

PRIORITY COMMUNICATION

Desulfurization of Thiophene via Hydrogen Transfer from Alkanes on Cation-Modified H-ZSM5

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H-ZSM5, Zn/H-ZSM5, and Co/H-ZSM5 catalyze thiophene desulfurization with high H₂S selectivity using propane as the exclusive hydrogen source. Desulfurization rates and selectivities were much higher than at the H₂ concentrations present during propane reactions. Zn⁺² and Co⁺² cations at exchange sites increased desulfurization rates. On H-ZSM5, desulfurization rates and selectivities with propane coreactants (20 kPa) were equivalent to those obtained with >200 kPa H₂; on Zn- and Co-exchanged H-ZSM5, the equivalent H₂ pressures were 50–100 kPa. These data show that alkane dehydrogenation can be coupled with thiophene hydrogenation on surfaces to increase thiophene desulfurization and propane dehydrogenation rates simultaneously. © 1999 Academic Press

INTRODUCTION

Sulfur removal from gasoline range (C₄–C₁₀) streams without hydrogenation of unsaturated molecules or the excessive use of costly H₂ remains a significant challenge. Thiophene and alkyl-thiophenes are less reactive than other organosulfur species present in these hydrocarbon streams (e.g., alkyl sulfides, mercaptans). Sulfur compounds produce SO_x during combustion in engines and during catalyst regeneration in catalytic cracking units, leading to local contamination and to the poisoning of automotive exhaust catalysts. The ubiquitous presence of light alkanes in refinery and petrochemical streams and their frequent use for H₂ generation led us to consider the direct use of hydrocarbons in desulfurization reactions; these reactions are favored by thermodynamics at temperatures typical of cracking, dehydrogenation, and aromatization processes.

Our recent finding that reactions of light alkanes at 700–900 K on cation-exchanged zeolites are limited by the rate of removal of hydrogen as H₂ (1–4) suggested the use of the resulting high chemical potential of adsorbed hydrogen species by coupling alkane reactions with “hydrogenation” reactions. Stoichiometric hydrogen scavengers such as O₂, CO, and CO₂ can remove hydrogen formed in C–H activation steps and increase alkane dehydrogenation selectiv-

ity on H-ZSM5 and Zn/H-ZSM5 (5). Here we report the desulfurization of thiophene to form H₂S and useful unsaturated hydrocarbons using propane as the exclusive hydrogen source on catalysts based on H-ZSM5 and Zn- and Co-exchanged H-ZSM5. Propane coreactants (20 kPa) led to desulfurization rates and H₂S selectivities much higher than expected at the H₂ pressures prevalent during propane–thiophene reactions (1–3 kPa) and similar to those obtained at 50–300 kPa H₂. Catalytic desulfurization occurred without significant formation of benzothiophene or of unreactive sulfur–catalyst adducts and without requiring gas phase H₂. These results show that dehydrogenation reactions can be coupled kinetically with hydrogenation reactions of thiophene or its fragments. In this way, thiophene desulfurization and propane dehydrogenation rates both increase, because rate-determining steps in the two reactions are replaced with alternate steps, which appear to involve surface-mediated transfer of hydrogen species from C–H activation steps to thiophene-derived fragments.

METHODS

Na-ZSM5 (Zeochem, Si/Al = 14.5) was exchanged four times with a fresh solution of 0.16 M NH₄NO₃ at 353 K for 16 h in order to form NH₄-ZSM5 and then treated in dry air at 773 K for 20 h to form H-ZSM5. The residual Na content was <0.03 wt% by atomic absorption. Co/H-ZSM5 and Zn/H-ZSM5 were prepared by exchange of H-ZSM5 with 0.05 M Co(NO₃)₂ (Aldrich, 99%) and 0.005 M Zn(NO₃)₂ (Aldrich, >98.0%) solutions at 353 K for 16 h and 5 h, respectively, and then treated in dry air at 773 K for 20 h. Co and Zn contents were 0.91 wt% Co (Co/Al = 0.15) and 0.96 wt% Zn (Zn/Al = 0.14). Co and Zn exist as isolated divalent cations at exchange sites, and they replace two OH groups during exchange. Evidence for their location and local structure was obtained by isotopic exchange (D₂–OH) and X-ray absorption studies (6, 7).

Thiophene reaction rates were measured in a flow microreactor using C₄H₄S (1 kPa), C₃H₈ (20 kPa)/C₄H₄S (1 kPa),



or H₂ (0–200 kPa)/C₄H₄S (1 kPa) reactants at 773 K. Isotopic tracer studies using 1-¹³C–C₃H₈ (20 kPa)/C₄H₄S (1 kPa) were carried out in a gradientless batch reactor (3). Propane (Praxair, >99.5%, purified by 13X trap), 1-¹³C–propane (Isotec, 99% chemical purity, 98% isotopic purity), and thiophene (Aldrich, >99%) were used as reactants. H₂ (Praxair, UHP) and He (Praxair, UHP) were purified using O₂ (Matheson) and 13X sieve traps. Reactant and product concentrations and isotopic compositions were measured by gas chromatography and mass spectrometry, respectively, using procedures previously reported (8). Initial thiophene desulfurization rates were obtained by extrapolation to initial time on stream using measured first-order deactivation kinetics. Rates are reported per Al site in the zeolite and also per residual OH group after exchange. D₂ exchange with OH groups was used to measure the density of residual OH groups (7). Propane conversions were <15% in all experiments. Thiophene conversions varied over a much wider range and, when required, were converted to rate constants using the first-order kinetics measured in independent experiments. The rate constants correspond to rates given as mole thiophene/mole OH-s.

RESULTS AND DISCUSSION

Desulfurization rates for pure thiophene and for thiophene/propane mixtures are shown in Table 1 on H-ZSM5, Co/H-ZSM5, and Zn/H-ZSM5. These rates correspond to thiophene conversions between 10 and 15% for pure thiophene reactants and 65 and 85% for thiophene/propane reactants. The equilibrium thiophene conversion at the reaction conditions of Table 1 is >99% when C₆–C₈ aromatics are the predominant products of propane–thiophene reactions. On all catalysts, pure thiophene reacts slowly to form H₂S, benzothiophene, and dibenzothiophene. The larger organosulfur compounds form by unimolecular desulfur-

ization steps that produce H₂S and subsequent reactions of the hydrocarbon fragments or by direct bimolecular Diels–Alder pathways (9, 10).

The presence of propane (20 kPa) markedly increased desulfurization rates on all three catalysts (Table 1). On H-ZSM5, thiophene desulfurization turnover rates (per Brønsted acid site) increased almost tenfold ($0.067 \times 10^{-3} \text{ s}^{-1}$ to $0.64 \times 10^{-3} \text{ s}^{-1}$) when propane was added to thiophene reactants. This rate comparison underestimates the promoting effect of propane coreactants because of the higher thiophene conversion (and lower residual thiophene concentration) in the presence of propane. An integral reactor analysis using the measured first-order kinetics gave rate constants that increased from 1.55 to 26.2 cm³/mol OH · s when propane (20 kPa) was added to thiophene (1 kPa). As shown below, this increase in turnover rate constant is much greater than expected from the low H₂ concentrations (<1 kPa) present during reactions of propane on H-ZSM5.

Similar effects of propane coreactants were observed on Co/H-ZSM5 and Zn/H-ZSM5 (Table 1). Desulfurization turnover rates (per residual OH group) for propane–thiophene mixtures were higher on Co/H-ZSM5 ($1.1 \times 10^{-3} \text{ s}^{-1}$) and Zn/H-ZSM5 ($1.3 \times 10^{-3} \text{ s}^{-1}$) than on H-ZSM5 ($0.64 \times 10^{-3} \text{ s}^{-1}$), despite the lower conversions (and larger residual thiophene concentrations) in the latter. The corresponding first-order rate constants were also higher on Co/H-ZSM5 (39.9 cm³/mol OH · s) and Zn/H-ZSM5 (60.5 cm³/mol OH · s) than on H-ZSM5 (26.2 cm³/mol OH · s). The moderate desulfurization rates obtained on H-ZSM5 show that acid sites can catalyze propane–thiophene reactions. Co and Zn cations, however, increase the rate of these reactions, even though they replace acid sites, because they also appear to provide binding sites for thiophene reactants (11, 12). This promoting effect occurs even though cations increase hydrogen recombinative desorption rates

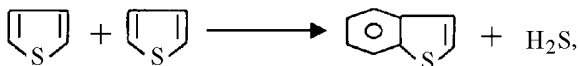
TABLE 1

Comparison of Thiophene Desulfurization Rates and (H₂S/Benzothiophene) Molar Ratios with and without Propane (773 K, 1 kPa C₄H₄S, 0 or 20 kPa C₃H₈, Balance He)

	Desulfurization rate (per Al, 10 ⁻³ , s ⁻¹)		Desulfurization rate (per OH group, 10 ⁻³ , s ⁻¹)		(H ₂ S/Benzothiophene) molar ratio	
	Thiophene only	With 20 kPa propane	Thiophene only	With 20 kPa propane	Thiophene only	With 20 kPa propane
H-ZSM5 (H/Al = 0.97)	0.065	0.62	0.067	0.64	3.4	31
Co/H-ZSM5 (Co/Al = 0.15) (OH/Al = 0.71)	0.19	0.79	0.26	1.1	5.6	71
Zn/H-ZSM5 (Zn/Al = 0.14) (OH/Al = 0.72)	0.14	0.91	0.19	1.3	5.0	56

and thus decrease the chemical potential of surface hydrogen species during propane reactions (4).

Propane coreactants also influence thiophene desulfurization selectivity (Table 1). On all catalysts, pure thiophene led to high selectivity to benzothiophene (BT) ($H_2S/BT = 3.4\text{--}5.6$), an undesired product of concerted or unconcerted bimolecular scavenging of the hydrocarbon fragments formed in C–S bond activation steps by another thiophene molecule. The exclusive decomposition of thiophene,



would lead to equimolar amounts of benzothiophene and H_2S . Table 1 shows (H_2S/BT) ratios greater than one, suggesting that either benzothiophene reacts further via Diels–Alder reactions to form additional H_2S molecules along with larger organosulfur compounds (e.g., dibenzothiophene) or that hydrogen is extracted from sacrificial adsorbed hydrocarbons in order to account for the higher than stoichiometric formation of H_2S . On all catalysts, propane coreactants increased (H_2S/BT) ratios by about a factor of 10 (Table 1). Adsorbed hydrogen atoms or gas phase alkenes formed during propane dehydrogenation reactions provide an alternate path for the removal of the unsaturated hydrocarbons formed during sulfur removal from thiophene. This is in agreement with a recent theoretical study (9), which suggested that thiophene desulfurization can take place on zeolitic acid sites when H_2 is present. This study proposed desulfurization pathways involving ring opening of thiophene on acid sites, desorption of H_2S , and hydrogenation of the resulting unsaturated hydrocarbon to form butadiene. At the conditions of our study, H atoms from either H_2 or propane can perform this last step, as well as sequential hydrogenation of alkynes and dienes to alkenes, with the ultimate formation of aromatics via dehydrocyclodimerization pathways that occur readily on cation-exchanged H-ZSM5.

The use of adsorbed H atoms formed in C–H bond activation steps, directly and without the intermediate involvement of gas phase H_2 formed during propane reactions, was confirmed by comparing first-order thiophene desulfurization rate constants (k) using H_2/C_4H_4S and C_3H_8/C_4H_4S reactant mixtures on H-ZSM5 (Fig. 1) and on Zn/H-ZSM5 (Fig. 2). The effect of H_2 was similar on Co/H-ZSM5 and those results will be reported in detail elsewhere (13). On all catalysts, H_2 and propane coreactants have similar qualitative effects on thiophene desulfurization reactions. Both H_2 and C_3H_8 increased thiophene desulfurization rate constants and (H_2S/BT) selectivity ratios by providing a source of hydrogen for S removal as H_2S . These hydrogen species also hydrogenate unsaturated thiophene-derived carbon fragments and introduce the resulting hydrocarbons into oligomerization-cracking cycles that lead to the alkene and

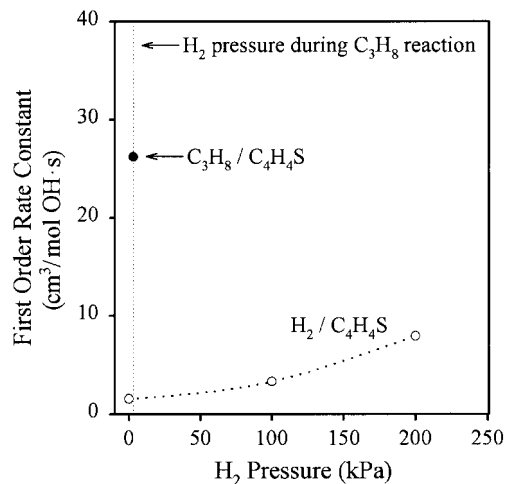


FIG. 1. Comparison of first-order thiophene desulfurization rate constants in the presence of propane or hydrogen on H-ZSM5 (773 K, 1 kPa C_4H_4S , 20 kPa C_3H_8 or 0–200 kPa H_2 , balance He).

aromatic products typically formed in reactions of light alkanes on cation-exchanged H-ZSM5 (2). The H_2 pressures required in order to reach the rate constants and selectivities obtained with propane (20 kPa), however, are higher than those present during propane dehydrogenation and aromatization on H-ZSM5 and Zn/H-ZSM5 (0–3 kPa; Figs. 1 and 2).

H_2 pressures are very low during propane or propane–thiophene reactions at the conversions of our study (<1 kPa on H-ZSM5; <2–3 kPa on Zn/H-ZSM5). These pressures are shown as dotted vertical lines in Figs. 1 and 2 at 773 K and 10–15% propane conversion levels. Thiophene desulfurization rate constants with C_3H_8 coreactants (20 kPa) are much higher than those obtained when 1–3 kPa H_2 was added to

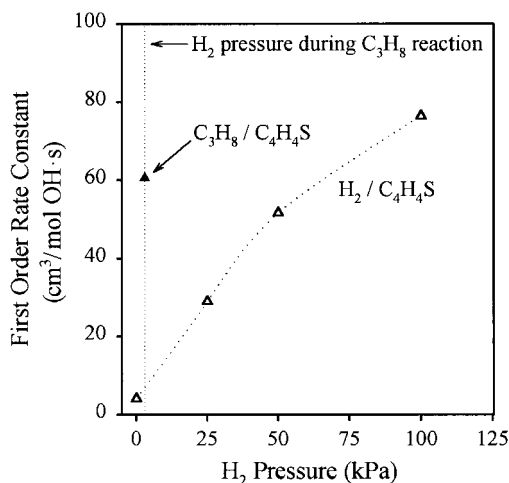


FIG. 2. Comparison of first-order thiophene desulfurization rate constants in the presence of propane or hydrogen on Zn/H-ZSM5 (773 K, 1 kPa C_4H_4S , 20 kPa C_3H_8 or 0–100 kPa H_2 , balance He).

thiophene reactant streams (Figs. 1 and 2). Therefore, the observed thiophene desulfurization reactions occur using alkanes as a direct source of hydrogen atoms; they do not involve reactions of the gas phase H_2 molecules formed during propane reactions.

The effects of H_2 are weaker on H-ZSM5 than on cation-exchanged H-ZSM5, because H-ZSM5 dissociates H_2 slowly (3). As a result, the chemical potential of hydrogen is lower on the surface than in the gas phase. The reverse of this step—the recombinative desorption of hydrogen to form H_2 —is also slow and controls the rate and selectivity of propane reactions on H-ZSM5. This desorption bottleneck leads to a high hydrogen surface chemical potential, which corresponds to a surface in (virtual) equilibrium with a H_2 pressure much higher than in the contacting gas phase (1, 3, 4, 14).

On H-ZSM5, thiophene desulfurization rate constants using propane (20 kPa) were higher than those obtained even at 200 kPa H_2 (Fig. 1). In effect, C–H bond activation occurs more rapidly on H-ZSM5 than H–H activation. As a result, propane is kinetically preferred over H_2 as a source of hydrogen for thiophene desulfurization reactions on H-ZSM5. Desorption bottlenecks caused by slow recombinative desorption steps preserve a high chemical potential of adsorbed hydrogen species, which favors the rapid hydrogenation of adsorbed thiophene or of its decomposition fragments.

On Zn/H-ZSM5, thiophene desulfurization rates are influenced by H_2 pressure more strongly than on H-ZSM5 (Figs. 1 and 2). Zn (and Co) cations catalyze recombinative desorption of adsorbed hydrogen and therefore also dissociative H_2 chemisorption. Surface and gas phase hydrogen pools communicate more effectively when these cations are present. As a result, H atoms from H_2 contribute more effectively to surface hydrogen than on H-ZSM5 and they compete with those formed in C–H bond activation steps. The resulting surface hydrogen chemical potential corresponds to an equivalent pressure considerably lower than on H-ZSM5, but still higher than in the contacting H_2 gas phase. These conclusions were confirmed quantitatively by measurements of the D-content in products formed from C_3H_8 – D_2 mixtures (3). Thiophene desulfurization rate constants using propane coreactants on Zn/H-ZSM5 ($60.5 \text{ cm}^3/\text{mol OH} \cdot \text{s}$) are equivalent to those obtained using 50–100 kPa H_2 (51.7 – $76.5 \text{ cm}^3/\text{mol OH} \cdot \text{s}$). The exact nature of the H-species transferred from propane to thiophene or its fragments remains unclear. It is likely, however, that the chemical potential of hydrogen on these surfaces is reflected in the hydrogen content of the unsaturated carbocations and alkoxide species prevalent on zeolite surfaces during hydrocarbon and alcohol reactions at high temperatures (15, 16).

H_2 and propane have similar effects on (H_2S /BT) selectivity ratios, which increase with increasing H_2 concentra-

tion or with the presence of propane on all catalysts. As also found for desulfurization rates, H_2 concentration effects on selectivity are much stronger on Zn/H-ZSM5 than on H-ZSM5 because Zn cations increase H_2 dissociation rates and thus the ability of gas phase H_2 to participate in hydrogenation reactions. On H-ZSM5, propane coreactants (20 kPa) lead to (H_2S /BT) ratios higher than those obtained even at 200 kPa H_2 . On Zn/H-ZSM5, H_2 pressures of 50–100 kPa lead to (H_2S /BT) ratios similar to those obtained with 20 kPa propane, an equivalence also found for thiophene desulfurization rates. A similar equivalence was found when deactivation rate constants using propane or H_2 as coreactants were compared. Both coreactants decreased deactivation rates, apparently by hydrogenating unsaturated deposits, but the H_2 pressures required to reach deactivation rates similar to those with propane (0.06 h^{-1} deactivation rate constant) were 50–100 kPa on Zn/H-ZSM5 and >200 kPa on H-ZSM5 (13).

A previous attempt at desulfurization reactions using hydrocarbons as a hydrogen source involved the concurrent dehydrogenation of more reactive hydrocarbons (decalin, methylcyclohexane) in the presence of significant H_2 partial pressures (600 kPa) at 673 K on carbon-supported Mo (17). These authors concluded that H_2 was involved in bifunctional hydrodesulfurization pathways, but that the rate of dehydrogenation was faster than the desulfurization rate; thus, no net consumption of H_2 occurred. The proposed mechanisms involved dehydrogenation on the carbon support and H_2 desorption on Mo sites, with the resulting H_2 participating along with the H_2 fed in conventional thiophene desulfurization reactions. In our work, more refractory light alkanes were used and the hydrogen formed was used directly before recombinative desorption, thus exploiting the high chemical potential of hydrogen at surfaces catalyzing alkane reactions limited by hydrogen desorption bottlenecks.

Propane reaction pathways in the absence of thiophene have been described in several previous studies (2, 3, 8, 18–20). The mechanism of desulfurization of thiophene using light alkanes was probed using $^{13}\text{C}_3\text{H}_7\text{CH}_3/\text{C}_4\text{H}_4\text{S}$ reactant mixtures in our study (6). The presence of thiophene increased the rate of aromatics formation from propane (measured from the appearance of ^{13}C -labeled aromatics), apparently as the result of the scavenging of surface hydrogen and of alkenes formed from propane by desulfurization reactions of thiophene. Thus, the coupling between a dehydrogenation reaction limited by hydrogen removal and a hydrogenation reaction that requires adsorbed hydrogen species leads to synergistic effects that increase the rate of both dehydrogenation and hydrogenation steps. While reactions of pure $^{13}\text{C}_3\text{H}_7\text{CH}_3$ on H-ZSM5 led to a random isotopomer distribution of ^{13}C in all products (2), the initial products of $^{13}\text{C}_3\text{H}_7\text{CH}_3/\text{C}_4\text{H}_4\text{S}$ mixtures contained an excess of toluene isotopomers with one ^{13}C (6).

This suggests that alkenes formed from $^{13}\text{C}_3\text{H}_6$ exit the oligomerization-cracking cycles, which cause the intramolecular isotopic scrambling, more rapidly when thiophene desulfurization occurs concurrently with propane dehydrocyclodimerization.

Similar kinetic coupling can occur during reactions of more reactive larger alkanes, cycloalkanes, and alkenes during catalytic cracking and aromatization reactions. Also, the removal of less refractory organosulfur compounds, such as mercaptans and sulfides, is likely to be feasible using similar dehydrogenation-hydrogenation kinetic coupling. Therefore, the proposed approach should apply in general to the desulfurization of the typical sulfur compounds in gasoline during processing of hydrocarbon streams. The reactions described provide plausible pathways for the formation of H_2S and of larger organosulfur compounds during catalytic cracking and a potential approach for the enhancement of sulfur removal within catalytic cracking processes by introducing lighter hydrocarbon fractions at specific positions along riser fluid bed reactors.

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