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

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Isotopically labeled reactants (D2 and C3D8) were used in order to probe H2S formation pathways during thiophene desulfurization on Co/H-ZSM5 at 773 K using H2 or propane as co-reactants. With D2/C4H4S or C3D8/C4H4S 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 hydrogen sulfide formation reaction. C3H8/C4H4S and C3D8/C4H4S 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 hydrogen atoms from C4H4S or deuterium atoms from D2 or C3D8, 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 C3D8/C4H4S than with D2/C4H4S reactants, indicating that propane is more effective than dihydrogen as a source of hydrogen for desulfurization reaction. C3H8/C4H4S and C3D8/C4H4S 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 C3H8/D2/C4H4S, C3H8/C4H4S, and D2/C4H4S mixtures confirmed that propane is a more effective source of hydrogen than H2. The deuterium content in all products formed from C3H8/D2/C4H4S mixtures was lower than in products formed from C3H8/H2 reactants. These findings suggest that thiophene inhibits the hydrogen adsorption–desorption steps responsible for the incorporation of D-atoms into adsorbed intermediates from D2 and for the desorption of dihydrogen during propane reactions.

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 H2 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 H2S. Subsequent studies using 13C-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 H2S formation.

Here, we probe H2S formation pathways during thiophene desulfurization using H2 or C3H8 as co-reactants on Co/H-ZSM5 at 773 K. Isotopically labeled hydrogen sources (D2 or C3D8) were used to determine whether hydrogen atoms from C3H8 or deuterium atoms from D2 or C3D8 were involved in hydrogen sulfide formation. Kinetic isotope effects obtained for propane conversion and for thiophene desulfurization rates using C3H8/C4H4S and C3D8/C4H4S 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 C3H8/D2/C4H4S, C3H8/C4H4S, or D2/C4H4S reactant mixtures were compared in order to determine the relative effectiveness of D2 and C3H8 as hydrogen sources in desulfurization reactions. The deuterium content in the products formed from C3H8/D2/C4H4S 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 C3H8/D2/C4H4S and C3H8/D3 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(NO₃)₂·6H₂O, 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 AlO₆ species, as shown by isotopic exchange of D₂ with zeolitic OH groups (D₂-OH) (13) and by ²⁷Al-NMR studies (14). Previous D₂-OH and infrared studies showed that Co²⁺ cations replace on average ~1.2 acidic OH groups, suggesting the presence of a mixture of Co²⁺–O–Co²⁺ dimers and Co²⁺ 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 H₂ up to 1273 K; Co K-edge X-ray absorption spectra showed that Co cations remain as divalent cations during reactions of C₃H₈ at 773 K (13).

D₂/C₃H₈S, C₃D₈/C₄H₄S, C₅H₈/C₄H₄S, and C₃H₈/D₂/C₄H₄S reaction measurements were carried out in a recirculating batch reactor at 773 K. Recirculation rates were kept above 4 cm³ 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 cm³ s⁻¹) for 1 h at 773 K before reaction measurements at 773 K and 110 kPa total pressure. D₂ (Matheson) and C₄H₄S (Aldrich, 99%) partial pressures were 10 and 1 kPa, respectively, and the partial pressures of C₃D₈ (Isotec, 99.5%, 99% D) and C₁H₈ (Praxair, 99.5%) were 20 kPa. Reactant and product concentrations were measured as a function of contact time by injecting 0.2 cm³ 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 cm³ 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 H₂O 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 D₂/C₄H₄S Mixtures on Co/H-ZSM5

Reactions of D₂/C₄H₄S 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 (H₂S, D₂S, and HDS) reflect, at least in part, the relative contributions of intramolecular hydrogen transfer and of hydrogen addition using D₂ as the hydrogen source. Such details require, however, that isotopic exchange between thiophene and D₂ 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 D₂–C₃H₄S 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 D₂ 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

![Deuterium Fraction vs Thiophene Conversion](image-url)
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 C4H4S and D2 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 C4H4S/D2 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 D2. D2 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 D2. 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 D2. Hydrogen sulfide is not only a product of the direct decomposition of thiophene to form H2S 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 D2. The latter pathway is in agreement with theoretical studies of the acid catalyzed desulfurization of thiophene (16).

**Reactions of C3D8/C4H4S Reactant Mixtures on Co/H-ZSM5**

A similar set of experiments using C3D8/C4H4S reactant mixtures was used to probe hydrogen transfer pathways using propane as the hydrogen source in intermolecular transfer pathways. The relative effectiveness of H2 and propane was previously examined by measurements of thiophene desulfurization rates using H2–thiophene and propane–thiophene reactants (2). Table 1 shows the comparison of thiophene desulfurization rates using H2 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 H2 (25 kPa) and leads to higher thiophene desulfurization rates. Desulfurization rates comparable to those with propane (at 20 kPa) are obtained only at H2 pressures of 50–100 kPa (Table 1).

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 C3D8/C4H4S 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 C3D8. 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 C4H4S than in C3D8.

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 13C 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 D2/C4H4S 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 C3D8/C4H4S mixtures on Co/H-ZSM5 [773 K, 1 kPa C4H4S, 0–100 kPa H2 or 20 kPa C3H8, Balance He, Co/Al = 0.17].

**Table 1**

<table>
<thead>
<tr>
<th>Gas phase pressure of hydrogen source (kPa)</th>
<th>Thiophene desulfurization rate (per residual OH group, 10^-3, s^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.26</td>
</tr>
<tr>
<td>25 (H2)</td>
<td>0.83</td>
</tr>
<tr>
<td>50 (H2)</td>
<td>1.01</td>
</tr>
<tr>
<td>100 (H2)</td>
<td>1.29</td>
</tr>
<tr>
<td>20 (C3H8)</td>
<td>1.08</td>
</tr>
</tbody>
</table>

Note: Previously reported in (2).
Thiophene Conversion (%)

Deuterium Fraction

0 20 40 60 80 100

0.0

0.2

0.4

0.6

0.8

1.0

Deuterium Fraction

0 20 40 60 80 100

0.0

0.2

0.4

0.6

0.8

1.0

Thiophene Conversion (%)

Reactants (Figs. 2a and 2b) than for D2/C4H4S 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 C3H8 (20 kPa) than with H2 (25 kPa) co-reactants on Co/H-ZSM5 (Table 1). Although these C3D8/C4H4S and D2/C4H4S 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 C3D8/C4H4S and C3H8/C4H4S Reactant Mixtures on Co/H-ZSM5**

Kinetic isotope effects obtained from the relative rates of C3D8/C4H4S and C3H8/C4H4S 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 C3D8/C4H4S and C3H8/C4H4S 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 C3D8 than with C3H8 ($k_H/k_D = 1.65$) (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.

**C3H8/D2/C4H4S Reactions on Co/H-ZSM5**

Propane dehydrogenation reactions are limited by hydrogen removal and cations act as active sites for the recombinative desorption of H2 (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 C3H8/D2 reactions (17, 19, 21). Previously, the presence of thiophene was shown to inhibit propane conversion rates on Co/H-ZSM5 (3). Here, we use C3H8/D2/C4H4S and C3H8/D2 reactant mixtures in order to probe how the function of Co cations is influenced by thiophene.

The addition of D2 to C3H8/C4H4S 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 D2 to contribute to the hydrogen content in the pool of reactive intermediates. The product selectivities are similar.
to those measured in C₃H₈/C₄H₄S reactions (Table 2), because only small amounts of D₂ (10 kPa) were added and propane (20 kPa) is a more effective source of hydrogen than D₂.

The presence of propane in C₃H₈/D₂/C₄H₄S mixtures led to significantly higher thiophene desulfurization rates and lower selectivity to sulfur compounds than with D₂/C₄H₄S 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 C₃H₈ on the rate of desulfurization and on the selectivity to sulfur compounds of D₂/C₄H₄S mixtures is stronger than that of D₂ on C₃H₈/C₄H₄S reactants (Table 2), again because C₃H₈ is more effective than H₂ in the desulfurization of thiophene on Co/H-ZSM5 (2).

A comparison of propane conversion rates using C₃H₈/D₂/C₄H₄S or C₃H₈/D₂ reactant mixtures shows that the presence of thiophene leads to lower propane turnover rates, as also found earlier using C₃H₈ and C₃H₈/C₄H₄S 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 C₃H₈/D₂/C₄H₄S and C₃H₈/D₂ 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 (C₃H₈/D₂/C₄H₄S or C₃H₈/D₂) 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

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>C₃D₈/C₄H₄S</th>
<th>C₃H₈/C₄H₄S</th>
<th>C₃H₈/D₂/C₄H₄S</th>
<th>D₂/C₄H₄S</th>
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<tr>
<td>Initial propane turnover rate (per Al, 10⁻³ s⁻¹)</td>
<td>1.78</td>
<td>1.82</td>
<td>1.90</td>
<td>—</td>
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<tr>
<td>Initial propene formation rate from propane (per Al, 10⁻³ s⁻¹)</td>
<td>0.98</td>
<td>0.97</td>
<td>0.95</td>
<td>—</td>
</tr>
<tr>
<td>Initial thiophene desulfurization rate (per Al, 10⁻³ s⁻¹)</td>
<td>0.92</td>
<td>1.52</td>
<td>1.75</td>
<td>0.65</td>
</tr>
<tr>
<td>Product selectivity (%) (at 20% thiophene conversion)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>4.7</td>
<td>5.1</td>
<td>5.5</td>
<td>4.1</td>
</tr>
<tr>
<td>Ethene</td>
<td>12.2</td>
<td>8.9</td>
<td>6.2</td>
<td>7.0</td>
</tr>
<tr>
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<td>5.4</td>
<td>4.3</td>
<td>6.5</td>
<td>3.3</td>
</tr>
<tr>
<td>Propene</td>
<td>55.3</td>
<td>53.6</td>
<td>48.8</td>
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<tr>
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<td>2.5</td>
<td>2.2</td>
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<tr>
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<td>22.2</td>
<td>31.9</td>
</tr>
<tr>
<td>S compounds</td>
<td>0.5</td>
<td>1.9</td>
<td>2.4</td>
<td>15.9</td>
</tr>
</tbody>
</table>

FIG. 3. The effect of thiophene co-reactant on the deuterium content in products (benzene: solid symbols and toluene: open symbols) of C₃H₈/D₂ and C₃H₈/D₆/C₄H₄S reactions on Co/H-ZSM5: (circles) C₃H₈/D₂ reactions and (triangles) C₃H₈/D₆/C₄H₄S reactions [Si/Al = 14.5, Co/Al = 0.31, 773 K, 20 kPa C₃H₈, 10 kPa D₂, and 0 or 1 kPa C₄H₄S].
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 D2 reactant is diluted with H2 and HD. Increasing contact time for both reactant mixtures, because both chemical conversion of propane (and thiophene) to hydrocarbon products.

A comparison of C3H8/D2/C4H4S reactions with C3H8/C4H4S and D2/C4H4S reactions also showed that propane is a more effective hydrogen source for thiophene desulfurization reactions. The deuterium content in the products formed from C3H8/D2/C4H4S mixtures was lower than in products formed from C3H8/D2 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 D2.

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