

## Coupling Alkane Dehydrogenation with Hydrogenation Reactions on Cation-Exchanged Zeolites

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Thiophene desulfurization was achieved using hydrogen surface species formed during dehydrogenation of alkanes on H-ZSM5 modified by exchanged cations (M = Co, Mo, Zn) with the selective formation of H<sub>2</sub>S without direct involvement of the H<sub>2</sub> formed in alkane reactions. Thiophene reactions in the absence of a hydrogen source (H<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>) lead to significant formation of benzothiophene and dibenzothiophene by-products. Propane markedly increases desulfurization rates and H<sub>2</sub>S selectivities, while inhibiting catalyst deactivation on all catalysts. Rates, selectivities, and deactivation rates using propane (20 kPa) as a direct hydrogen source are equivalent to those obtained at >200 kPa H<sub>2</sub> on H-ZSM5 and to 50-100 kPa H<sub>2</sub> on Co/H-ZSM5 and much higher than at the H<sub>2</sub> pressures prevalent during alkane reactions (1-2 kPa). Alkane reactions on M/H-ZSM5 are limited by hydrogen desorption bottlenecks that lead to surface hydrogen chemical potentials higher than those in the contacting H<sub>2</sub> gas phase. The addition of these hydrogen species to thiophene leads to the observed desulfurization, which provides an alternate path for hydrogen removal and leads to higher alkane dehydrogenation rates. This synergistic coupling occurs on H-ZSM5, but cations appear to provide a promotional effect. Cations provide recombinative desorption sites that decrease the availability and chemical potential of adsorbed hydrogen, but they also appear to be involved in providing alternate binding sites for hydrodesulfurization reactions.

### 1. INTRODUCTION

Sulfur compounds in crude oil often remain in fuels, leading to their release and to the poisoning of exhaust catalysts. Environmental concerns and legislation will lead to a significant decrease in the sulfur content of diesel and gasoline fuels (400 to <40 ppm) [1]. Catalytic cracking (FCC) naphtha contributes most of the sulfur compounds in gasoline [1]. Some desulfurization via hydrogen transfer to form H<sub>2</sub>S occurs during FCC, but thiophene and alkylthiophenes remain largely unreacted and can adsorb on FCC catalysts, leading to SO<sub>x</sub> release during regeneration [2]. Sulfur removal from FCC naphtha requires hydrodesulfurization processes that lead to significant hydrogenation of high-octane alkenes and aromatics. Thiophene desulfurization without significant saturation and H<sub>2</sub> requirements would provide alternate process options and mechanistic details of largely unexplored hydrogen transfer reactions. This study explores one example of such chemistry - the desulfurization of thiophene with selective formation of H<sub>2</sub>S using alkanes as direct hydrogen sources on cation-exchanged zeolites.

Alkane dehydrogenation and dehydrocyclodimerization on cation-modified H-ZSM5 lead to hydrogen removal bottlenecks that limit reaction rates and lead to the formation of hydrogen-rich cracking products [3, 4]. This bottleneck causes the chemical potential of adsorbed hydrogen to be significantly higher than that of H<sub>2</sub> in the contacting gas phase, leading to the hydrogenation of adsorbed species that can cause the undesired formation of hydrogen-rich light alkanes as a side product of dehydrogenation and aromatization steps [5]. These observations led to the use of concurrent desired hydrogenation reactions to remove the desorption bottleneck and to upgrade unsaturated molecules such as O<sub>2</sub>, CO, and CO<sub>2</sub> [6]. Here, we report the hydrodesulfurization of thiophene using surface hydrogen formed in-situ during propane dehydrogenation reactions on H-ZSM5 modified by exchanged Co, Zn, and Mo.

## 2. EXPERIMENTAL METHODS

### 2.1. Catalyst Preparation and Elemental Analysis

Na-ZSM5 (Zeochem, Si/Al = 14.5) was converted to the ammonium form (NH<sub>4</sub>-ZSM5) by exchange with a 0.16 M NH<sub>4</sub>NO<sub>3</sub> solution (Fisher, Certified ACS, >98.0%) at 353 K for 16 h four times using fresh NH<sub>4</sub>NO<sub>3</sub> solutions to ensure complete exchange. The zeolite sample was filtered and washed with deionized water. Samples were dried in air at 398 K for 20 h and calcined at 773 K for 20 h in flowing dry air to convert to the proton form of the zeolite (H-ZSM5). Co/H-ZSM5 was prepared by ion exchange of H-ZSM5 at 353K for 16 h in a 0.05 M Co(NO<sub>3</sub>)<sub>2</sub> solution (Aldrich, 99%). The sample was filtered, washed with deionized water, dried in air at 398 K for 20 h, and then treated in flowing dry air at 773 K for 20 h. Atomic absorption spectroscopy (Galbraith Laboratories, Inc.) measured a Co content of 0.91 wt% (Co/Al = 0.15). Co<sup>+2</sup> isolated cations are located at the exchange site and replace two Brønsted acid sites during exchange. These characterization data will be reported elsewhere [7]. Zn/H-ZSM5 was prepared by aqueous exchange methods that lead to the predominant formation of Zn<sup>+2</sup> cations bridging two Al sites [8]. Mo/H-ZSM5 was prepared by solid-state exchange methods using MoO<sub>3</sub>/H-ZSM5 physical mixtures, which lead to the formation of (Mo<sub>2</sub>O<sub>5</sub>)<sup>+2</sup> dimers interacting with two Al sites [9].

### 2.2. Catalytic Thiophene Desulfurization

Thiophene desulfurization studies were performed in a tubular reactor with plug-flow hydrodynamics. Rates, selectivities, and deactivation behavior were measured at 773 K using C<sub>3</sub>H<sub>8</sub> (20 kPa)/C<sub>4</sub>H<sub>4</sub>S (1 kPa), H<sub>2</sub> (0-200 kPa)/C<sub>4</sub>H<sub>4</sub>S (1 kPa), or pure C<sub>4</sub>H<sub>4</sub>S (1 kPa) reactants. C<sub>3</sub>H<sub>8</sub> (Praxair, >99.5%) was purified using O<sub>2</sub>/H<sub>2</sub>O traps (Matheson) and C<sub>4</sub>H<sub>4</sub>S (Aldrich, >99%) was used without purification. H<sub>2</sub> (Praxair, UHP) and He (Praxair, UHP) were purified using O<sub>2</sub> and 13X sieve traps (Matheson). Reactant and product concentrations were measured by gas chromatography (Hewlett-Packard 6890) using capillary (HP-1 Crosslinked Methyl Siloxane, 50m x 0.32mm, 1.05 μ film) and packed columns (Hayesep-Q, 80/100 mesh, 10' x 0.125") and flame ionization and thermal conductivity detection. Thiophene reaction rates are reported as molar thiophene conversion rates per Al or per residual OH group after exchange. Isotopic exchange (D<sub>2</sub>-OH) experiments were used to determine the number of residual OH groups [8, 9]. Sulfur selectivities are reported on a sulfur basis as the percentage of sulfur from the converted thiophene that appears in each sulfur-containing product. 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 rate expression obtained in independent kinetic experiments. The rate constants correspond to rates expressed as mole thiophene/mole OH-s. The deactivation behavior of the catalysts was studied at a constant space velocity.

### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of Propane on Thiophene Desulfurization

Thiophene desulfurization rates (per OH group) on H-ZSM5, Co/H-ZSM5, and Zn/H-ZSM5 are shown in Figure 1 with and without  $C_3H_8$  as a co-reactant. In the absence of  $C_3H_8$ , desulfurization proceeds slowly and leads to  $H_2S$ , benzothiophene (BT), and dibenzothiophene. The larger sulfur compounds can form via thiophene desulfurization to  $H_2S$  and subsequent reaction of thiophene fragments with another thiophene or via bimolecular Diels-Alder reactions of two thiophene molecules [10, 11]. Propane (20 kPa) markedly increases thiophene desulfurization rates on all three catalysts, apparently by increasing the availability of hydrogen adatoms required for C-S bond activation and for the hydrogenation of thiophene fragments. The rates reported in Figure 1 were obtained at high but similar  $C_4H_4S$  conversions (65-85%), which are not limited by thermodynamics [12], and low  $C_3H_8$  conversions (<15%). Thus, they reflect the relative catalytic activities of these materials in spite of the integral reactor conditions imposed by the high thiophene conversions. A kinetic analysis using the measured first order rate dependence on  $C_4H_4S$  concentration was used to rigorously calculate reaction rate constants ( $k$ ). For example, the addition of propane increases the value of  $k$  from 1.55 to 26.2  $cm^3/mole$  OH-s on H-ZSM5 and from 6.45 to 39.9  $cm^3/mole$  OH-s on Co/H-ZSM5.

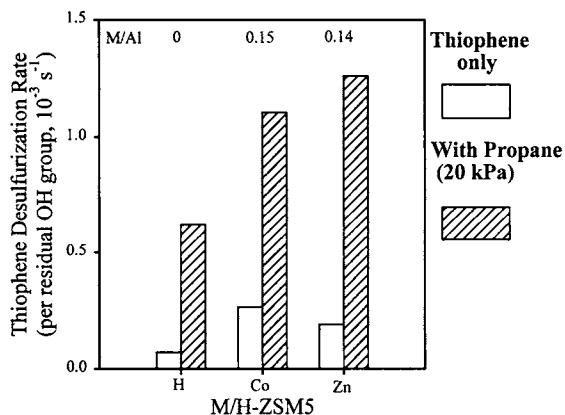


Figure 1: Comparison of thiophene desulfurization rates with and without propane [773 K, 1 kPa  $C_4H_4S$ , 0 or 20 kPa  $C_3H_8$ , balance He]

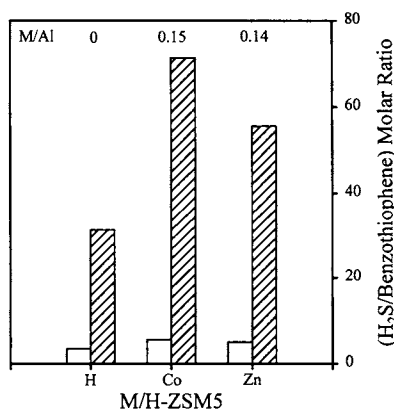


Figure 2: Comparison of ( $H_2S$ /benzothiophene) molar ratio with and without propane [773 K, 1 kPa  $C_4H_4S$ , 0 or 20 kPa  $C_3H_8$ , balance He]

The availability of reactive adsorbed hydrogen species with  $C_3H_8$  as a co-reactant also influences thiophene desulfurization selectivity (Figure 2). The ( $H_2S$ /BT) ratio is significantly higher when  $C_3H_8$  is present; hydrogen species are used to hydrogenate unsaturated thiophene fragments and to decrease the probability of direct or indirect thiophene self-reactions that lead to more refractory organosulfur compounds.

In addition, the coupling of propane dehydrogenation with thiophene desulfurization not only increases the rate of thiophene desulfurization, but also increases the rate of propane

conversion based on our preliminary results using  $^{13}\text{C}$ -labeled propane and unlabeled thiophene reactants, in agreement with the concept of kinetic coupling.

### 3.2. Effect of Cations on Thiophene Desulfurization

The effect of Co, Mo, and Zn cations on the rate of propane-thiophene reactions is shown in Table 1 for a set of samples with similar M/Al ratios. Also reported in Table 1 are the OH densities of each sample, obtained from  $\text{D}_2$ -OH isotopic exchange measurements after cation exchange. H-ZSM5, which contains predominantly Brønsted acid sites associated with Al sites (OH/Al $\sim$ 1), catalyzes propane-thiophene reactions, suggesting that such sites can be used to activate both propane and thiophene reactants. This is in agreement with a recent theoretical study which showed that thiophene desulfurization occurs on acidic zeolites in the presence of  $\text{H}_2$  [10]. Thiophene desulfurization was proposed to proceed via a two-step pathway: opening of the thiophene ring on the Brønsted acid site, and removal of sulfur as  $\text{H}_2\text{S}$  and formation of butadiene in the presence of  $\text{H}_2$ . Butadiene is expected to be too reactive to be isolated and is rapidly converted to aromatics on H-ZSM5. Reaction rates (normalized by the number of Al atoms) are slightly higher on Co- and Zn-exchanged samples than on H-ZSM5, even though each divalent cation has replaced about two Brønsted acid sites during exchange. In the case of Mo/H-ZSM5, the severe conditions required for solid-state exchange lead to significant dealumination [9], and desulfurization rates are lower than on H-ZSM5 because of their very low OH/Al ratios (Table 1).

Reaction rates normalized instead by the number of residual OH groups show a much greater effect of cations, suggesting that cations enhance the activity of the catalysts, either by providing parallel desulfurization pathways or by introducing bifunctional desulfurization pathways (Table 1). Cations appear to have two counteracting effects on propane-thiophene reactions. Cations increase the rate of recombinative hydrogen desorption during alkane reactions and thus decrease the availability of surface hydrogen for desulfurization reactions [4-6]. On the other hand, cations can provide binding sites for thiophene adsorption and reactions, which can intercept recombinative desorption steps and scavenge hydrogen before desorption as  $\text{H}_2$ . Na and K cations in H-ZSM5 have been shown to bind sulfur compounds, such as thiophene and  $\text{H}_2\text{S}$  [13, 14].

Table 1: Comparison of thiophene desulfurization rates on H-ZSM5 and M/H-ZSM5 (M=Co, Mo, Zn) [773 K, 1 kPa  $\text{C}_4\text{H}_4\text{S}$ , 20 kPa  $\text{C}_3\text{H}_8$ , balance He]

Catalyst	M/Al Ratio	OH/Al Ratio	Desulfurization Rate (per Al, $10^{-3}, \text{s}^{-1}$ )	Desulfurization Rate (per OH group, $10^{-3}, \text{s}^{-1}$ )
H-ZSM5	0	0.97	0.62	0.64
Co/H-ZSM5	0.15	0.71	0.79	1.11
Mo/H-ZSM5	0.18	0.25	0.22*	0.88*
Zn/H-ZSM5	0.14	0.72	0.91	1.26

\* measured at 3 kPa; corrected to 1 kPa thiophene using measured rate expression

### 3.3. $\text{C}_3\text{H}_8$ and $\text{H}_2$ as Hydrogen Sources on H-ZSM5 and Co/H-ZSM5

$\text{C}_3\text{H}_8$  and  $\text{H}_2$  were compared as hydrogen sources by measuring thiophene desulfurization rates and selectivities using  $\text{C}_3\text{H}_8/\text{C}_4\text{H}_4\text{S}$  and also  $\text{H}_2/\text{C}_4\text{H}_4\text{S}$  reactant mixtures with varying  $\text{H}_2$  concentrations on H-ZSM5 and Co/H-ZSM5 (Table 2).

Table 2: Comparison of thiophene desulfurization rates and (H<sub>2</sub>S/BT) molar ratios in the presence of H<sub>2</sub> or propane on H-ZSM5 and Co/H-ZSM5 [773 K, 1 kPa C<sub>4</sub>H<sub>4</sub>S, 0-200 kPa H<sub>2</sub> or 20 kPa C<sub>3</sub>H<sub>8</sub>, balance He]

H-ZSM5			Co/H-ZSM5		
Gas Phase Pressure of Hydrogen Source (kPa)	Thiophene Desulfurization Rate (per residual OH group, 10 <sup>-3</sup> , s <sup>-1</sup> )	(H <sub>2</sub> S/BT) Molar Ratio	Gas Phase Pressure of Hydrogen Source (kPa)	Thiophene Desulfurization Rate (per residual OH group, 10 <sup>-3</sup> , s <sup>-1</sup> )	(H <sub>2</sub> S/BT) Molar Ratio
0	0.067	3.45	0	0.26	5.56
100 (H <sub>2</sub> )	0.13	5.67	25 (H <sub>2</sub> )	0.83	27.9
200 (H <sub>2</sub> )	0.28	6.57	50 (H <sub>2</sub> )	1.01	43.0
20 (C <sub>3</sub> H <sub>8</sub> )	0.62	31.3	100 (H <sub>2</sub> )	1.29	129
			20 (C <sub>3</sub> H <sub>8</sub> )	1.08	71.4

At the pressures and conversions of our study, C<sub>3</sub>H<sub>8</sub> reactions lead to gas phase H<sub>2</sub> pressures of 0-0.5 kPa on H-ZSM5 and 0-2 kPa on Co/H-ZSM5. The higher H<sub>2</sub> pressures on Co/H-ZSM5 reflect the effect of cations on the rate and H<sub>2</sub> selectivity of propane reactions, as previously reported also on Ga- and Zn-exchanged H-ZSM5 [4, 15]. The direct use of hydrogen from alkanes without the involvement of H<sub>2</sub>, is demonstrated by the higher desulfurization rates obtained with C<sub>3</sub>H<sub>8</sub> (at 20 kPa) than with H<sub>2</sub> at pressures even higher than those existing during propane reactions on both H-ZSM5 and Co/H-ZSM5 (Table 2).

On H-ZSM5, desulfurization rates and (H<sub>2</sub>S/BT) ratios using 20 kPa propane exceed those obtained with 200 kPa H<sub>2</sub> (Table 2). Increasing H<sub>2</sub> pressures slightly increase desulfurization rates and H<sub>2</sub>S selectivities; these effects are directionally similar to those obtained when propane is introduced as a hydrogen source and they suggest that H adatoms formed from propane and H<sub>2</sub> are kinetically similar. Clearly, the H<sub>2</sub> available during propane-thiophene reactions cannot account for the high desulfurization rates obtained using propane as the hydrogen source. The (H<sub>2</sub>S/BT) ratio also reflects hydrogen availability and the effectiveness of the hydrogen source. (H<sub>2</sub>S/BT) ratios are higher with C<sub>3</sub>H<sub>8</sub> (20 kPa) than with 200 kPa H<sub>2</sub> (Table 2) confirming our conclusion that propane reactants lead to hydrogen surface concentrations that exceed those that would exist in equilibrium with 200 kPa H<sub>2</sub> on H-ZSM5. A hydrogen desorption bottleneck on H-ZSM5 leads to high chemical potentials of adsorbed hydrogen species, which are effectively used in hydrogenation reactions of thiophene species with the selective formation of H<sub>2</sub>S and aromatics via pathways similar to those involved using H<sub>2</sub> as the hydrogen source.

On Co/H-ZSM5, desulfurization rates with 20 kPa C<sub>3</sub>H<sub>8</sub> are similar to those achieved with 50-100 kPa H<sub>2</sub> (Table 2). (H<sub>2</sub>S/BT) ratios increase with increasing H<sub>2</sub> pressure and reach values similar to values obtained with C<sub>3</sub>H<sub>8</sub> co-reactants also at 50-100 kPa H<sub>2</sub>. This equivalent H<sub>2</sub> pressure (50-100 kPa) is lower on Co/H-ZSM5 than on H-ZSM5 (>200 kPa), because Co cations catalyze hydrogen adsorption-desorption steps. As a result, the availability of surface hydrogen is lower than on H-ZSM5 and H<sub>2</sub> can be more effectively used as a source of hydrogen than on H-ZSM5. Thiophene desulfurization rates for H<sub>2</sub>/C<sub>4</sub>H<sub>4</sub>S mixtures with H<sub>2</sub> pressures (1-2 kPa) typically present during propane reactions, however, were lower than for C<sub>3</sub>H<sub>8</sub>/C<sub>4</sub>H<sub>4</sub>S mixtures; therefore, desulfurization does not require gas phase H<sub>2</sub> on Co/H-ZSM5. Zn cations in H-ZSM5 show similar effects on the rate of hydrogen removal and on the equivalent H<sub>2</sub> pressure obtained during propane-thiophene reactions [12].

### 3.4. Effects of C<sub>3</sub>H<sub>8</sub> and H<sub>2</sub> on Catalyst Deactivation Rates

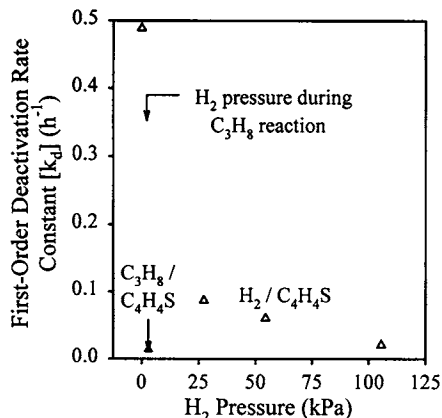


Figure 3: Comparison of first order deactivation rate constant ( $k_d$ ) in the presence of propane or H<sub>2</sub> on Co/H-ZSM5 [773 K, 1 kPa C<sub>4</sub>H<sub>4</sub>S, 20 kPa C<sub>3</sub>H<sub>8</sub> or 0-100 kPa H<sub>2</sub>, balance He, Co/Al=0.15]

Catalyst deactivation rates also depend on the availability of surface hydrogen species that decrease the level of unsaturation and increase the reactivity of strongly adsorbed carbonaceous deposits. Deactivation rates are proportional to the concentration of undeactivated catalytic sites. Treatment in 20% O<sub>2</sub> at 773 K restores initial desulfurization rates, suggesting that deactivation can be reversed by combustion of carbonaceous deposits. Deactivation rate constants ( $k_d$ ) with propane-thiophene reactants (0.014 h<sup>-1</sup>) are much lower than with pure thiophene (0.49 h<sup>-1</sup>). H<sub>2</sub> co-reactants also decrease deactivation rate constants, approaching the values obtained with propane at 50-100 kPa of H<sub>2</sub> (0.060-0.021 h<sup>-1</sup>) (Figure 3). Thus, reactions of propane-thiophene mixtures on Co/H-ZSM5 show deactivation behavior that reflects a surface with hydrogen

chemical potential similar to that present with 50-100 kPa H<sub>2</sub> in the contacting gas phase.

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