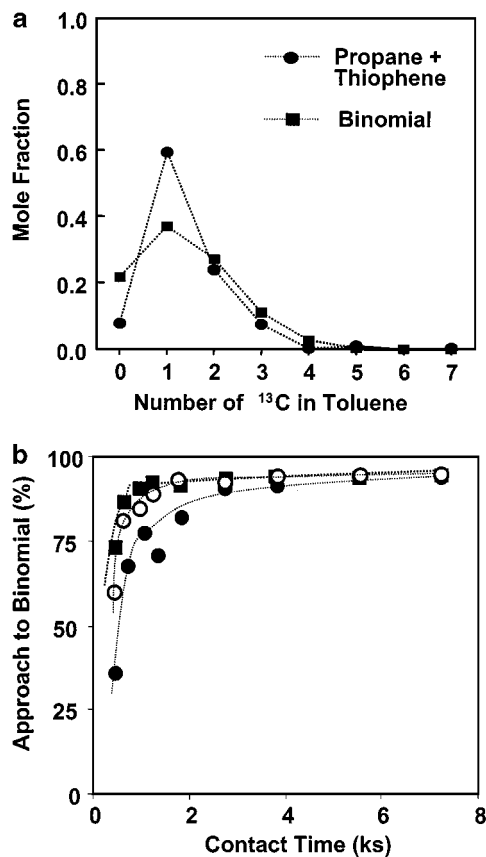

FIG. 5. (a) ^{13}C distribution in toluene on H-ZSM5 (contact time: 0.6 ks, propane conversion: 4.9%, thiophene conversion: 40.4%) in comparison with binomial distribution. (b) Approach to binomial distribution versus contact time during reactions of propane only on H-ZSM5 (solid squares), propane only on Co/H-ZSM5 (open circles), and propane–thiophene on H-ZSM5 (solid circles) (H-ZSM5; Si/Al = 14.5; 773 K; 20 kPa C_3H_8, 1 kPa C_4H_4S, balance He).

TABLE 3

Propane Turnover Rates and Product Site-Time Yields from Propane during Reactions of Propane Only and Propane–Thiophene Mixtures on H-ZSM5 and Co/H-ZSM5

Turnover rate or site-time yield (per Al, 10^{-3}, s^{-1})	H-ZSM5		Co/H-ZSM5	
	C_3H_8	C_3H_8–C_4H_4S	C_3H_8	C_3H_8–C_4H_4S
Propane	1.32	0.76	4.85	1.93
Methane	0.23	0.18	0.26	0.19
Ethene	0.45	0.19	0.62	0.22
Ethane	0.06	0.04	0.15	0.12
Propene	0.53	0.17	3.11	0.83
Butenes	0.04	0.03	0.18	0.15
C_6–C_8 Aromatics	0.03	0.12	0.41	0.43

Note. Si/Al = 14.5, Co/Al = 0.17; 773 K; 20 kPa C_3H_8, 1 kPa C_4H_4S, balance He; C_3H_8 conversion = $\sim$2%.

the mixture of all isotopomers expected if intramolecular or intermolecular scrambling had occurred. Since the scrambled propane isotopomers would form via the reverse step of propane dehydrogenation, the lack of carbon scrambling in propane indicates that propane dehydrogenation to propene is essentially an irreversible step when thiophene is present. A similar analysis of propane, during reactions of pure 2–^{13}C–C_3H_8, shows that the concentration of propane isotopomers other than 2–^{13}C–C_3H_8 increases with increasing propane conversion. This leads us to conclude that thiophene scavenges propene-derived intermediates and the hydrogens required for propene hydrogenation steps. Thus, thiophene decreases the rate of propene hydrogenation to form propane (k_{-1}) or increases the rate of propene conversion to aromatics (k_2') (Scheme 1), or both.

Thiophene remains essentially unlabeled, indicating that carbon atoms in thiophene do not exchange with species formed from propane (Fig. 6). The ^{13}C fractions in 2-methylthiophene and 3-methylthiophene increased with increasing contact time, and they reached values of $\sim$0.067 (Fig. 6). This is the value expected if a single carbon atom (in the methyl group) came from propane with the expected 33% probability of carrying the isotopic label. This suggests that methylthiophenes form via alkylation of thiophene with propane-derived and isotopically scrambled intermediates, followed by β-scission of alkyl branches to retain methyl groups. Surprisingly, benzothiophene contains 7–9% ^{13}C (Fig. 6), suggesting that it is not formed exclusively via bimolecular Diels–Alder reactions of thiophene (11). Instead, it appears that only about 50% forms via this route, which would form only unlabeled products; the remaining benzothiophene forms in alkylation reactions similar to those leading to methylthiophenes, but with cyclization instead of β-scission of the C_{5+} alkyl branches. Such a route would lead to an equal number of carbon atoms from propane and thiophene in each benzothiophene molecule and to a ^{13}C content of 16.7%. This alkylation

route accounts for $\sim$50% of the benzothiophenes formed. Yet, benzothiophene selectivities are still much lower for thiophene–propane mixtures than for pure thiophene reactants (1, 2). Benzothiophene formation rates during reactions of pure thiophene and during reactions of propane–thiophene mixtures on Co/H-ZSM5, at roughly similar remaining thiophene concentrations, are shown in Table 2. Benzothiophene formation rates are much lower when propane is present, indicating that propane co-reactants markedly decrease the rate of bimolecular Diels–Alder reactions of thiophene by providing abundant alkene and hydrogen adsorbed species that scavenge thiophene-derived species to form aromatics products. These reactions decrease the probability that such species react with thiophene to form larger organosulfur compounds and hydrogen-deficient deactivating residues.

^{13}C Content and Isotopomer Distribution of Reaction Products on Co/H-ZSM5

The ^{13}C fractions and isotopomer distributions in the products formed from 2–^{13}C–propane–thiophene mixtures on Co/H-ZSM5 resemble those obtained on H-ZSM5. Aliphatic hydrocarbons form only from propane, whereas aromatics contain carbon atoms from both propane and thiophene. Alkenes are formed via scission of larger hydrocarbons in oligomerization-cracking cycles as contact time increases, ultimately leading to binomial isotopomer distributions. Thiophene-derived species do not form alkenes, and aromatics appear to form via reactions of alkenes with thiophene-derived species. These results suggest that Co cations do not introduce alternate pathways in propane–thiophene reactions. These results are consistent with our previous finding that the effects of cations on
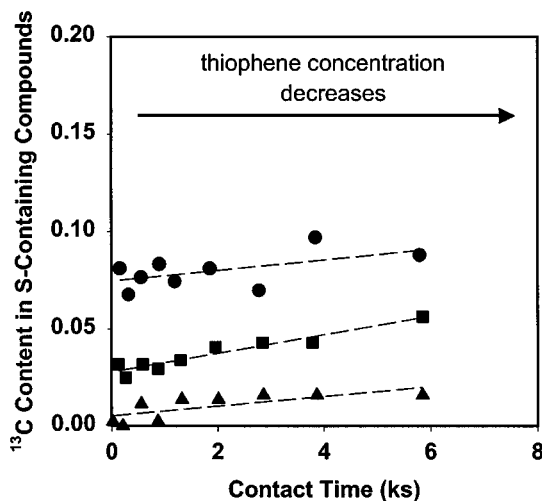

FIG. 6. ^{13}C contents in thiophene (triangles), methylthiophenes (squares), and benzothiophene (circles) on H-ZSM5 versus contact time (Si/Al = 14.5; 773 K; 20 kPa C_3H_8, 1 kPa C_4H_4S, balance He).

thiophene–propane reactions are much weaker than previously found for reactions of pure propane reactants (1).

Reaction Rates and Selectivities on H-ZSM5 and Co/H-ZSM5

The effects of thiophene on the rate of formation and the selectivity of individual hydrocarbons from the propane molecules in the propane–thiophene feed are examined in order to explore how thiophene influences propane dehydrogenation pathways on H-ZSM5 and Co/H-ZSM5.

The rate at which any product is formed from propane can be obtained from the ^{13}C fraction in that product, after accounting for the isotopic purity of propane. Site-time yields (molecules of propane appearing as a given product per Al site per second) for each product formed from propane are shown in Table 3 (at 2% propane conversion) and compared with those obtained with pure propane. Propane conversion turnover rates on both H-ZSM5 and Co/H-ZSM5 are much lower when thiophene is present. Methane site-time yields, which reflect the rate of acid-catalyzed primary cracking of propane, are also lower for propane–thiophene reactants. This suggests that thiophene inhibits the rate of acid-catalyzed reactions, via either competitive adsorption or irreversible titration, on H-ZSM5. Ethene and propene site-time yields also decrease when thiophene is added, but at least some of this decrease reflects their faster conversion to aromatics in the presence of thiophene. This latter reaction leads to much higher C_6–C_8 aromatics site-yields on H-ZSM5 (and slightly higher on Co/H-ZSM5) when thiophene is present. These data suggest that thiophene or thiophene-derived species increase aromatics formation rates at the expense of alkenes, by scavenging either alkenes or surface hydrogen species, both of which would increase the rate at which alkenes exit oligomerization-cracking cycles to form aromatics (k_2 and k_2' in Scheme 1).

The fraction of the carbon atoms in propane appearing as a given product reflects the carbon selectivity from the propane co-reactant. It can be calculated from the isotopic content of each reaction product. Figure 7a compares the aromatics selectivities from propane during propane–thiophene reactions with those obtained with pure propane on H-ZSM5. Aromatics selectivities are higher when thiophene is present, consistent with the scavenging of hydrogen or alkene species by thiophene. Figure 7b compares the ratio of aromatics to propene formed from propane during propane and propane–thiophene reactions. These ratios are higher when thiophene is present, indicating that more aromatics and fewer alkenes are formed. This is consistent with the scavenging of alkene species by thiophene, which increases the formation of aromatics and decreases the formation of alkenes, giving a higher ratio when thiophene is present than when only propane is present (Fig. 7b).
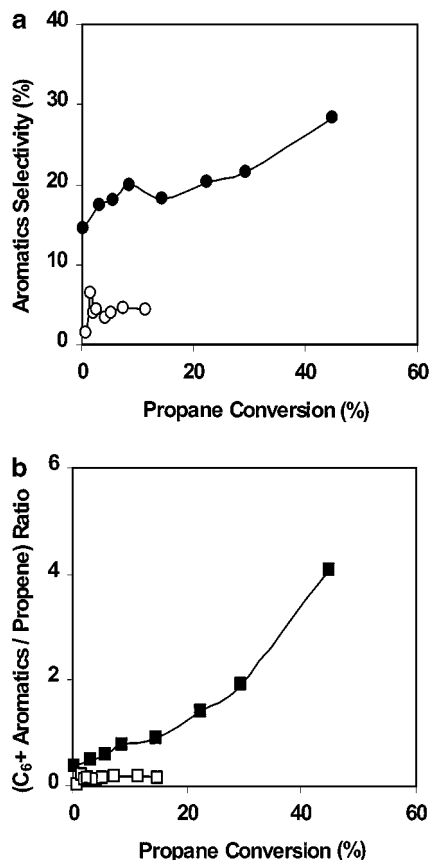

FIG. 7. (a) C_6–C_8 aromatics selectivity from propane during reactions of propane only (open circles) and propane–thiophene (solid circles). (b) Ratio of (C_{6+} aromatics/propene) during reactions of propane only (open squares) and propane–thiophene (solid squares) (H-ZSM5; 773 K; 20 kPa C_3H_8, 1 kPa C_4H_4S, balance He).

The total rate of propane dehydrogenation, given by the sum of the site-time yields for alkenes and aromatics, is lower when thiophene is present as a co-reactant (Table 3). It appears that thiophene inhibits the ability of exchanged Co cations to catalyze propane dehydrogenation steps, a role previously ascribed to their ability to desorb hydrogen as H_2. Since the overall reaction occurs via the sequential pathways in Scheme 1, the total dehydrogenation rate reflects the value of the rate constant k_1 shown in this Scheme.

The presence of thiophene inhibits both acid and metal functions in Co/H-ZSM5. Yet, interactions between thiophene with acid sites or metal cations were not detected by *in situ* infrared measurements during reaction on either H-ZSM5 or Co/H-ZSM5 (12). Similarly, no changes in the structure of Co cations were detected by X-ray absorption spectroscopy during reaction (12). Therefore, the inhibiting behavior of thiophene remains unclear. Any inhibition effects caused by oligomerized thiophene-derived species that block acid sites would have been detectable from their effect on the acidic OH infrared band during reaction. Similar effects on Co cations would have led to changes in the

local coordination detectable from near-edge or fine structure analysis of X-ray absorption spectra (12). Only the blockage of zeolite channels would lead to loss of accessibility of both cations and acid sites as deactivation proceeds. Such processes often arise because of the lack of spatial constraints around cation and acid sites present at external H-ZSM5 surfaces (13–15).

Molecular simulations suggest that thiophene decomposition on Brønsted acid sites form H_2S and unstable adsorbed butadiyne species in the absence of a hydrogen source, such as H_2 (16). Butadiyne species are strongly adsorbed and they can only desorb via reactions with another thiophene molecule to form benzothiophene or by the sacrificial use of hydrogen from another adsorbed unsaturated intermediate. The introduction of surface hydrogen species and hydrogen-rich intermediates, such as those available during alkane reactions, would lead to the conversion of butadiyne to adsorbed species with sufficient hydrogen to desorb as stable aromatics.

The effectiveness of alkene and hydrogen species formed from propane and hydrogen species formed from H_2 in the conversion of thiophene-derived fragments to aromatics are compared in Table 4. Table 4 shows the carbon selectivities for the products formed on Co/H-ZSM5 *from the thiophene component* in ^{13}C–C_3H_8/C_4H_4S and H_2/C_4H_4S reactant mixtures. The selectivity for thiophene conversion to aromatics (benzene, toluene, and xylene) is higher when propane is used as the hydrogen source, apparently because alkenes and hydrogen species formed from propane (at 20 kPa) are more effective in the conversion of butadiyne species to aromatics than hydrogen species formed from H_2 (at 25 kPa). The selectivity to benzothiophene with propane co-reactants is lower than with H_2 as the hydrogen source, consistent with the more effective scavenging of thiophene-derived species stranded on surfaces and available for bimolecular Diels–Alder reactions with another thiophene. Cracking products (methane, ethene, ethane, and propene)

formed from the thiophene component in H_2/C_4H_4S mixtures but not in C_3H_8/C_4H_4S mixtures. It appears that when H_2 is present, hydrogen surface species hydrogenate butadiyne species to species with sufficient hydrogen to undergo productive β-scission reactions. The resulting low concentrations of alkenes leads to ineffective chain growth and low concentrations of C_6–C_9 chains capable of dehydrocyclization reactions. The higher concentrations of alkenes when propane is present lead to effective chain growth and much higher aromatization rates for thiophene-derived intermediates. Thus, propane is more effective than H_2 at converting thiophene via chain growth and dehydrocyclization reactions to desired aromatic products. Propane provides the hydrogen atoms, either as adsorbed species or as hydrogen-rich alkenes, required to convert butadiyne to desorbable and stable aromatics. Therefore, the propane–thiophene coupling reaction removes sulfur from the thiophene molecule selectively as H_2S while dehydrogenating the propane molecule and forming aromatics. In addition, deactivation is inhibited because reactions of propane with stranded thiophene fragments allows their desorption; as a result, stoichiometric reactions become catalytic by the regeneration of the active sites required for thiophene decomposition reactions.

CONCLUSIONS

Propane–thiophene reactions on H-ZSM5 and Co/H-ZSM5 lead to the formation of aliphatic products (methane, ethene, ethane, propene, and butenes) exclusively from propane. In contrast, aromatic products (benzene, toluene, and xylenes) contain carbon atoms from both propane and thiophene. Thiophene-derived species do not contribute to the formation of alkenes because they do not enter into alkene oligomerization-cracking cycles. Instead, they react with alkenes to form aromatics, which in contrast with the butadiyne formed via thiophene decomposition, desorb as stable products. Alkene and hydrogen species formed from propane are more effective than H_2 in the conversion of thiophene-derived species to aromatics and they prevent the extensive cracking of thiophene fragments observed with H_2 as the hydrogen source. Thiophene scavenges surface hydrogen and alkene species formed during propane conversion reactions on H-ZSM5 and increases the rate at which alkenes exit as aromatics from oligomerization-cracking cycles, a role similar to metal cations that act as hydrogen desorption sites during propane reactions. The coupling of thiophene desulfurization with propane dehydrogenation allows the highly unsaturated fragments derived from thiophene to form desorbable and stable aromatics as final products, thus removing kinetic and thermodynamic bottlenecks in propane reactions. The coupling of thiophene desulfurization and propane aromatization reactions leads to the concurrent increase in the rate of both reactions.

TABLE 4

Carbon Selectivities from Thiophene during Reactions of Propane–Thiophene and H_2–Thiophene Mixtures on Co/H-ZSM5

	Co/H-ZSM5	
Carbon selectivity (%)	C_3H_8–C_4H_4S	H_2–C_4H_4S
C_1–C_2	0	10.8
Propene	0	5.5
C_4–C_5	0	0
Benzene	28.8	26.0
Toluene	47.7	24.5
Xylene	10.3	5.1
Alkylthiophenes	6.3	6.0
Benzothiophene	2.8	20.5

Note. Si/Al = 14.5, Co/Al = 0.17; 773 K; 20 kPa C_3H_8 or 25 kPa H_2, 1 kPa C_4H_4S, balance He; C_4H_4S conversion = ∼50%.

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