



Catalytic desulfurization of thiophene on H-ZSM5 using alkanes as co-reactants

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Abstract

Propane, *n*-hexane, *n*-decane, and hydrogen were used as co-reactants in the desulfurization of thiophene catalyzed by H-ZSM5 at 673 K. These co-reactants lead to hydrogen-rich intermediates, which are required for the removal of unsaturated fragments formed in thiophene decomposition reactions. Thiophene desulfurization rates increased with increasing alkane chain size, suggesting that the availability of hydrogen-rich intermediates increases with increasing alkane reactivity. Desulfurization rates with alkane co-reactants were significantly higher than those achieved with hydrogen. Sulfur is predominately removed as hydrogen sulfide (>80% S-selectivity) in the presence of alkane co-reactants, but much lower hydrogen sulfide selectivities were obtained when hydrogen was used and when thiophene decomposed in the absence of any co-reactants. The presence of thiophene did not alter the nature of the cracking, dehydrogenation, oligomerization, and cyclization pathways typical of alkane reactions or the overall rates of propane conversion on H-ZSM5. The selectivity for alkane conversion to aromatics, however, increased when alkane reactions occur concurrently with thiophene desulfurization, indicating that thiophene-derived intermediates contribute to the formation of aromatics by scavenging alkene intermediates formed from the alkane co-reactants. The higher alkene/alkane ratios observed during alkane reactions in the presence of thiophene are consistent with the scavenging of hydrogen-rich intermediates by thiophene-derived species via reactions that form aromatic molecules containing carbon atoms from both alkane and thiophene reactants.

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1. Introduction

The desulfurization of thiophene using propane molecules as co-reactants was recently reported on H-ZSM5 and cation-exchanged H-ZSM5 catalysts [1,2]. In this coupling reaction, propane provides adsorbed hydrogen and hydrogen-rich alkenes required for the removal of unsaturated adsorbed species

formed during thiophene desulfurization on Bronsted acid sites. Thiophene-derived intermediates desorb to form hydrocarbons and hydrogen sulfide selectively during propane–thiophene reactions, without the direct involvement of gas phase H₂ molecules formed during concurrent propane dehydrogenation and dehydrocyclodimerization reactions. These reaction pathways were confirmed using ¹³C and ²H isotopic tracer studies [3,4]. Previous studies have shown that hydrodesulfurization of thiophene can also be carried out using hydrogen on cation-exchanged zeolites [1,2,5–11].

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Here, we extend these previous studies to reactions of higher alkanes with thiophene in order to probe the effects of alkane size and reactivity on the rate, selectivity, and deactivation behavior of thiophene desulfurization reactions. *n*-Hexane and *n*-decane were chosen because, in contrast with propane, they undergo β -scission and cyclization without requiring chain growth. The reaction pathways of these larger alkanes are typical of those prevalent during catalytic cracking processes, in which thiophene desulfurization can also occur and lead to the consequent formation of hydrogen sulfide and organosulfur compounds larger than thiophene [12–16].

2. Experimental methods

Na-ZSM5 (Zeochem, Si/Al = 14.5) was exchanged three times with a 0.25 M NH_4NO_3 (Aldrich, 99.999%) solution at 353 K for 16 h. After each exchange, the slurry was filtered and washed with deionized water in order to obtain NH_4 -ZSM5. NH_4 -ZSM5 was treated in ambient air at 398 K overnight and then at 773 K in flowing dry air (Airgas, zero grade) for 20 h to form H-ZSM5. The synthesis and characterization of the H-ZSM5 samples have been reported elsewhere [17–19].

H-ZSM5 samples were treated in flowing dry air (Airgas, zero grade) at 773 K for 1 h before catalytic reactions. Catalytic rate and selectivity measurements were carried out at 673 or 773 K using a tubular flow reactor with plug-flow hydrodynamics. Thiophene (1 kPa, Aldrich, >99%) was added to a propane–He stream (20 kPa, Praxair, certified mixture) using a liquid metering pump (Cole-Parmer 74900). Thiophene/*n*-hexane (1 kPa/20 kPa; *n*-hexane, Aldrich, >99%) and thiophene/*n*-decane (1 kPa/6 kPa or 12 kPa; *n*-decane, Aldrich, >99%) reactants were introduced as premixed liquids into a flowing He stream using the same liquid metering pump. The two *n*-decane partial pressures (6 and 12 kPa) used were meant to provide a comparison with propane (at 20 kPa) and with *n*-hexane (20 kPa) at their respective equivalent “carbon” (or $-\text{CH}_2-$) partial pressures. All liquid reactants were vaporized immediately upon injection and transferred into the reactor and the analytical system through heated lines kept at 403 K. The reactant conversion levels were changed by varying the reactant space

velocity or by allowing deactivation to proceed with increasing time on stream. The effects of conversion on reaction selectivity were independent of which one of the two methods was used in order to change the reactant conversion level. Deactivation rates are reported as first-order rate constants, obtained from the exponential decay in rate with time on stream expected from first-order site deactivation processes.

Reactant and product concentrations in the reactor effluent were measured by gas chromatography (Hewlett-Packard 6890) using capillary (HP-1 cross-linked methyl silicone, 50 m \times 0.32 mm, 1.05 μm film) and packed columns (Hayesep-Q, 80/100 mesh, 10 ft \times 0.125 in.) and flame ionization and thermal conductivity detectors. Product identifications based on elution sequence were confirmed by mass spectrometric analysis after similar chromatographic separation protocols. Sulfur compounds were identified using a GC–MS system equipped with the same capillary column and with an electron-impact mass selective detector (Hewlett-Packard 5971). H_2S was measured and quantified using TCD areas relative to Ar (internal standard). Reaction rates are reported as turnover rates (reactant molar conversion rate/g-atom Al-s). Product selectivities are reported on a carbon basis as the percentage of the total carbon atoms converted in the reactant stream (alkane or alkane–thiophene) appearing as a given product. Sulfur selectivities are reported similarly, but based on the number of sulfur atoms present in the reacted thiophene molecules.

3. Results and discussion

Thiophene desulfurization reactions were studied using propane, *n*-hexane, and *n*-decane as co-reactants. These results are reported as thiophene desulfurization first-order rate constants, because the high thiophene conversions attained required that reaction rates be described using rigorous integral plug-flow hydrodynamic models. Independent kinetic studies have confirmed this first-order dependence of desulfurization reactions on thiophene concentration. These rate constants are reported in Table 1 for reactions of thiophene with *n*-decane (at 673 K), *n*-hexane (at 673 K), or propane (at 773 K). At similar $-\text{CH}_2-$ effective pressures, desulfurization rate constants were higher with *n*-decane (6 kPa) than with propane co-reactants

Table 1
Comparison of pure alkane and alkane–thiophene reactions on H-ZSM5 (Si/Al = 14.5)

Reactants	He/ C ₄ H ₄ S	C ₃ H ₈	C ₃ H ₈ / C ₄ H ₄ S	C ₆ H ₁₄	C ₆ H ₁₄ / C ₄ H ₄ S	C ₁₀ H ₂₂	C ₁₀ H ₂₂ / C ₄ H ₄ S	C ₁₀ H ₂₂	C ₁₀ H ₂₂ / C ₄ H ₄ S
Reaction temperature (K)	773	773	773	673	673	673	673	673	673
Reactants (alkane/thiophene) (kPa)	0/1	20/0	20/1	20/0	20/1	6/0	6/1	12/0	12/1
Alkane conversion to hydrocarbons (%)	–	18.5	9.6	63.0	60.1	38.8	37.3	34.2	33.6
Hydrocarbon formation rate (per Al 10 ⁻³ s ⁻¹)	–	1.4	1.5	22.9	21.9	47.1	43.3	72.0	71.3
Hydrocarbon deactivation rate constant (k _d) (h ⁻¹)	–	<0.001	0.055	0.014	0.18	0.0090	0.22	0.026	0.34
Thiophene conversion (%)	9.2	–	77.9	–	89.1	–	50.0	–	56.6
Thiophene desulfurization rate (per Al 10 ⁻³ s ⁻¹)	0.063	–	0.61	–	1.6	–	3.7	–	10.0
Thiophene desulfurization rate constant (k) (×10 ⁴ cm ³ /(mol Al-s))	0.015	–	0.25	–	0.88	–	0.90	–	3.4
Desulfurization deactivation rate constant (k _d) (h ⁻¹)	0.18	–	0.033	–	0.086	–	0.090	–	0.097

(20 kPa) (0.90 × 10⁻⁴ cm³/(mol Al-s) versus 0.25 × 10⁻⁴ cm³/(mol Al-s)), even at the lower temperatures used for the thiophene–decane mixtures (673 K versus 773 K). Desulfurization rate constants at 673 K were also higher with *n*-decane (12 kPa) than with *n*-hexane (20 kPa) co-reactants (3.4 × 10⁻⁴ cm³/(mol Al-s) versus 0.88 × 10⁻⁴ cm³/(mol Al-s)).

Hydrocarbon formation rates using pure alkanes and alkane–thiophene mixtures are also shown in Table 1. Hydrocarbon formation rates were not strongly influenced by the presence of thiophene, but the selectivity to aromatics was significantly higher for each alkane when thiophene is present (Table 3). The higher reactivity of larger alkanes led to higher rates of C–H bond activation and to more readily available hydrogen, hydrogen-rich adsorbed intermediates, and alkenes, all of which provide pathways for the reactive desorption of thiophene-derived unsaturated fragments formed on acid sites. *n*-Hexane and *n*-decane were significantly more effective reactants than propane, even at the lower temperatures used for the reactions of these larger alkanes.

First-order deactivation rate constants are shown in Table 1 for each alkane reactant and for the corresponding alkane–thiophene mixture. Deactivation rate constants for thiophene desulfurization reactions increased with increasing alkane chain size. Deactivation rates for dehydrocyclodimerization reactions also increased with alkane size; they were higher for

each alkane reactant when thiophene was present than for the respective pure alkane reactant. Such effects are consistent with the formation of more unsaturated intermediates during thiophene desulfurization and alkane dehydrocyclodimerization reactions as the hydrogen-to-carbon ratio decreases with increasing alkane chain length.

Thiophene desulfurization rate constants at 673 or 773 K for alkane–thiophene reactant mixtures were also compared to those measured at 773 K using hydrogen molecules as co-reactants (Table 2). Desulfurization rate constants (at 673 K) with *n*-hexane and

Table 2
Comparison of thiophene desulfurization rate constants in the presence of hydrogen or propane at 773 K, and hexane or decane at 673 K on H-ZSM5 (773 or 673 K, 1 kPa C₄H₄S, 0–200 kPa hydrogen, 20 kPa C₃H₈, 20 kPa C₆H₁₄, 6 kPa C₁₀H₂₂, or 12 kPa C₁₀H₂₂, balance He)

Gas phase pressure of hydrogen source (kPa)	Thiophene desulfurization rate constant (k) (×10 ⁴ cm ³ /(mol Al-s))
0 (773 K)	0.015
100 (H ₂) (773 K)	0.032
200 (H ₂) (773 K)	0.077
20 (C ₃ H ₈) (773 K)	0.25
20 (C ₆ H ₁₄) (673 K)	0.88
6 (C ₁₀ H ₂₂) (673 K)	0.90
12 (C ₁₀ H ₂₂) (673 K)	3.4
20 (C ₃ H ₈) (773 K) Zn/H-ZSM5	0.44

n-decane as co-reactants are not only greater than those with propane co-reactants, but also much greater than those achieved with 100–200 kPa H₂ at 773 K (Table 2). Even when Zn cations were exchanged into H-ZSM5 in order to provide hydrogen dissociation sites, *n*-hexane and *n*-decane are significantly more effective hydrogen sources for thiophene desulfurization than hydrogen (Table 2) [1].

The effects of thiophene co-reactants on the products formed from propane, *n*-hexane, and *n*-decane on H-ZSM5 are shown in Table 3. Hydrocarbon selectivities measured with and without thiophene are compared for each alkane in Table 3; these comparisons are presented at similar alkane conversion levels, because primary and secondary reaction path-

ways prevalent during alkane reactions can lead to significant effects of reactant conversion and reactor residence time on product distributions. For each alkane, the presence of thiophene led to higher selectivities to aromatic products, as reported previously for propane reactants [3]. Isotopic tracing of reaction products formed from mixtures of thiophene and ¹³C-labeled propane on H-ZSM5 and Co/H-ZSM5 showed that these higher aromatics selectivities were only partially caused by the contribution of thiophenic carbons to these aromatic products. The aromatics selectivity of the propane dehydrocyclodimerization reaction itself also increased when thiophene was present as a scavenger for propane-derived hydrogen and hydrogen-rich intermediates [3]. Reactions among

Table 3

Comparison of product selectivities (on a per total carbon basis of both reactants) during pure alkane and alkane–thiophene reactions on H-ZSM5 (Si/Al = 14.5)

Reactants	He/ C ₄ H ₄ S	C ₃ H ₈	C ₃ H ₈ / C ₄ H ₄ S	C ₆ H ₁₄	C ₆ H ₁₄ / C ₄ H ₄ S	C ₁₀ H ₂₂	C ₁₀ H ₂₂ / C ₄ H ₄ S	C ₁₀ H ₂₂	C ₁₀ H ₂₂ / C ₄ H ₄ S
Reaction temperature (K)	773	773	773	673	673	673	673	673	673
Reactants (alkane/thiophene) (kPa)	0/1	20/0	20/1	20/0	20/1	6/0	6/1	12/0	12/1
Hydrocarbon formation rate (per Al 10 ⁻³ s ⁻¹)	–	0.94	1.7	31.9	11.9	90.6	37.2	145.7	71.3
Thiophene desulfurization rate (per Al 10 ⁻³ s ⁻¹)	0.070	–	0.63	–	1.21	–	3.10	–	10.0
Alkane conversion to hydrocarbons (%)	–	11.2	7.9	30.9	33.6	31.9	31.8	33.0	32.6
Thiophene conversion (%)	9.6	–	69.9	–	67.9	–	46.6	–	56.6
Selectivity (%C)									
CH ₄	0.27	25.0	17.7	0.14	0.23	0.036	0.037	0.040	0.039
C ₂ H ₄	1.1	34.5	21.7	3.2	3.8	2.7	2.3	2.6	2.2
C ₂ H ₆	0	6.9	3.9	1.2	1.8	0.3	0.3	0.3	0.2
C ₃ H ₆	0.45	20.1	9.9	8.7	9.8	19.7	18.0	16.4	15.2
C ₃ H ₈	0	–	–	32.2	30.9	14.3	13.8	14.8	14.0
Butenes	0	4.0	2.0	8.5	8.4	21.0	20.5	19.0	19.5
Butanes	0	4.7	2.1	25.6	19.5	15.7	15.2	17.6	16.9
C ₅ –C ₆	2.0	0.53	0.60	14.1 ^a	10.6 ^a	23.8	24.6	24.9	25.9
C ₇ –C ₈	–	–	–	–	–	1.4	1.4	2.2	2.3
C ₆₊ aromatics	4.9	4.1	34.5	5.7	13.4	1.3	3.2	2.4	3.4
Alkene/alkane ratios									
C ₃	–	–	–	0.27	0.32	1.38	1.30	1.11	1.09
C ₄	–	0.85	0.92	0.33	0.43	1.34	1.35	1.08	1.15
Sulfur selectivity (%)									
Hydrogen sulfide	49.1	–	90.5	–	92.9	–	89.8	–	95.7
Methylthiophenes	5.8	–	2.8	–	3.5	–	6.2	–	3.4
Dimethylthiophenes	0	–	0.5	–	2.0	–	3.0	–	0.8
Benzothiophene	45.1	–	6.3	–	1.6	–	1.0	–	0.0

^a Excluding *n*-hexane.

unsaturated products of thiophene and hydrogen-rich intermediates formed from alkanes lead to synergistic effects that increase the rate of both alkane dehydrocyclodimerization and thiophene desulfurization reactions.

The alkene to alkane ratios for C₃ and C₄ products of alkane and alkane–thiophene reactions are also shown in Table 3. Alkene/alkane ratios are greater when thiophene is present as a co-reactant (Table 3). This indicates that thiophene scavenges hydrogen and hydrogen-rich intermediates, leading to a higher selectivity to unsaturated products.

The various sulfur compounds formed are also shown in Table 3 and reported as sulfur selectivities, defined as the percentage of the sulfur in the converted thiophene appearing within each reaction product.

When thiophene is used as the sole reactant, it reacts predominately via bimolecular Diels–Alder reactions to form equimolar amounts of benzothiophene and hydrogen sulfide (Table 3). When alkanes were present as a hydrogen source, the hydrogen sulfide selectivity increased markedly, concurrently with a decrease in the selectivity to larger organosulfur compounds. Thiophene reacts with hydrogen and hydrogen-rich species rather than with other thiophene molecules, leading to the selective formation of hydrogen sulfide.

Detailed product distributions are shown in Figs. 1–3 as a function of alkane or total (alkane + thiophene) reactant conversion for each alkane and alkane–thiophene mixture; in these experiments, the reactant conversion was varied by changing the reactant residence time, or by allowing deactivation

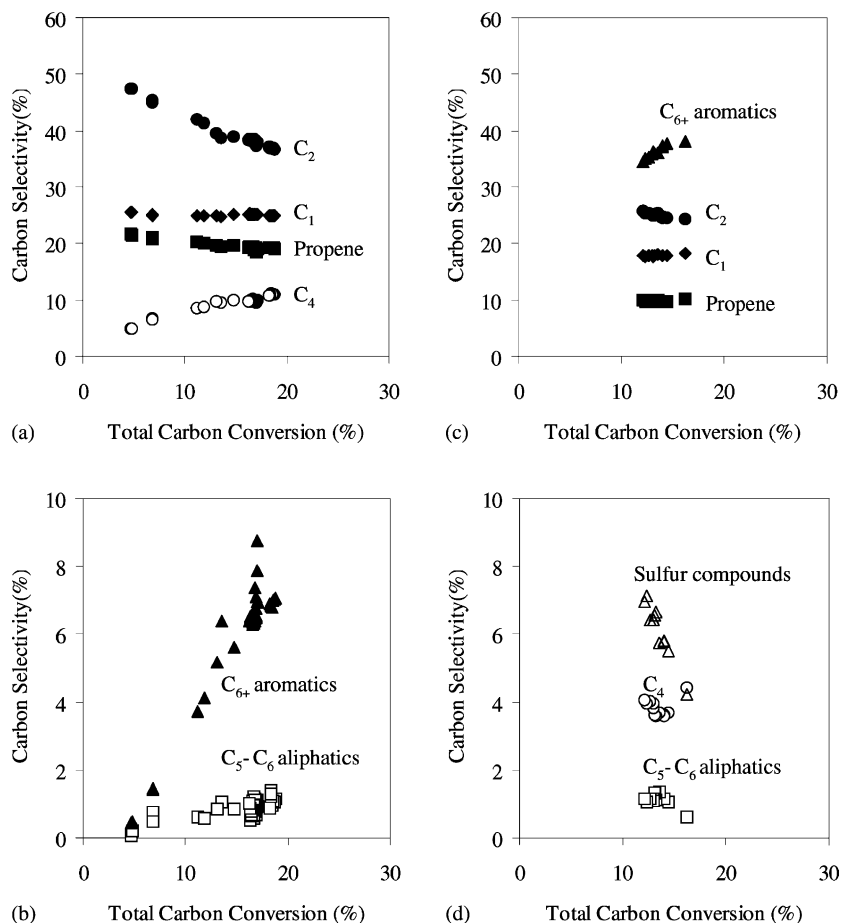


Fig. 1. Product selectivity of (a and b) propane and (c and d) propane–thiophene reactions on H-ZSM5 (Si/Al = 14.5) as a function of total carbon conversion ((a and b): 773 K, 20 kPa C₃H₈, balance He; (c and d): 773 K, 20 kPa C₃H₈, 1 kPa C₄H₄S, balance He).

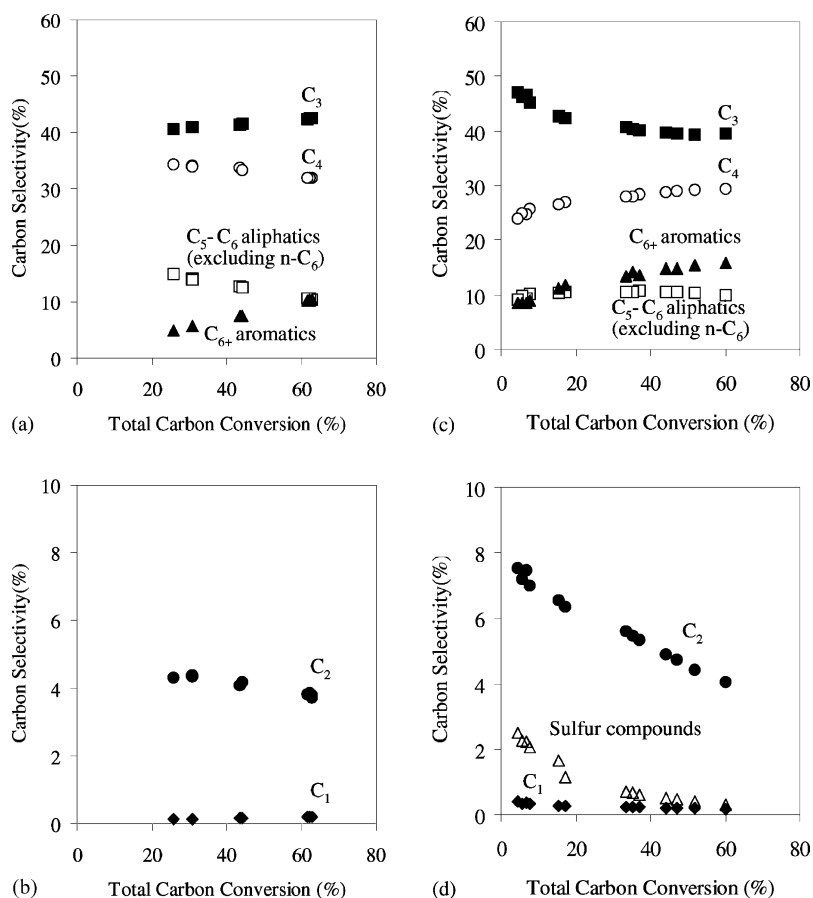
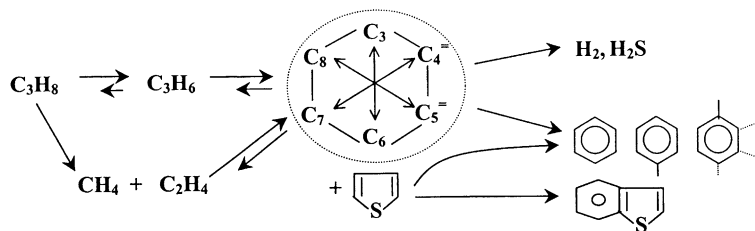


Fig. 2. Product selectivity of (a and b) hexane and (c and d) hexane–thiophene reactions on H-ZSM5 (Si/Al = 14.5) as a function of total carbon conversion: ((a and b): 673 K, 20 kPa C₆H₁₄, balance He; (c and d): 673 K, 20 kPa C₆H₁₄, 1 kPa C₄H₄S, balance He).

to proceed with increasing time on stream. C₁–C₂ products consist of methane, ethene, and ethane. The C₃ fraction contains both propene and propane and the C₄ products contain butenes and butanes; C₅–C₆ aliphatic products consist of pentenes, pentanes, hexenes, and hexanes. The C₆₊ aromatics fraction contains benzene, toluene, xylenes, as well as traces of higher aromatics. Alkylthiophenes and

benzothiophene were the predominant organosulfur compounds.

Product distributions for reactions of pure propane and of propane–thiophene reactants are shown in Fig. 1. At short contact times, C₁–C₂ products are formed via direct propane cracking, while propene and hydrogen are formed via propane dehydrogenation steps, as shown in the scheme below.



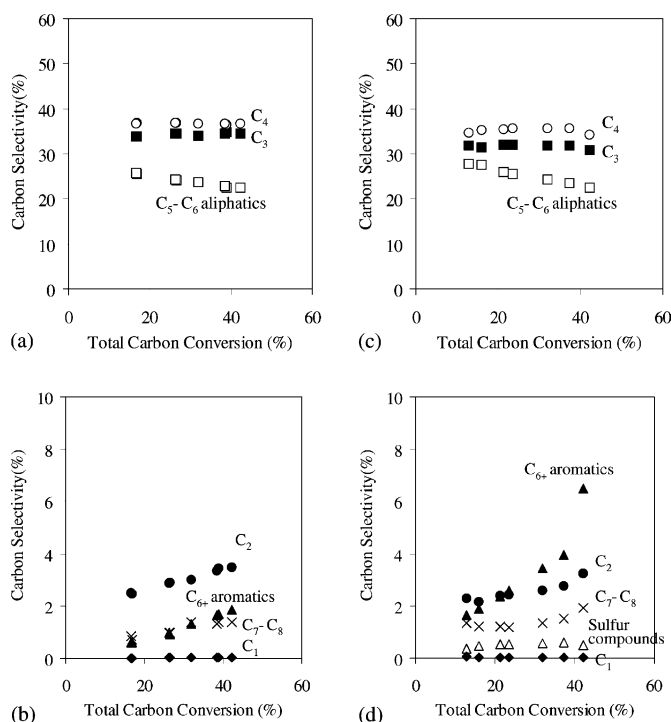


Fig. 3. Product selectivity of (a and b) decane and (c and d) decane–thiophene reactions on H-ZSM5 (Si/Al = 14.5) as a function of total carbon conversion: ((a and b): 673 K, 6 kPa C₁₀H₂₂, balance He; (c and d): 673 K, 6 kPa C₁₀H₂₂, 1 kPa C₄H₄S, balance He).

C₄ and C₆₊ products become more prevalent at higher conversions, because of their formation via secondary oligomerization and cracking reactions of alkenes. When thiophene was present, the selectivities to C₁–C₂, propene, and C₄ products were lower, while the selectivity to aromatics was higher (Fig. 1). Alkene intermediates react with thiophene to form aromatics, instead of participating in alternate pathways, such as hydrogenation or cracking, which lead to higher alkane selectivities. Previous studies have shown that the addition of alkenes to ethylthiophene increased its desulfurization reaction rate; this was attributed to the formation of carbocations from the added alkenes [13]. Thiophene does not appear to influence the types of reactions involved in propane conversion, but it reacts with hydrogen-rich intermediates derived from propane and leads to an increase in the overall selectivity for alkane conversion to aromatics.

C₃ and C₄ hydrocarbons are the predominant initial products of *n*-hexane cracking on H-ZSM5 at 673 K (Fig. 2), suggesting that cracking pathways in the

reaction scheme proposed above for propane become dominant as a result of the more stable carbocation intermediates available for larger chains. Cracking reactions initially involve direct β -scission reactions of hexane-derived adsorbed intermediates. C₂–C₄ alkene selectivities decreased with increasing conversion, while selectivities to C₂–C₄ alkane and C₆₊ aromatics products increased. The alkenes formed in primary cracking steps are consumed via hydrogenation to form alkanes and via oligomerization/cracking reactions to form aromatics with increasing residence time. Thiophene does not influence the nature of *n*-hexane cracking pathways, but it leads to higher selectivities to aromatics, with a concurrent decrease in the cracking selectivity (to C₃ and C₄ hydrocarbons), as also observed for propane reactants. It appears that these selectivity changes reflect reactions of unsaturated thiophene-derived fragments with alkenes to form aromatics containing carbon atoms from both thiophene and *n*-hexane as also observed for propane–thiophene mixtures.

n-Decane reactions include multiple cracking events, even at short residence times, suggesting that several C–C bonds are cleaved in one surface sojourn. Initial β -scission along the chain to form C₃–C₆ hydrocarbons is followed by sequential secondary cracking of these molecules (Fig. 3), with the ultimate formation of mixtures containing predominately C₃–C₄ molecules. As for propane and hexane co-reactants, thiophene addition to *n*-decane did not strongly influence the types of reactions, but it increased slightly the selectivity to aromatics while decreasing the selectivity to C₃–C₄ products.

The percentage of the sulfur removed that appears as hydrogen sulfide is shown in Fig. 4a as a function of thiophene conversion for pure thiophene feeds, for hydrogen–thiophene mixtures, and for each alkane–thiophene mixture. H₂S selectivities for all alkane–thiophene reactions are significantly higher than for reactions of pure thiophene or of H₂–thiophene mixtures (Fig. 4a). During reactions of pure thiophene, bimolecular Diels–Alder pathways lead to the preferential reaction of thiophene-derived fragments with another thiophene to give one hydrogen sulfide molecule and one benzothiophene molecule. Thus, it appears that the rate-controlling step in H₂S formation is the transfer of hydrogen from alkane-derived intermediates to unsaturated thiophene-derived fragments, as proposed in previous studies from the effects of hydride transfer agents on desulfurization rates [13] and from theoretical studies of acid-catalyzed thiophene desulfurization [20]. These conclusions are consistent with reports that cracking catalysts with higher hydrogen transfer activity tend to form fewer heavier sulfur compounds in fluid catalytic cracking processes [15].

Alkanes provide the hydrogen atoms required for desorption and desulfurization of these heavier organosulfur compounds, either via direct hydrogen transfer or via reactions of stranded unsaturated species with hydrogen-rich alkenes. The scavenging of thiophene-derived unsaturated intermediates using adsorbed hydrogen and hydrogen-rich intermediates or gas phase alkenes decreases the rate of bimolecular Diels–Alder reactions; this leads in turn to the formation of larger organosulfur compounds and to low H₂S selectivity. Fig. 4b shows the molar ratio of H₂S to organosulfur compounds as a function of thiophene conversion for pure thiophene, for

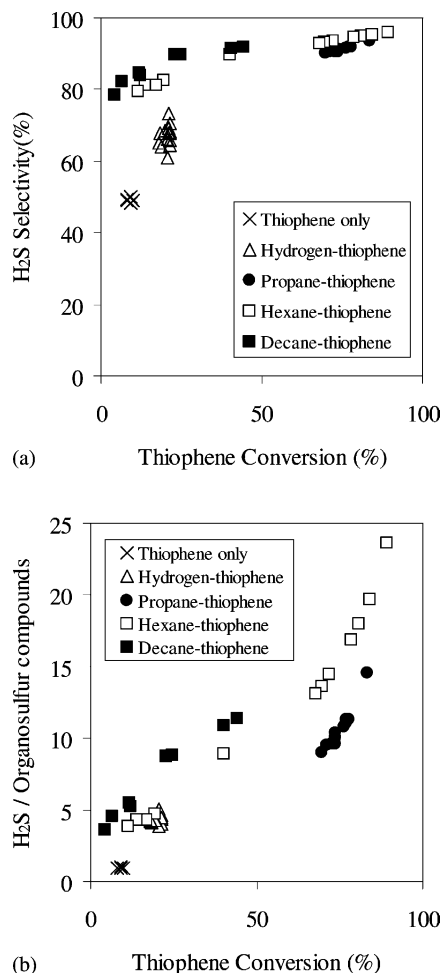


Fig. 4. (a) Hydrogen sulfide selectivity of alkane–thiophene reactions on H-ZSM5 (Si/Al = 14.5) as a function of thiophene conversion: thiophene only (773 K, 1 kPa C₄H₄S, balance He), hydrogen–thiophene (773 K, 200 kPa hydrogen, 1 kPa C₄H₄S, balance He), propane–thiophene (773 K, 20 kPa C₃H₈, 1 kPa C₄H₄S, balance He), hexane–thiophene (673 K, 20 kPa C₆H₁₄, 1 kPa C₄H₄S, balance He), decane–thiophene (673 K, 6 kPa C₁₀H₂₂, 1 kPa C₄H₄S, balance He). (b) Hydrogen sulfide/organosulfur compound molar ratio for alkane–thiophene reactions on H-ZSM5 (Si/Al = 14.5) as a function of thiophene conversion: thiophene only (773 K, 1 kPa C₄H₄S, balance He), hydrogen–thiophene (773 K, 200 kPa hydrogen, 1 kPa C₄H₄S, balance He), propane–thiophene (773 K, 20 kPa C₃H₈, 1 kPa C₄H₄S, balance He), hexane–thiophene (673 K, 20 kPa C₆H₁₄, 1 kPa C₄H₄S, balance He), decane–thiophene (673 K, 6 kPa C₁₀H₂₂, 1 kPa C₄H₄S, balance He).

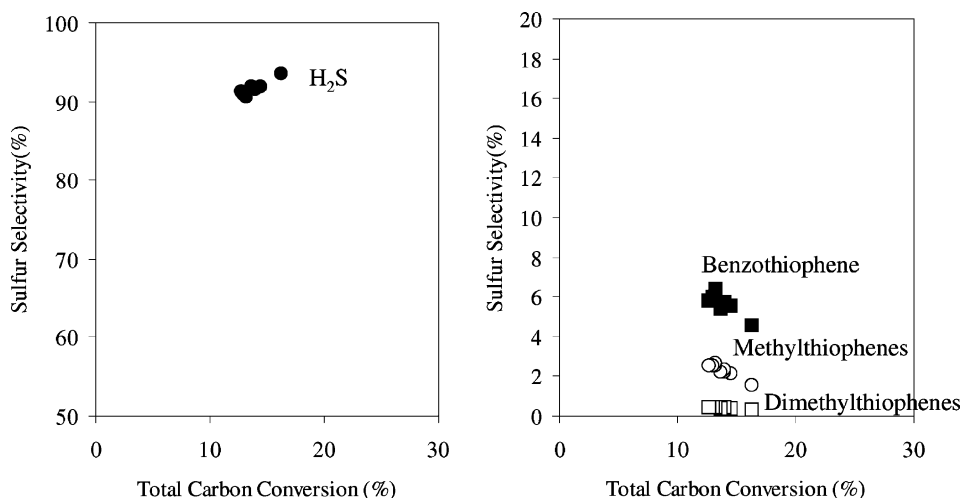


Fig. 5. Product sulfur selectivity of propane–thiophene reactions on H-ZSM5 (Si/Al = 14.5) as a function of total carbon conversion: 773 K, 20 kPa C_3H_8 , 1 kPa C_4H_4S , balance He.

the three alkane co-reactants used in this study, and for H_2 co-reactants. This ratio was larger with H_2 co-reactants than with pure thiophene feeds; it was even larger when alkanes were used as co-reactants. This selectivity ratio increased with increasing alkane chain length, apparently because of the higher reactivity and hydrogen transfer rates prevalent when higher alkanes are used as co-reactants, which is also

reflected in the observed increase of thiophene desulfurization rates with increasing alkane chain length (Table 1).

The detailed sulfur speciation among reaction products are shown in Figs. 5–7 for each alkane–thiophene mixture as a function of total (alkane + thiophene) reactant conversion. For all alkane co-reactants, hydrogen sulfide is the predominant sulfur compound

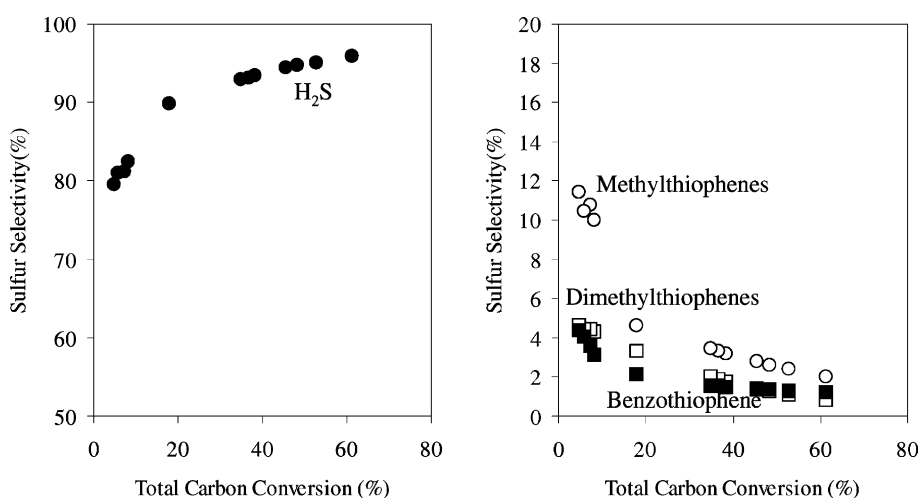


Fig. 6. Product sulfur selectivity of hexane–thiophene reactions on H-ZSM5 (Si/Al = 14.5) as a function of total carbon conversion: 673 K, 20 kPa C_6H_{14} , 1 kPa C_4H_4S , balance He.

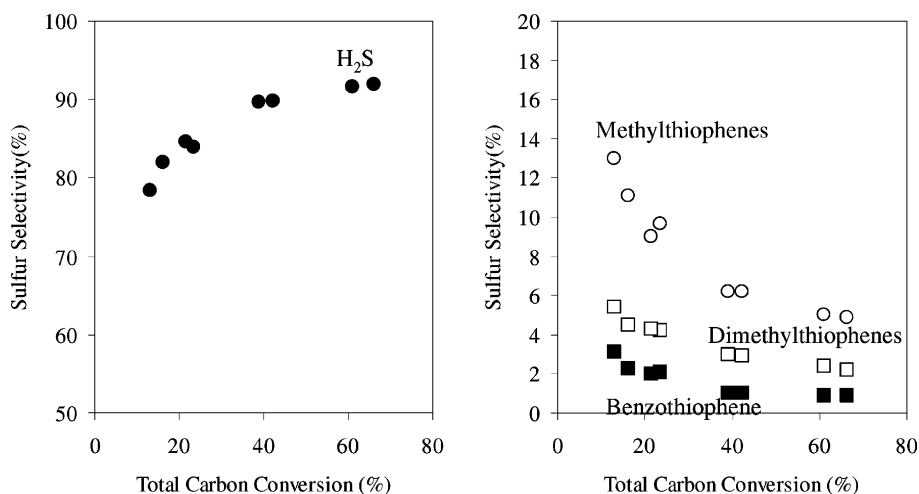


Fig. 7. Product sulfur selectivity of decane–thiophene reactions on H-ZSM5 (Si/Al = 14.5) as a function of total carbon conversion: 673 K, 6 kPa $C_{10}H_{22}$, 1 kPa C_4H_4S , balance He.

formed, but small amounts of organosulfur compounds (methylthiophene, dimethylthiophene, and benzothiophene) are also formed via alkylation of thiophene or via bimolecular Diels–Alder reactions (Figs. 5–7). With propane co-reactants, benzothiophene was the most prevalent organosulfur compound, while hexane and decane co-reactants led to the predominant formation of alkyl–thiophenes (Figs. 5–7). The lower reactivity of propane compared with that of larger alkanes led to lower rates for the scavenging of thiophene-derived precursors, which are required as intermediates in the formation of larger organosulfur compounds. With all three alkane co-reactants, the selectivity to methylthiophene is greater than that for dimethylthiophene (Figs. 5–7) and the H_2S selectivity increases with increasing conversion at the expense of the formation of organosulfur compounds (Figs. 5–7). This indicates that organosulfur compounds react further with increasing residence time to form hydrogen sulfide and hydrocarbon products in secondary desulfurization reactions.

4. Conclusions

Propane, *n*-hexane, and *n*-decane were used as an effective co-reactant in the selective desulfurization of thiophene to form hydrogen sulfide and hydrocar-

bons on H-ZSM5 at 673 K. Thiophene desulfurization rates, rate constants, and deactivation rates increased with increasing alkane chain size. The higher reactivity of larger alkanes leads to their more effective use as a source of hydrogen and hydrogen-rich intermediates, which are involved in reactions with unsaturated fragments formed in thiophene desulfurization reactions. All three alkanes are also more effective desulfurization co-reactants than H_2 (100–200 kPa, 773 K), even when H_2 dissociation sites, in the form of Zn cations, are introduced onto H-ZSM5 catalysts during synthesis. The presence and scavenging reactions of thiophene molecules do not alter the nature of alkane reaction pathways on H-ZSM5, but the selectivity for alkane conversion to aromatics increases as a result of the selective reaction of alkane-derived species with unsaturated fragments formed in thiophene decomposition and desulfurization reactions.

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