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Deuterium Isotopic Tracer Studies of Thiophene Desulfurization Pathways Using Propane or Dihydrogen as Co-reactants

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Isotopically labeled reactants (D_2 and C_3D_8) were used in order to probe H_2S formation pathways during thiophene desulfurization on Co/H-ZSM5 at 773 K using H_2 or propane as co-reactants. With D_2/C_4H_4S or C_3D_8/C_4H_4S reactants, both D and H were present in the hydrogen sulfide formed, suggesting that desulfurization can occur via both direct thiophene decomposition with intramolecular hydrogen transfer and deuterium addition from D_2 or C_3D_8. Thiophene, however, becomes readily deuterated via rapid exchange with D-containing intermediates formed from D_2 or C_3D_8, suggesting that thiophene protonation-deprotonation steps are fast. These isotopic equilibration processes prevent a definitive assessment of the contributions of these two pathways to hydrogen sulfide formation. The D-content in hydrogen sulfide and in hydrocarbons are higher with C_3D_8/C_4H_4S than with D_2/C_4H_4S reactants, indicating that propane is more effective than dihydrogen as a source of hydrogen for desulfurization reaction. C_3H_8/C_4H_4S and C_3D_8/C_4H_4S reactants gave similar reactions rates for hydrocarbon formation, suggesting that C–H bond activation steps do not limit hydrocarbon formation rates. A normal kinetic isotope effect was observed for thiophene desulfurization, indicating that the abstraction of fragments from propane-derived intermediates for reactions with thiophene is more difficult for deuterated intermediates. A comparison of thiophene desulfurization rates with $C_3H_8/D_2/C_4H_4S$, C_3H_8/C_4H_4S, and D_2/C_4H_4S mixtures confirmed that propane is a more effective source of hydrogen than H_2. The deuterium content in all products formed from $C_3H_8/D_2/C_4H_4S$ mixtures was lower than in products formed from C_3H_8/D_2 reactants. These findings suggest that thiophene inhibits the hydrogen adsorption–desorption steps responsible for the incorporation of D-atoms into adsorbed intermediates from D_2 and for the desorption of dihydrogen during propane reactions. © 2002 Elsevier Science (USA)

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

INTRODUCTION

Recently, we reported that thiophene desulfurization rates increase significantly when coupled with propane dehydrogenation reactions on cation-modified H-ZSM5 (1, 2). The higher thiophene desulfurization rates observed with propane co-reactants do not reflect reactions of thiophene with the H_2 formed via dehydrogenation of the alkane co-reactants. Instead, thiophene-derived intermediates appear to react directly with propane-derived intermediates to form sulfur-free hydrocarbons and H_2S. Subsequent studies using ^{13}C-labeled propane and unlabeled thiophene showed that alkenes form only from propane, while thiophene scavenges surface alkene and hydrogen species formed from propane to form aromatics containing carbon atoms from both thiophene and propane (3). Previous studies have also shown that hydrodesulfurization of thiophene occurs on cation-exchanged zeolites (1, 2, 4–11). These studies did not provide any experimental evidence for the pathways involved in H_2S formation.

Here, we probe H_2S formation pathways during thiophene desulfurization using H_2 or C_3H_8 as co-reactants on Co/H-ZSM5 at 773 K. Isotopically labeled hydrogen sources (D_2 or C_3D_8) were used to determine whether hydrogen atoms from C_4H_4S or deuterium atoms from D_2 or C_3D_8 were involved in hydrogen sulfide formation from D_2/C_4H_4S or C_3D_8/C_4H_4S mixtures. Kinetic isotope effects obtained for propane conversion and for thiophene desulfurization rates using C_3H_8/C_4H_4S and C_3D_8/C_4H_4S mixtures were used to probe the relative kinetic relevance of propane and thiophene activation steps in catalytic desulfurization turnovers. The isotopic and chemical identity of products of $C_3H_8/D_2/C_4H_4S$, C_3H_8/C_4H_4S, or D_2/C_4H_4S reactant mixtures were compared in order to determine the relative effectiveness of D_2 and C_3H_8 as hydrogen sources in desulfurization reactions. The deuterium content in the products formed from $C_3H_8/D_2/C_4H_4S$ reflects the ability of the exchanged Co cations to catalyze hydrogen adsorption–desorption steps. The effect of thiophene on the rate of these steps was examined by comparing the D-content in products formed from $C_3H_8/D_2/C_4H_4S$ and C_3H_8/D_2 mixtures. These measurements are reported here only for Co/H-ZSM5, but previous studies have suggested that similar reaction pathways are involved on H-ZSM5 and Co/H-ZSM5 catalysts (3, 12).

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EXPERIMENTAL

Co/H-ZSM5 samples were prepared by exchange of H-ZSM5 (prepared from Na-ZSM5; Zeochem, Si/Al = 14.5) with aqueous solutions of cobalt nitrate ($Co(NO_3)_2 \cdot 6H_2O$, Aldrich, 99%) at 353 K. These solutions were filtered and washed with 2 l deionized water. They were dried in ambient air at 398 K overnight and then treated in flowing dry air (Airgas, zero grade) at 773 K for 20 h. A more detailed description of the synthesis and characterization of the H-ZSM5 and Co/H-ZSM5 samples has been reported elsewhere (13). The Co content was 1.7 wt% (atomic absorption), corresponding to a Co/Al ratio of 0.31 (Galbraith Laboratories, Inc.) and the samples have minimal extraframework AlO_x species, as shown by isotopic exchange of D_2 with zeolitic OH groups (D_2–OH) (13) and by ^{27}Al-NMR studies (14). Previous D_2–OH and infrared studies showed that Co^{2+} cations replace on average ~1.2 acidic OH groups, suggesting the presence of a mixture of Co^{2+}–O–Co^{2+} dimers and Co^{2+} monomers, each bridging two next nearest neighbor Al sites (13). Temperature programmed reduction studies showed that Co cations in Co/H-ZSM5 do not reduce in H_2 up to 1273 K; Co K-edge X-ray absorption spectra showed that Co cations remain as divalent cations during reactions of C_3H_8 at 773 K (13).

D_2/C_4H_4S, C_3D_8/C_4H_4S, C_3H_8/C_4H_4S, and $C_3H_8/D_2/C_4H_4S$ reaction measurements were carried out in a recirculating batch reactor at 773 K. Recirculation rates were kept above 4 cm^3 s^{-1} in order to ensure low propane and thiophene conversions per pass (<2%). Catalyst samples (~0.05 g) were treated in flowing air (1.67 cm^3 s^{-1}) for 1 h at 773 K before reaction measurements at 773 K and 110 kPa total pressure. D_2 (Matheson) and C_4H_4S (Aldrich, 99%) partial pressures were 10 and 1 kPa, respectively, and the partial pressures of C_3D_8 (Isotec, 99.5%, 99% D) and C_3H_8 (Praxair, 99.5%) were 20 kPa. Reactant and product concentrations were measured as a function of contact time by injecting 0.2 cm^3 syringe gas samples 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 content in the products was measured by injecting a 0.3 cm^3 gas sample into a gas chromatograph equipped with the same capillary column and an electron-impact mass selective detector (Hewlett-Packard 5971). Deuterium atoms in hydrogen sulfide were found to undergo isotopic exchange with trace amounts of H_2O in the syringe. Therefore, the residence time of samples within the syringe was minimized, by injecting samples into the GC-MS immediately after they were extracted from the reactor.

Reaction rates are reported as turnover rates (moles of propane or thiophene converted per g-atom Al, per s). Product selectivities are reported as the percentage of converted reactant or reactants (during propane-thiophene reactions) appearing as a given product, based on carbon numbers. The deuterium content and the D-isotopomer distribution in all products and in unreacted reactants were determined from mass spectrometric data using matrix methods that account for ion fragmentation (15).

RESULTS AND DISCUSSION

Reactions of D_2/C_4H_4S Mixtures on Co/H-ZSM5

Reactions of D_2/C_4H_4S mixtures were used to probe the origin of the hydrogen atoms in the hydrogen sulfide formed during thiophene decomposition on Co/H-ZSM5. Specifically, the relative amounts of D and H in the hydrogen sulfide molecules formed (H_2S, D_2S, and HDS) reflect, at least in part, the relative contributions of intramolecular hydrogen transfer and of hydrogen addition using D_2 as the hydrogen source. Such details require, however, that isotopic exchange between thiophene and D_2 be sufficiently slow relative to hydrogen sulfide formation in order to ensure accurate extrapolation of the isotopic content to zero contact time, where the results reflect the relative contributions from the isotopically pure reactants.

The deuterium fraction in benzene, propene, hydrogen sulfide, and thiophene during D_2–C_4H_4S reactions on Co/H-ZSM5 at 773 K are shown as a function of contact time in Fig. 1. At short contact times and low thiophene conversions, some deuterium is detected in hydrogen sulfide, indicating that some D-atoms from D_2 participate in the removal of sulfur from thiophene (Fig. 1). The deuterium fraction in hydrogen sulfide molecules is significantly lower than one, indicating that intramolecular hydrogen transfer within thiophene also plays a significant role in the

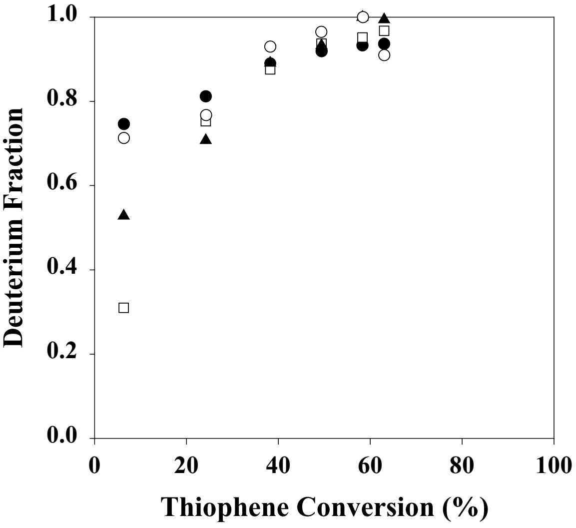

FIG. 1. Deuterium fraction in products during reactions of D_2/C_4H_4S on Co/H-ZSM5: (solid circles) benzene, (open circles) propane, (solid triangles) hydrogen sulfide, (open squares) thiophene [Co/H-ZSM5, Co/Al = 0.31, 773 K, 20 kPa D_2, 1 kPa C_4H_4S].

formation of hydrogen sulfide. Indeed, for all but the lowest contact time shown in Fig. 1, the deuterium contents in benzene, propene, thiophene, and hydrogen sulfide are similar within the accuracy of the isotopic content measurements. The rapid isotopic equilibration between C_4H_4S and D_2 renders these conclusions about the nature of the hydrogen addition steps dependent on this one initial data point. This initial point, however, clearly shows that the D content in hydrogen sulfide, benzene, and propene exceed that in the thiophene co-reactant. Thus, both hydrogen addition and intramolecular hydrogen transfer appear to contribute to the hydrogen sulfide detected during desulfurization of C_4H_4S/D_2 mixtures on Co/H-ZSM5.

We conclude that the protonation–deprotonation of thiophene is faster than desulfurization turnovers leading to rapid isotopic exchange between thiophene and D_2. D_2 exchanges rapidly with acidic OH groups in Co/H-ZSM5 at the conditions of these experiments (13). Hydrogen addition occurs via intramolecular hydrogen transfer and via deuterium addition from D_2. In addition, the formation of desorbable hydrocarbons (e.g., benzene, propene) involves longer surface residence times than hydrogen sulfide formation and desorption, as well as significant participation of D-atoms from D_2. Hydrogen sulfide is not only a product of the direct decomposition of thiophene to form H_2S and highly unsaturated adsorbed carbonaceous deposits, but it is also formed via hydrogenation of S-containing fragments using deuterium from a surface pool nearly equilibrated with gas phase D_2. The latter pathway is in agreement with theoretical studies of the acid catalyzed desulfurization of thiophene (16).

Reactions of C_3D_8/C_4H_4S Reactant Mixtures on Co/H-ZSM5

A similar set of experiments using C_3D_8/C_4H_4S reactant mixtures was used to probe hydrogen transfer pathways using propane as the hydrogen source in intermolecular transfer pathways. The relative effectiveness of H_2 and propane was previously examined by measurements of thiophene desulfurization rates using H_2–thiophene and propane–thiophene reactants (2). Table 1 shows the comparison of thiophene desulfurization rates using H_2 or propane as the hydrogen source on Co/H-ZSM5 (Co/Al = 0.17). These data show that propane (20 kPa) is a more effective source of hydrogen than H_2 (25 kPa) and leads to higher thiophene desulfurization rates. Desulfurization rates comparable to those with propane (at 20 kPa) are obtained only at H_2 pressures of 50–100 kPa (Table 1).

TABLE 1

Comparison of Thiophene Desulfurization Rates and (H_2S/Benzothiophene) Molar Ratios in the Presence of H_2 or Propane on Co/H-ZSM5 [773 K, 1 kPa C_4H_4S, 0–100 kPa H_2 or 20 kPa C_3H_8, Balance He, Co/Al = 0.17]

Gas phase pressure of hydrogen source (kPa)	Thiophene desulfurization rate (per residual OH group, 10^{-3}, s^{-1})
0	0.26
25 (H_2)	0.83
50 (H_2)	1.01
100 (H_2)	1.29
20 (C_3H_8)	1.08

Note. Previously reported in (2).

The relative contributions of D-atoms from propane and H-atoms from thiophene in the formation of benzene, toluene, and hydrogen sulfide can be obtained from the deuterium fraction in these molecules and in the propane and thiophene co-reactants (Figs. 2a and 2b). The D/H ratio in the C_3D_8/C_4H_4S reactant mixture is 40, suggesting that the deuterium fraction in a pool of adsorbed intermediates in isotopic quasi-equilibrium with these reactants would be 0.975. The initial aromatics and hydrogen sulfide products formed, however, contain only a 0.6–0.7 D-fraction (Figs. 2a and 2b), indicating that protium atoms from thiophene contribute to this surface pool more effectively than D-atoms from C_3D_8. Both propane and thiophene contribute hydrogens to the surface pool of intermediates responsible for the formation of all products, but C–H bond activation and exchange with this surface pool are faster in C_4H_4S than in C_3D_8.

The initial D-content in hydrogen sulfide resembles that measured for all hydrocarbon products, but it is much higher than the D-content in the thiophene co-reactants (Figs. 2a and 2b). Previous isotopic carbon tracing studies using ^{13}C have shown that only propane contributes carbon atoms to the propene molecules formed from propane–thiophene mixtures, but that aromatic molecules contain carbon atoms from both propane and thiophene (3). Therefore, hydrogen atoms from propane participate in the removal of sulfur from thiophene and thiophene desulfurization involves both intramolecular hydrogen addition and D-atom transfer from propane-derived intermediates. The similar deuterium contents in aromatics and in hydrogen sulfide suggest that intermolecular hydrogen transfer steps use a pool of hydrogen-containing intermediates involved also in the oligomerization-cracking cycles responsible for the formation of aromatics and larger alkenes in propane–thiophene reactions. As in the case of D_2/C_4H_4S reactant mixtures, thiophene acquires deuterium during propane–thiophene reactions, because it exchanges readily, probably via protonation–deprotonation events, with a surface pool of intermediates containing significant deuterium atoms from perdeuterated propane. This process interferes with a more quantitative analysis of the relative rates of intramolecular and hydrogen addition pathways involved in hydrogen sulfide formation during propane–thiophene reactions.

The deuterium content in the products increases more rapidly with contact time in the case of C_3D_8/C_4H_4S

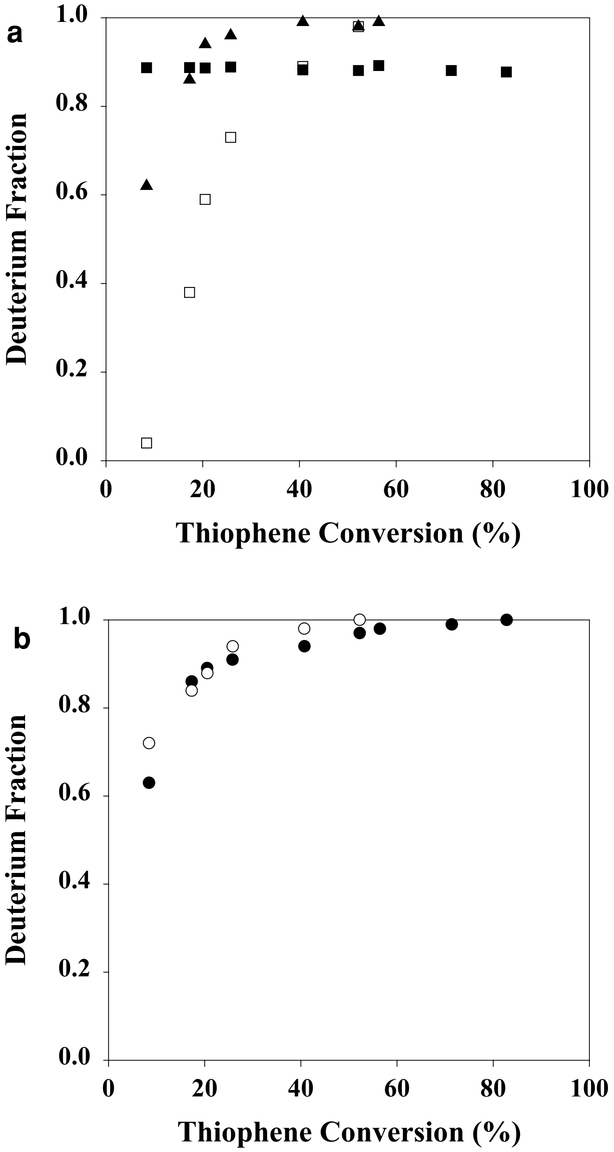

FIG. 2. (a) Deuterium fraction in reactants and products during reactions of C_3D_8/C_4H_4S on Co/H-ZSM5: (solid squares) propane, (open squares) thiophene, and (solid triangles) hydrogen sulfide [Co/H-ZSM5, Co/Al = 0.31, 773 K, 20 kPa C_3D_8, 1 kPa C_4H_4S]. (b) Deuterium fraction in products during reactions of C_3D_8/C_4H_4S on Co/H-ZSM5: (solid circles) benzene and (open circles) toluene [Co/H-ZSM5, Co/Al = 0.31, 773 K, 20 kPa C_3D_8, 1 kPa C_4H_4S].

reactants (Figs. 2a and 2b) than for D_2/C_4H_4S reactants (Fig. 1), suggesting that propane is a more effective hydrogen source than dihydrogen on Co/H-ZSM5 catalysts. This is consistent with the higher rate of thiophene desulfurization obtained with C_3H_8 (20 kPa) than with H_2 (25 kPa) co-reactants on Co/H-ZSM5 (Table 1). Although these C_3D_8/C_4H_4S and D_2/C_4H_4S reaction studies are unable to measure the definite contributions from the two plausible hydrogen sulfide formation pathways, it is clear that a co-reactant able to act as a hydrogen source influences the rate of formation of hydrogen sulfide, suggesting a role of hydrogen atoms from the co-reactants in the hydrogenation of both the sulfur and the carbon moieties in thiophene molecules. In this role, propane is much more effective than dihydrogen, as also proposed from earlier from steady-state desulfurization rate measurements (1, 2).

Kinetic Isotope Effects in Desulfurization Reactions of C_3D_8/C_4H_4S and C_3H_8/C_4H_4S Reactant Mixtures on Co/H-ZSM5

Kinetic isotope effects obtained from the relative rates of C_3D_8/C_4H_4S and C_3H_8/C_4H_4S reactant mixtures can be used to probe the kinetic relevance of C–H bond activation steps in propane and in thiophene during the kinetic coupling of their respective reactions. Propene is formed only from the propane co-reactant during propane–thiophene reactions (3). Initial propane turnover rates and initial propene formation rates for C_3D_8/C_4H_4S and C_3H_8/C_4H_4S reactions are shown in Table 2. No kinetic isotope effects were observed for total propane conversion ($r_H/r_D = 1.02$) or for propene formation ($r_H/r_D = 0.99$) rates when thiophene was present as a co-reactant (Table 2). This indicates that C–H bond activation steps do not limit propane conversion rates in the presence of thiophene. Initial thiophene desulfurization rates are significantly lower with C_3D_8 than with C_3H_8 ($k_H/k_D = 1.65$) (Table 2). This suggests that rate-limiting steps in thiophene desulfurization involve the abstraction of hydrogen or hydrogen-rich fragments from reactive propane-derived surface intermediates in order to render thiophene-derived fragments desorbable as stable molecules. The abstraction of such species appears to be slower when such propane-derived species contain deuterium than when they contain protium.

$C_3H_8/D_2/C_4H_4S$ Reactions on Co/H-ZSM5

Propane dehydrogenation reactions are limited by hydrogen removal and cations act as active sites for the recombinative desorption of H_2 (17–20), thus increasing the overall rate of propane reactions. The effectiveness of cations at performing hydrogen removal steps can be probed by measuring the D content in the products of C_3H_8/D_2 reactions (17, 19, 21). Previously, the presence of thiophene was shown to inhibit propane conversion rates on Co/H-ZSM5 (3). Here, we use $C_3H_8/D_2/C_4H_4S$ and C_3H_8/D_2 reactant mixtures in order to probe how the function of Co cations is influenced by thiophene.

The addition of D_2 to C_3H_8/C_4H_4S reaction mixtures slightly increased thiophene desulfurization rates on Co/H-ZSM5 (Table 2), because it provides an additional source of hydrogen for desulfurization reactions. Co cations catalyze hydrogen adsorption–desorption steps and allow gas phase D_2 to contribute to the hydrogen content in the pool of reactive intermediates. The product selectivities are similar

TABLE 2

Initial Propane Turnover Rates, Propene Formation Rates, and Thiophene Desulfurization Rates and Product Selectivities at 20% Thiophene Conversion of C_3D_8/C_4H_4S, C_3H_8/C_4H_4S, $C_3H_8/D_2/C_4H_4S$, and D_2/C_4H_4S Reactions on Co/H-ZSM5 [Si/Al = 14.5, Co/Al = 0.31; 773 K, 20 kPa C_3H_8, 10 kPa D_2, 1 kPa C_4H_4S, Balance He]

	C_3D_8/C_4H_4S	C_3H_8/C_4H_4S	$C_3H_8/D_2/C_4H_4S$	D_2/C_4H_4S
Initial propane turnover rate (per Al, 10^{-3}, s^{-1})	1.78	1.82	1.90	—
Initial propene formation rate from propane (per Al, 10^{-3}, s^{-1})	0.98	0.97	0.95	—
Initial thiophene desulfurization rate (per Al, 10^{-3}, s^{-1})	0.92	1.52	1.75	0.65
Product selectivity (%) (at 20% thiophene conversion)				
Methane	4.7	5.1	5.5	4.1
Ethene	12.2	8.9	6.2	7.0
Ethane	5.4	4.3	6.5	3.3
Propene	55.3	53.6	48.8	23.5
Butenes	2.5	2.2	8.3	2.6
C_6–C_8 aromatics	19.4	23.7	22.2	31.9
S compounds	0.5	1.9	2.4	15.9

to those measured in C_3H_8/C_4H_4S reactions (Table 2), because only small amounts of D_2 (10 kPa) were added and propane (20 kPa) is a more effective source of hydrogen than D_2.

The presence of propane in $C_3H_8/D_2/C_4H_4S$ mixtures led to significantly higher thiophene desulfurization rates and lower selectivity to sulfur compounds than with D_2/C_4H_4S reactants, because of the availability and effectiveness of the additional source of accessible hydrogen and hydrogen-rich reactive intermediates provided by propane (Table 2). The effect of C_3H_8 on the rate of desulfurization and on the selectivity to sulfur compounds of D_2/C_4H_4S mixtures is stronger than that of D_2 on C_3H_8/C_4H_4S reactants (Table 2), again because C_3H_8 is more effective than H_2 in the desulfurization of thiophene on Co/H-ZSM5 (2).

A comparison of propane conversion rates using $C_3H_8/D_2/C_4H_4S$ or C_3H_8/D_2 reactant mixtures shows that the presence of thiophene leads to lower propane turnover rates, as also found earlier using C_3H_8 and C_3H_8/C_4H_4S reactants (3). These inhibition effects remain puzzling, because no significant coverage of cations or acidic OH groups by intermediates or unreactive fragments was detected by in situ infrared spectroscopy during steady-state reactions on Co/H-ZSM5 (3, 12). Interactions between thiophene and acidic OH groups were detected by infrared, albeit at much lower temperatures (~300 K) (12, 22, 23). Also, X-ray absorption spectra did not detect any changes in Co structure or any residual inorganic sulfur compounds, even after extended contact with thiophene/propane reactants at typical reaction temperatures (3, 12).

The deuterium content in the products formed from $C_3H_8/D_2/C_4H_4S$ and C_3H_8/D_2 mixtures were compared in order to detect any changes in the ability of Co cations to form dihydrogen as a result of the presence of thiophene (Fig. 3). All products formed from a given reactant mixture ($C_3H_8/D_2/C_4H_4S$ or C_3H_8/D_2) contain similar deuterium fractions, suggesting that they form from adsorbed reactive intermediates with uniform isotopic composition. All isotopomers show a binomial distribution at all contact times, consistent with the quasi-equilibrated nature of C–H bond activation, a step that occurs reversibly and significantly faster than catalytic turnovers required for

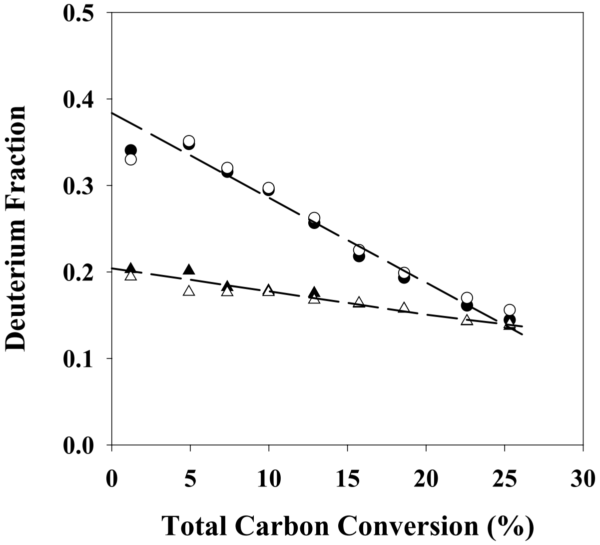

FIG. 3. The effect of thiophene co-reactant on the deuterium content in products (benzene: solid symbols and toluene: open symbols) of C_3H_8/D_2 and $C_3H_8/D_2/C_4H_4S$ reactions on Co/H-ZSM5: (circles) C_3H_8/D_2 reactions and (triangles) $C_3H_8/D_2/C_4H_4S$ reactions [Si/Al = 14.5, Co/Al = 0.31, 773 K, 20 kPa C_3H_8, 10 kPa D_2, and 0 or 1 kPa C_4H_4S].

chemical conversion of propane (and thiophene) to hydrocarbon products.

The deuterium content in all products decreased with increasing contact time for both reactant mixtures, because the initially pure D_2 reactant is diluted with H_2 and HD molecules formed in propane dehydrogenation and aromatization reactions. Products formed from $C_3H_8/D_2/C_4H_4S$ mixtures contain less deuterium than those formed from C_3H_8/D_2 mixtures, suggesting that hydrogen adsorption–desorption steps on Co cations are inhibited by thiophene (Fig. 3). This is consistent with the inhibition effects of thiophene on propane conversion reactions, which are kinetically influenced by the rate of hydrogen removal via recombinative desorption steps. The identity of the adsorbed species responsible for this inhibition remains unclear, in view of the absence of detectable co-adsorbed species from infrared and X-ray absorption spectroscopy (3, 12).

CONCLUSIONS

Reaction mixtures of D_2/C_4H_4S and C_3D_8/C_4H_4S were used to probe hydrogen sulfide formation pathways in thiophene desulfurization reactions. The deuterium content in the hydrogen sulfide initially formed was higher than that in unreacted thiophene molecules, indicating that hydrogen sulfide is not only formed by direct decomposition of thiophene, but also by hydrogenation of S-containing fragments using hydrogens from either D_2 or C_3D_8. Rapid isotopic equilibration of thiophene with intermediates derived from C_3D_8 or D_2 prevents a quantitative measure of the contributions of intermolecular and intramolecular hydrogen transfer to the formation of hydrogen sulfide. Both mechanisms are evident, however, from the deuterium content in hydrogen sulfide formed from D_2/C_4H_4S and C_3D_8/C_4H_4S mixtures and propane is clearly a more effective hydrogen source than H_2 in thiophene desulfurization on Co/H-ZSM5.

Kinetic isotope effects obtained for propane conversion, propene formation, and thiophene desulfurization rates using C_3H_8/C_4H_4S and C_3D_8/C_4H_4S reactant mixtures were used to establish the relative kinetic relevance of C–H bond activation steps on these reactions. No isotope effects were observed for propane conversion or propene formation rates during propane–thiophene reactions, indicating that C–H bond activation does not control propane conversion rates. A normal kinetic isotope effect was observed for thiophene desulfurization suggesting that the rate-limiting step for thiophene desulfurization involves hydrogen abstraction from propane-derived reactive surface intermediates.

A comparison of $C_3H_8/D_2/C_4H_4S$ reactions with C_3H_8/C_4H_4S and D_2/C_4H_4S reactions also showed that propane is a more effective hydrogen source for thiophene desulfurization reactions. The deuterium content in the products formed from $C_3H_8/D_2/C_4H_4S$ mixtures was lower than in products formed from C_3H_8/D_2 mixtures, suggesting a lower D-content in the pool of adsorbed intermediates when thiophene is present. This indicates that thiophene inhibits the ability of metal cations to catalyze the hydrogen adsorption–desorption steps responsible for the introduction of D-atoms into this surface pool from D_2.

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