Kinetic, infrared, and X-ray absorption studies of adsorption, desorption, and reactions of thiophene on H-ZSM5 and Co/H-ZSM5

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Temperature programmed desorption and infrared and X-ray absorption near-edge spectroscopies were used during adsorption and reactions of thiophene in order to probe adsorbed intermediates and catalytic structures responsible for thiophene reactions with propane or H_2 on H-ZSM5 and Co/H-ZSM5. Infrared spectra showed that thiophene interacts with acidic OH groups in H-ZSM5 *via* hydrogen bonding at ambient temperature. No additional bands were detected on Co/H-ZSM5, suggesting the absence of specific interactions with Co cations. During adsorption at ambient temperatures, infrared bands assigned to CH_2 groups near C=C bonds or S-atoms and to S–H species were detected and H-ZSM5 and Co/H-ZSM5 acquired colors typical of thiophene oligomers. Slightly above ambient temperatures, benzene and H_2S formed from pre-adsorbed thiophene. These results indicate that hydrogen-bonded thiophene undergoes ring opening or oligomerization near ambient temperature on acidic OH groups in H-ZSM5. Some of the adsorbed thiophene (20–50%) interacts weakly with channel walls or with residual Na cations and desorbs unreacted. The remaining adsorbed thiophene desorbs as H_2S, aromatic hydrocarbons, and organosulfur compounds, such as methylthiophene and benzothiophene, or forms irreversibly adsorbed unsaturated organic deposits. *In situ* infrared studies during thiophene and thiophene–propane reactions at 773 K on H-ZSM5 and Co/H-ZSM5 showed that surface coverages of thiophene-derived intermediates were low on acidic OH groups and Co cations. Co K-edge X-ray absorption near-edge spectra measured during these reactions confirmed that Co^{2+} cations do not reduce or sulfide; their local environment, however, changes slightly, apparently because of interactions of strongly adsorbed species with Co cations. Sulfur K-edge X-ray absorption spectra detected small amounts of organosulfur species, but no inorganic sulfides, after thiophene, thiophene–H_2, and thiophene–propane reactions, consistent with the observed stability of exchanged cations against reduction and sulfidation. S : Al ratios were less than 0.04 at. on all samples; these amounts represent less than 1% of the S-atoms removed from thiophene as H_2S during catalytic propane–thiophene reactions.

Introduction

Recent studies have shown that thiophene desulfurization proceeds with the selective formation of H_2S and sulfur-free hydrocarbons using hydrogen species and alkenes formed in concurrent propane dehydrogenation and aromatization reactions on H-ZSM5 and cation-exchanged H-ZSM5.[1,2] The reaction occurs without significant involvement of the H_2 molecules formed in propane dehydrogenation reactions. The reaction pathways involved in the kinetic coupling of thiophene and propane reactions were discussed previously.[3,4] In this previous study, it was mentioned that the coverage of acidic OH groups by intermediates derived from thiophene or propane was very low during reaction; no thiophene adsorption on acid sites was detected during propane–thiophene reactions at 773 K on H-ZSM5 or Co/H-ZSM5. It was also stated, without the experimental evidence, that *in situ* X-ray absorption spectroscopy did not detect any marked changes in the local structure or oxidation state of the exchanged Co^{2+} cations. The experimental evidence for these statements, and its implications for the mechanism and site requirements of thiophene desulfurization reactions, are presented here together with complementary studies of the desorption and chemical reactions of thiophene pre-adsorbed on H-ZSM5 and Co/H-ZSM5. Temperature-programmed desorption of pre-adsorbed thiophene, and infrared and X-ray absorption near-edge (XANES) spectra collected during adsorption and reactions of thiophene, were used to explore possible reactive intermediates and catalytic structures present during reactions of thiophene with either propane or H_2 on H-ZSM5 and Co/H-ZSM5.

Studies investigating the interactions of thiophene with different acidic zeolites and alumina-based materials have been reported.[5–10] Garcia and Lercher used infrared spectroscopy to examine the adsorption and surface chemistry of thiophene on H-ZSM5, Na-ZSM5, and K-ZSM5 near ambient temperature and during subsequent temperature ramping.[5,6] The products evolved were identified using mass spectrometry, but without measurements of the amounts desorbed. Here, we bring together results obtained from infrared spectroscopy during thiophene adsorption at ambient temperature and during subsequent thermal treatments in He, with temperature programmed desorption studies on H-ZSM5 and Co/H-ZSM5, during which we monitor the adsorption, purge,

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and desorption stages using quantitative mass spectrometry. We attempt to determine the identity and amount of the products formed using gas chromatography. These experiments aim to probe the interactions and reactions of thiophene on H-ZSM5 and Co/H-ZSM5 at ambient temperature and during subsequent desorption or reactions of thiophene as the temperature increases. In addition, infrared studies during reactions of thiophene and thiophene–propane mixtures at 773 K on H-ZSM5 and Co/H-ZSM5 were used to probe the interactions of propane and thiophene with acid sites or metal cations during steady-state catalytic reactions.

In situ Co K-edge XANES was used to detect any structural changes of Co cations in Co/H-ZSM5 during thiophene–propane reactions, and specifically any reduction or sulfidation of these cations in the presence of thiophene. Sulfur K-edge X-ray absorption was used to determine the amount and type of sulfur species retained by the catalysts after thiophene reactions.

Experimental methods

Catalyst synthesis

Na-ZSM5 (Zeochem, Si : Al = 14.5) (~20 g) was converted to NH_4-ZSM5 by three exchanges with 0.5 M aqueous NH_4NO_3 (Aldrich, 99.999%) solutions (1 L exchange solution) at 353 K. The samples were filtered and washed with 2 L deionized water, treated in ambient air at 398 K overnight, and then in flowing dry air (Airgas, zero grade) at 773 K for 20 h in order to form H-ZSM5. Co/H-ZSM5 samples were prepared by aqueous exchange of H-ZSM5 (~2.5 g) at 353 K for varying periods of time using a 0.05 M aqueous solution of cobalt nitrate [$Co(NO_3)_2 \cdot 6H_2O$, Aldrich, 99%] (1 L exchange solution). After exchange, samples were filtered to retain the solids, which were washed with 2 L deionized water, dried in ambient air at 398 K overnight, and treated in flowing dry air (Airgas, zero grade) at 773 K for 20 h. The Co and Na content were measured by atomic absorption spectroscopy (Galbraith Laboratories, Inc.). The Na content in H-ZSM5 and Co/H-ZSM5 were below 0.14 wt.%. The structural characterization and catalytic behavior of these H-ZSM5 and Co/H-ZSM5 samples were reported previously.[1,11–13]

In situ infrared spectroscopic studies

Infrared spectra were collected using a Fourier-transform infrared spectrometer (Mattson, Research Series 10000) and a Praying-Mantis diffuse reflectance attachment (Harrick Scientific, DRP-XXX) with a controlled environment flow cell (Harrick Scientific, HVC-DR2). The cell was equipped with CaF_2 windows. Catalyst powder samples were placed within a cylindrical receptacle on top of a porous quartz disk and gases flowed upwards through the disk and the sample. Samples were treated in flowing dry air (Airgas, zero grade) for 1 h at 773 K before thiophene adsorption. Thiophene (Aldrich, $>99\%$, 1 kPa) in a He (Praxair, UHP) or H_2 (Praxair, UHP) carrier was passed through samples at ambient temperature in order to probe the thiophene interactions during adsorption at low temperatures. Thiophene was then removed from the He or H_2 carrier and the temperature increased in flowing He to 773 K at 0.167 K s^{-1}. *In-situ* infrared spectra were also measured during thiophene and thiophene–propane (Praxair, $>99.5\%$) reactions at 773 K on H-ZSM5 and Co/H-ZSM5. Diffuse reflectance measurements were converted to pseudo-absorbances using the Kubelka–Munk function.[14] KBr was used to collect a background spectrum at the same temperature as the zeolite samples. Spectra were collected in the 1000–4000 cm^{-1} wavenumber range with a resolution of 4 cm^{-1}.

Temperature programmed desorption and reactions of adsorbed thiophene

The kinetics of desorption and chemical reactions of adsorbed thiophene on H-ZSM5, Co/H-ZSM5 (Co/Al = 0.12), and Na-ZSM5 were measured as the sample temperature was increased using a flow microreactor. Samples were first treated in flowing dry air (Airgas, zero grade) for 1 h at 773 K. Helium (Praxair, UHP) was then used to purge the reactor for 0.5 h, as it was cooled from 773 K to ambient temperature. Thiophene was adsorbed by exposing samples to thiophene (1 kPa) in a flow of either He (Praxair, UHP) or H_2 (Praxair, UHP) at ambient temperature for 0.33 h. Thiophene was then removed from the carrier gas and weakly-adsorbed thiophene was desorbed by flowing the carrier gas for an additional 1 h. The temperature was then increased to 773 K at 0.167 K s^{-1} and held at 773 K for 1 h. The effluent was analyzed continuously during adsorption, purge, and desorption/reaction steps using an on-line mass spectrometer (Leybold Inficon Inc., Transpector). In addition, syringe samples of the effluent were collected for gas chromatographic analysis (Hewlett-Packard 6890) using capillary (HP-1 crosslinked methyl-silicone, 50 m $\times$ 0.32 mm, 1.05 μ film) and packed (Hayesep-Q, 80/100 mesh, $10' \times 0.125''$) columns and flame ionization and thermal conductivity detection. Both mass spectrometry and gas chromatography data were used in order to identify products and to measure the concentrations of thiophene and reaction products. The following masses were used for each reaction product: H_2S (34 amu), benzene (78 amu), toluene (91 amu), methylthiophene (97 amu), and benzothiophene (134 amu).

Cobalt K-edge XANES during thiophene–propane reactions

Cobalt K-edge X-ray absorption studies were carried out at the Stanford Synchrotron Research Laboratory (SSRL) using beamlines 2-3 and 4-1 and an unfocused Si (111) double-crystal upward-reflecting monochromator with parallel geometry. The spectra were acquired at 5 eV increments between 7461–7691 eV, 0.35 eV increments from 7691 to 7730 eV, and 0.04 A^{-1} increments from 7730 to 8791 eV. The intensities of the incident photon beam, the transmitted beam after the sample, and the transmitted beam after a reference Co foil were measured using three N_2-purged ionization chambers. The energy was calibrated by simultaneously measuring the spectrum of the sample and of the Co foil and fixing the first inflection point in the Co foil spectrum at its reported absorption energy (7709 eV). X-ray absorption spectra were measured using an *in situ* capillary cell and a portable gas feed manifold.[15] Samples were treated in flowing dry air (Airgas, zero grade) at 773 K before *in situ* measurements. Spectra were acquired during thiophene (Aldrich, $>99\%$)/propane (Praxair, $>99.5\%$) reactions at 773 K. The X-ray absorption spectrum of cobalt sulfide (Alfa Aesar, 99.5%) was also collected at ambient conditions for comparison. This sample was diluted with boron nitride to obtain a 5 wt.% Co sample. X-ray absorption data were analyzed using WinXAS (version 1.2).[16,17] A linear fit to the pre-edge region was subtracted from the spectra, and they were then normalized using a fifth-order polynomial fit to the post-edge fine structure (EXAFS) region.

Sulfur K-edge XANES

Sulfur K-edge X-ray absorption studies were also performed at the Stanford Synchrotron Research Laboratory (SSRL) using beamline 6-2 with an unfocused Si (111) double-crystal upward-reflecting monochromator with parallel geometry. The spectra were collected using a Lytle cell and a fluorescence detector[18] both purged with He at 1.67 cm^3 s^{-1}. The spectra were taken at 0.125 eV increments in the 2460 to 2490 eV energy region. The beam path was also purged with He.

$Na_2S_2O_3$ was used as a reference compound and the edge energies of S^{2-} and S^{6+} in $Na_2S_2O_3$ were assumed to be located at 2468.6 and 2477.5 eV, respectively. Spectra were measured on samples exposed to ambient air at room temperature after reactions of thiophene, thiophene/H_2, or thiophene/propane reactants at 773 K for about 2 h. The catalyst samples were mounted using Kapton tape and spectra were measured at ambient temperature.

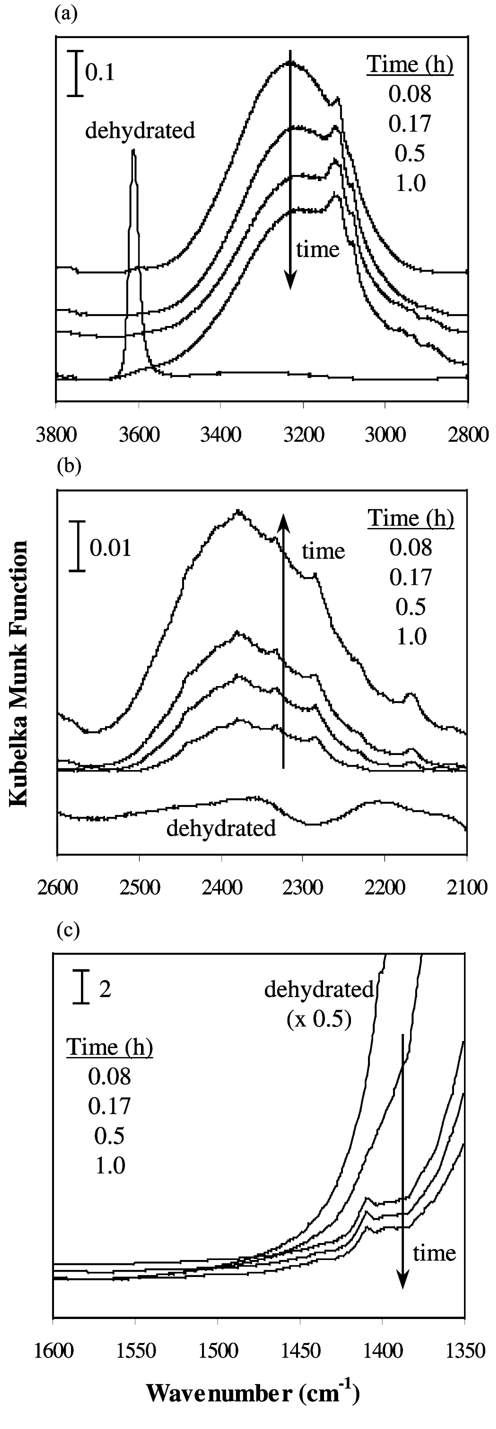


Fig. 1 (a) Infrared spectra of OH region of H-ZSM5 (Si/Al = 14.5) in contact with thiophene/He at 303 K with increasing time compared to spectrum of dehydrated sample in He at 773 K. (b) Infrared spectra of hydrogen bonding between SH groups in mercaptans and acidic OH groups on H-ZSM5 (Si : Al = 14.5) in contact with thiophene : He at 303 K with increasing time compared to spectrum of dehydrated sample in He at 773 K. (c) Infrared spectra of deformation vibrations of CH_2 groups close to a double bond (*CH_2–CH = CH_2) or a sulfur atom (*CH_2–S–) of H-ZSM5 (Si : Al = 14.5) in contact with thiophene : He at 303 K with increasing time compared to spectrum of dehydrated sample in He at 773 K.

Results and discussion

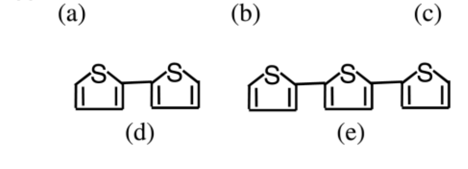
Infrared spectroscopy studies

Infrared spectra of adsorbed thiophene and of OH groups in H-ZSM5 and Co/H-ZSM5 were measured both during the initial adsorption of thiophene at ambient temperature and during treatment in He with increasing temperature. The infrared spectra of thiophene adsorbed on H-ZSM5 at 303 K are shown in Fig. 1a–c as a function of time of contact with thiophene. These spectra are compared to the initial spectrum of H-ZSM5 after dehydration in He at 773 K and before thiophene adsorption in these figures.

The band at 3610 cm^{-1} in fresh H-ZSM5 samples (Fig. 1a) corresponds to acidic OH groups at framework Al sites in H-ZSM5.[19–21] The adsorption of thiophene at ambient temperature led to the disappearance of this band and to its replacement by a broader band centered at ∼3200 cm^{-1} (Fig. 1a). These spectral changes reflect hydrogen-bonding interactions of thiophene with acidic OH groups in H-ZSM5.[5]

As H-ZSM5 remained in contact with thiophene for longer times, the intensity of this broad band at ∼3200 cm^{-1} decreased (Fig. 1a) and the intensity of new bands at 2900 cm^{-1}, 2350 cm^{-1}, and 1410 cm^{-1} increased. The band at 3610 cm^{-1} for free acidic OH groups, however, was not restored (Fig. 1a–c). Also, infrared bands appeared at 3120, 3080, and 1250 cm^{-1}—they correspond to a condensed thiophene phase within zeolite channels. The band at 2900 cm^{-1} is assigned to stretching vibrations of CH_2 groups located near a C–C double bond (*e.g.*, *CH_2–CH=CH_2) (Scheme 1a) or a sulfur atom (*e.g.*, *CH_2–S–) (Scheme 1b).[5] The band at 2350 cm^{-1} has been assigned to an interaction similar to the hydrogen bonding between S–H groups in mercaptans and O–H groups.[5] The band at 1410 cm^{-1} is assigned to the fundamental ring stretching vibration due to hydrogen bonding of thiophene.[5] On H–Y this band is attributed to conjugated C=C bonds,[7] while on γ-Al_2O_3, it was assigned to weakly bonded thiophene species present at high coverages.[9] These spectral changes show that thiophene molecules initially attached to OH groups *via* weak hydrogen bonding at ambient temperatures react at ∼303 K to form products that remain adsorbed on acidic OH groups.

Garcia and Lercher assigned the 2900 cm^{-1} and 2350 cm^{-1} bands to an alkene-thiol species formed via ring opening of thiophene.[5] Saintigny *et al.* carried out molecular simulations of thiophene adsorption and reactions of thiophene on acid sites.[22] Their proposed ring opening and desulfurization reactions do not lead to CH_2 groups near a C–C double bond or sulfur atom, but they involve a S–H group hydrogen-bonded to an acidic OH.[22] The S–H bands in the spectra of thiophene adsorbed near ambient temperatures may indicate that ring opening occurs at these low temperatures. The band corre-



Scheme 1 Structures of (a) CH_2 group near a C–C double bond, (b) CH_2 group near a sulfur atom, (c) 2,4-di-(thienyl)-thiolane, (d) dimeric thiophene, and (e) trimeric thiophene.

sponding to CH_2 groups located near a C–C double bond or to a sulfur atom and liquid thiophene are likely to arise from thiophene oligomers. Oligomers of thiophene such as 2,4-di-(thienyl)-thiolane (Scheme 1c), thiophene dimers (Scheme 1d), and trimers (Scheme 1e) form on acid catalysts.[23–25] These thiophene oligomerization reactions are discussed in more detail below.

The infrared spectra for Co/H-ZSM5 after exposure to thiophene were very similar to those obtained on H-ZSM5. Thus, it appears that Co cations did not bind thiophene species as infrared-active structures near ambient temperatures. During thiophene adsorption on Na-ZSM5, Garcia and Lercher observed infrared bands at 3109 and 3089 cm^{-1}, corresponding to C–H stretching vibrations, and a band at 1396 cm^{-1}, which they assigned to a perturbed ring stretching vibration ν_5 in species interacting strongly with cations.[5] Therefore, we would expect that an electron-rich molecule, such as thiophene, would interact with Co cations acting as Lewis acids. Bands similar to those observed by Garcia and Lercher on Na-ZSM5[5] may be present in Co/H-ZSM5 but may have been obscured by the broad bands at $\sim$3100 cm^{-1} corresponding to condensed thiophene. These condensed thiophene bands were not detected in previous studies[5] because of the much lower thiophene pressures used (10^{-6}–10^{-1} kPa *vs.* 1 kPa here). The OH bands in the fresh sample and the bands corresponding to OH perturbed by hydrogen-bonded thiophene were unaffected by the presence of cations, but their intensities were slightly lower because some of the OH groups were replaced by Co during exchange.[3] Co cations decrease the number of acidic OH groups but not their chemical properties. This was shown by comparing infrared spectra for pyridine adsorbed on Co/H-ZSM5 and on H-ZSM5 and noting that the frequency of the adsorbed pyridine bands was not affected by Co cations.[26] In addition, the adsorption of thiophene with H_2 or He as a carrier gas led to identical spectra, as expected from the absence of H_2 activation pathways at ambient temperatures on either H-ZSM5 or Co/H-ZSM5.

Fig. 2a–c show infrared spectra of H-ZSM5 during thermal treatment of pre-adsorbed thiophene (303 K, 1 h) using He as a carrier gas. The broad band at 3200 cm^{-1} became weaker as temperature increased (Fig. 2a). At 373 K, the intensity of the broad band at 3200 cm^{-1} weakened without any significant recovery of the 3610 cm^{-1} band corresponding to unperturbed acidic OH groups (Fig. 2a). This indicates that hydrogen-bonded thiophene continues to react as the sample is heated above ambient temperature. The broad band at 3200 cm^{-1} continues to weaken and the intensity of the free acidic OH band is fully recovered as the temperature increases, indicating that products are formed by desorption of species adsorbed on acidic OH groups. The bands at 2900 cm^{-1}, corresponding to CH_2 groups near a C–C double bond or sulfur atom, and the band at 1410 cm^{-1} for hydrogen-bonded thiophene,[5] conjugated C=C bonds,[7] or high-coverage thiophene species,[9] respectively, became initially more intense with increasing temperature, but ultimately weakened at higher temperatures (Fig. 2a–c). The 2350 cm^{-1} band for hydrogen-bonded S–H at OH groups also weakened with increasing temperature (Fig. 2b). The analysis of the effluent stream (reported below) shows that H_2S and benzene were evolved in this temperature range. The spectral and product evolution described here for H-ZSM5 are similar to those measured on Co/H-ZSM5 samples.

A quantitative analysis of these infrared data was carried out using the integrated intensity of the 1410 cm^{-1} band (Fig. 2c), corresponding to thiophene species or conjugated C=C bonds as a function of temperature (Fig. 3). This integrated intensity was normalized using that for the zeolite framework band at 1200 cm^{-1}, which corresponds to framework vibrations and it is used here as an internal standard. The concentration of these intermediates increased as temperature increased from 300 to 450 K, and then decreased at higher temperatures. Ring opening and oligomerization appear to be initially favored by higher temperatures, but ultimately the products formed either desorb or dehydrogenate further into active organic or organosulfur surface species with lower infrared absorption cross-sections. The band at 1410 cm^{-1}, corresponding to these intermediates, is also detected on Co/H-ZSM5, suggesting that Co cations do not influence

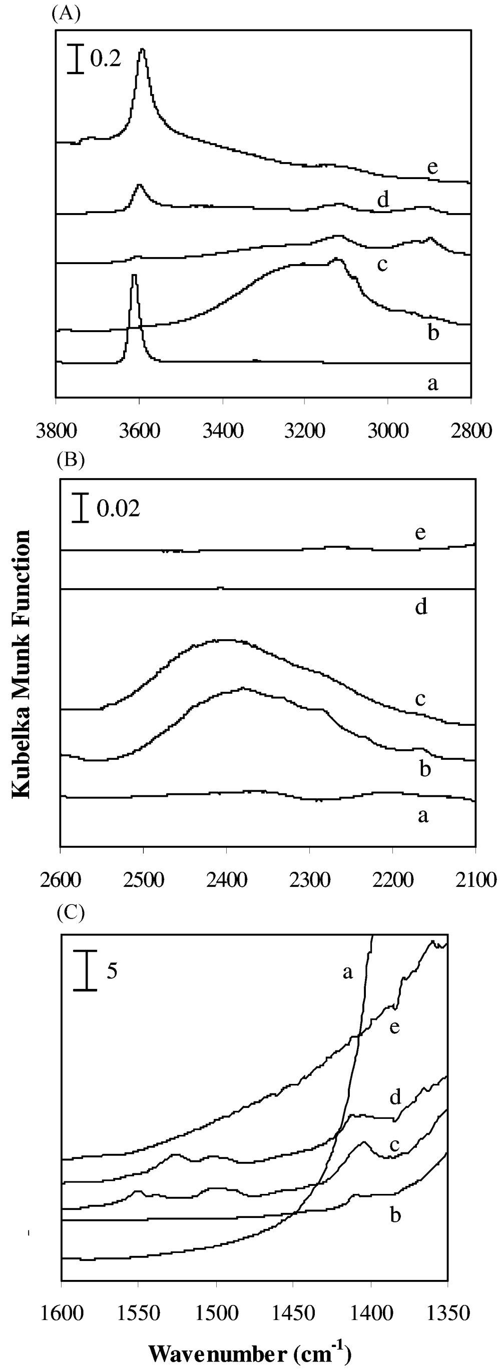


Fig. 2 (A) Infrared spectra of OH region of (a) dehydrated H-ZSM5 sample (Si/Al = 14.5), (b) thiophene adsorbed in He stream after 1 h, and adsorbed thiophene during treatment in He at (c) 373 K (d) 573 K (e) 773 K. (B) Infrared spectra of hydrogen bonding between SH groups in mercaptans and acidic OH groups of (a) dehydrated H-ZSM5 sample (Si/Al = 14.5), (b) thiophene adsorbed in He stream after 1 h, and adsorbed thiophene during treatment in He at (c) 373 K (d) 573 K (e) 773 K. (C) Infrared spectra of deformation vibrations of CH_2 groups close to a double bond ($*CH_2–CH = CH_2$) or a sulfur atom ($*CH_2$–S-) of (a) dehydrated H-ZSM5 sample (Si/Al = 14.5), (b) thiophene adsorbed in He stream after 1 h, and adsorbed thiophene during treatment in He at (c) 373 K (d) 573 K (e) 773 K.

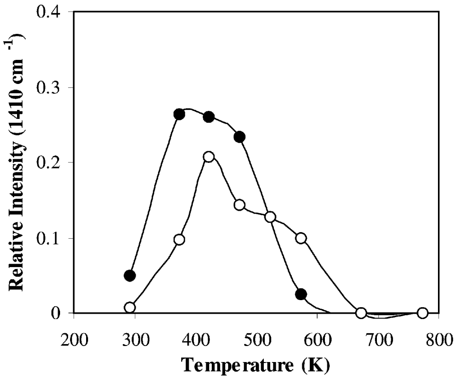


Fig. 3 Intensity of infrared band at 1410 cm^{-1} (CH_2 groups close to a double bond or sulfur atom) relative to infrared band at 1200 cm^{-1} (zeolite T–O–T framework) during thiophene temperature programmed desorption in He on H-ZSM5 (●) and Co/H-ZSM5 (○) [Si/Al = 14.5, Co/Al = 0.17].

the density or type of adsorbed species. Co cations led to the retention of these adsorbed intermediates up to higher temperatures when He was used as the carrier gas. This may reflect the greater extent of unsaturation of adsorbed species when Co cations are present and provide sites for the removal of H_2 as the temperature increases. These hydrogen-deficient species are expected to bind more strongly to surface sites. Indeed, the analysis of the effluent stream discussed below shows that some larger products (*e.g.* toluene and methylthiophene) desorb at higher temperatures on Co/H-ZSM5 than on H-ZSM5.

The role of acidic OH groups in thiophene adsorption and reactions was inferred from *in situ* infrared spectra of Na-ZSM5 during thiophene adsorption at ambient temperature and during heating in a He carrier gas. Neither OH groups nor hydrogen-bonded thiophene were detected (bands at 3610 cm^{-1} and 3200 cm^{-1}, respectively), as expected from the absence of OH groups in Na-ZSM5 (Fig. 4). Infrared bands at 3150 cm^{-1} and 3100 cm^{-1} were observed (Fig. 4), indicating that a condensed thiophene phase is present within zeolite channels, as also found for H-ZSM5 and Co/H-ZSM5 (Fig. 2a and 2c). Similar conclusions were reported previously on NaY zeolite.[27] On Na-ZSM5, however, another study[5] assigned bands at 3109 and 3089 cm^{-1} to C–H stretches and those at 1396 cm^{-1} to perturbed fundamental ring stretching vibrations ν_5 in thiophene interacting strongly with Na^+ cations. The bands corresponding to these modes may be present within the broad envelope of bands for condensed thiophene; yet, the shape of this envelope does not change, and no new features appear as the condensed thiophene phase desorbs as temperature increases from ambient to 573 K. All thiophene-derived infrared bands disappeared without any intervening changes in frequency and without the appearance of new bands, as the temperature increased from ambient to 773 K. Therefore, no ring opening and oligomerization reactions of thiophene-derived species were detected by the infrared measurements on Na-ZSM5.

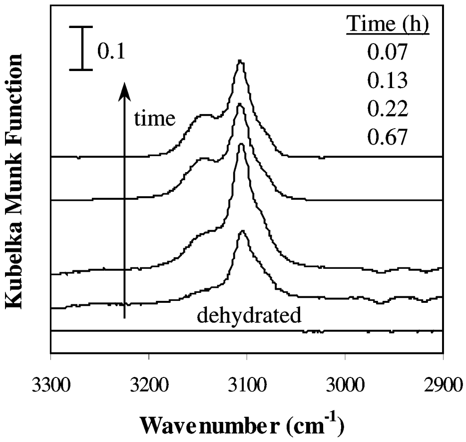


Fig. 4 Infrared spectra of Na-ZSM5 (Si/Al = 14.5) in contact with thiophene/He at 303 K with increasing time compared to spectrum of dehydrated sample in He at 773 K.

Temperature programmed desorption of pre-adsorbed thiophene

The desorption of pre-adsorbed thiophene and the evolution of its reaction products were studied using He or H_2 carrier gases as H-ZSM5, Co/H-ZSM5, and Na-ZSM5 samples were heated from ambient temperature to 773 K. The amount of thiophene adsorbed during exposure to 1 kPa thiophene at ambient temperature was measured from the differences in thiophene concentrations between inlet and outlet streams. The adsorption *vs.* time curves for thiophene in He and H_2 carrier gases are similar in shape on H-ZSM5. They are also similar in shape for H-ZSM5, Co/H-ZSM5, and Na-ZSM5, but the amounts adsorbed differ. Saturation thiophene coverages were reached in 0.25–0.33 h. After saturation, thiophene was removed from the carrier gas and the sample was purged with He for 1 h in order to remove weakly-adsorbed species. The amount of thiophene retained by the sample (Table 1) was estimated by subtracting the amount desorbed during the purge cycle from the amount adsorbed during exposure to the thiophene-containing stream.

The total amount of thiophene retained during the adsorption cycle corresponds to ~2 thiophene molecules per Al on all samples (Table 1). The infrared data shown in the previous section showed that ring opening and oligomerization occurred on H-ZSM5 and Co/H-ZSM5, but not on Na-ZSM5, during thiophene adsorption at ambient temperature (Fig. 1a–c). H-ZSM5 turned bright orange and Co/H-ZSM5 a paler orange color, during thiophene adsorption at ambient temperature, but Na-ZSM5 retained its original white color. Thiophene oligomers are colored and become darker as the extent of oligomerization increases, because electrons are more effectively delocalized over larger conjugated structures, leading to photon absorption in the visible range. Oligomers shift from colorless dimers, to pale yellow trimers, and ultimately to red for larger structures.[28,29] The large amounts of thiophene formed and the color changes observed suggest the formation of oligomeric thiophene species during thiophene adsorption at ambient temperature on H-ZSM5 and Co/H-ZSM5, but not on Na-ZSM5.

Thiophene oligomerization occurs on acid catalysts.[23–25] For example, thiophene forms predominantly trimers [2,4-di-(2-thienyl)-thiolane] on phosphoric acid,[23] and larger oligomers on cation-exchanged Y-zeolite and mordenite[24] and on montmorillonite.[25] On H-ZSM5 and Co/H-ZSM5, the extent of oligomerization becomes limited, apparently by the limited volume within ZSM5 channels, and the reaction stops after ~0.3 h and saturation thiophene coverages are reached. Thiophene oligomers should not form on Na-ZSM5 because of the absence of acid sites; therefore, thiophene adsorbs molecularly within Na-ZSM5 pores, possibly *via* specific interactions with Na cations.

Infrared data showed that oligomerization and ring opening reactions form thiophene oligomers and alkene–thiol species, respectively, which give rise to infrared bands for CH_2 groups near double bonds or sulfur atoms and to SH groups. These species appear to account also for the perturbation of the OH bands by hydrogen bonding. The formation of CH_2 and SH species, however, would additionally require hydrogen transfer, intramolecularly within the thiophene structures or intermolecularly from neighboring adsorbed organic species.

Table 1 Comparison of amounts of thiophene adsorbed, removed by He or H_2, retained at room temperature, desorbed as thiophene during temperature programmed desorption, and desorbed as other products during temperature programmed desorption on H-ZSM5, Co/H-ZSM5, and Na-ZSM5 in He or H_2 [1 kPa thiophene, balance He or H_2, 303 K, Si/Al = 14.5, Co/Al = 0.12]

Catalyst	Carrier gas	Thiophene adsorbed (molecules/Al)	Thiophene removed (molecules/Al)	Thiophene retained (molecules/Al)	Thiophene desorbed Unreacted (molecules/Al)	Thiophene desorbed as Other Products (molecules/Al)
H-ZSM5	He	1.85	0.23	1.62	0.38	0.072
H-ZSM5	H_2	1.91	0.48	1.43	0.61	0.0083
Co/H-ZSM5	He	2.33	0.56	1.77	0.76	0.10
Co/H-ZSM5	H_2	2.63	0.78	1.85	0.90	0.037
Na-ZSM5	He	2.14	0.49	1.65	0.95	Not quantified

During purging, some weakly-adsorbed thiophene desorbs and the amounts of thiophene that remain adsorbed are shown in Table 1. The thiophene retained on H-ZSM5 and Co/H-ZSM5 interacts with OH groups, leading to the replacement of the free acidic OH band in H-ZSM5 with a band for stretches of OH groups perturbed by hydrogen bonding with adsorbed thiophene or thiophene-derived species, such as oligothiophenes or alkene–thiols. Similar amounts of thiophene, however, remain on Na-ZSM5, even though this sample contains no acidic OH groups. The thiophene remaining after purging on Na-ZSM5 may be associated with Na cations[5] or merely physisorbed on channel walls with a significant heat of adsorption.

After removal of weakly-bound thiophene at ambient temperature, the desorption of reaction products and of unreacted thiophene was monitored by online mass spectrometry as a function temperature (Fig. 5) using He as the carrier gas. Thiophene desorbs in two separate peaks centered at 400 and 575 K; the second peak is much smaller than the first peak. Two desorption peaks were also observed when H_2 was used as the carrier gas during thiophene desorption. On Na-ZSM5, unreacted thiophene also desorbed in two peaks, but the higher temperature peak accounted for a much larger fraction of the total amount of desorbed thiophene than on H-ZSM5 or Co/H-ZSM5. Previous studies have also reported two desorption peaks on Na-ZSM5,[5] which were simply described as weakly and strongly adsorbed thiophene without any structural speculation.

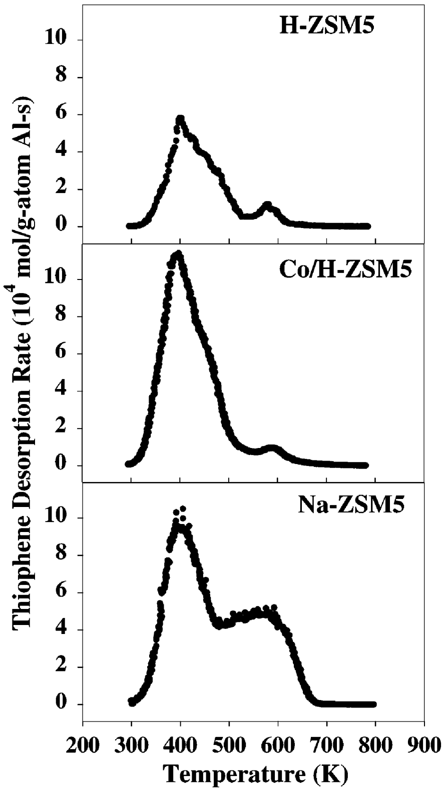


Fig. 5 Thiophene temperature programmed desorption in He on H-ZSM5 (Si/Al = 14.5), Co/H-ZSM5 (Co/Al = 0.12), and Na-ZSM5 after adsorption of thiophene [0.167 K s^{-1}, 1.67 cm^3 s^{-1}].

The thiophene species desorbing at ~400 K are likely to be bound to framework oxygens *via* van der Waals interactions, while the desorption peak at 575 K appears to reflect stronger interactions with specific sites, such as Na cations. Indeed, this desorption peak is much larger on Na-ZSM5 than on H-ZSM5 or Co/H-ZSM5, both of which contain only trace amounts of Na. The amount of unreacted thiophene desorbed in the second peak (thiophene/Al = 0.03–0.04) is similar to the amount of Na in H-ZSM5 and Co/H-ZSM5 (Na/Al ~ 0.01–0.06). The corresponding amount desorbed for the Na-ZSM5 sample (thiophene/Al = 0.4), however, is less than expected from its Na content (Na/Al ~ 1). We note that these desorption peaks do not include any adsorbed thiophene that has reacted to form stable adsorbed species.

Clearly, the species responsible for desorption of unreacted thiophene are not associated with acidic OH groups, because desorption profiles for H-ZSM5 and Co/H-ZSM5 are similar to those for Na-ZSM5 samples containing no framework Al–OH species. Thus, it appears that the hydrogen-bonded thiophene species detected by infrared near ambient temperature undergo oligomerization and ring opening reactions before they desorb. Indeed, the amount of thiophene desorbed is much smaller than the amount retained after adsorption and purging at ambient temperature (Table 1). This is also the case for Na-ZSM5, for which the absence of acid sites makes the reasons for this behavior unclear. Garcia and Lercher have concluded that all adsorbed thiophene desorbs without reaction on Na-ZSM5.[5]

Table 1 also shows the amounts of thiophene retained and desorbed for H-ZSM5 and Co/H-ZSM5 when H_2 was used as the carrier gas. The amounts of thiophene desorbed are greater when H_2 is present on both H-ZSM5 and Co/H-ZSM5 than when He is used as the carrier gas. This suggests that the reactions that strand thiophene on the surface are dehydrogenation reactions, such as oligomerization to dimer and trimer thiophene species and ring opening reactions to form alkene–thiol species, the products of which can be hydrogenated to form desorbable hydrocarbons and H_2S when H_2 is available as a reactant.

Several products were detected during heating of these samples after thiophene adsorption. H_2S formed slightly above ambient temperature (Fig. 6a) on both H-ZSM5 and Co/H-ZSM5. The amounts of H_2S desorbed are plotted in relative units (signal intensity for 34 amu relative to 4 amu) because a calibration of the mass spectrometer for H_2S was unavailable. This low-temperature pathway for H_2S formation is consistent with the ring opening reactions detected near ambient

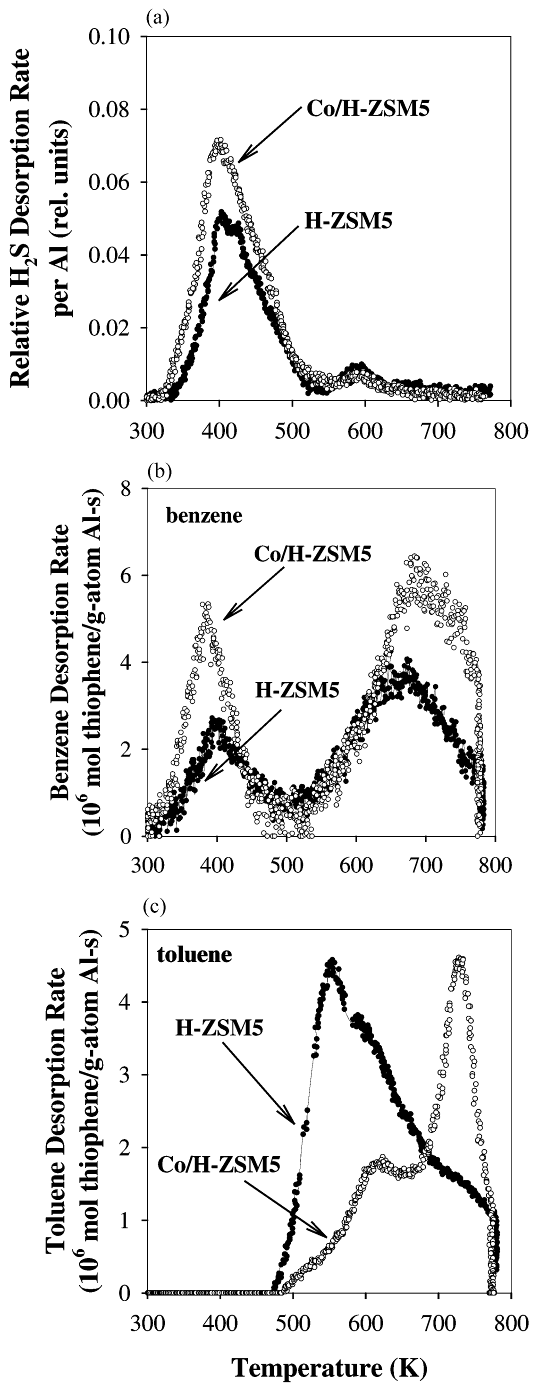


Fig. 6 (a) H_2S desorption rates relative to He (per Al) during temperature programmed desorption of pre-adsorbed thiophene on H-ZSM5 and on Co/H-ZSM5 using He as a carrier gas [Si/Al = 14.5, Co/Al = 0.12, 0.167 K s^{-1}, 1.67 cm^3 s^{-1}, isothermal at 773 K for 1 h]. (b) Benzene desorption rates during temperature programmed desorption of pre-adsorbed thiophene on H-ZSM5 and on Co/H-ZSM5 using He as a carrier gas [Si/Al = 14.5, Co/Al = 0.12, 0.167 K s^{-1}, 1.67 cm^3 s^{-1}, isothermal at 773 K for 1 h]. (c) Toluene desorption rates during temperature programmed desorption of pre-adsorbed thiophene on H-ZSM5 and on Co/H-ZSM5 using H_2 as a carrier gas [Si/Al = 14.5, Co/Al = 0.12, 0.167 K s^{-1}, 1.67 cm^3 s^{-1}, isothermal at 773 K for 1 h].

temperature by infrared spectroscopy. Benzene also desorbs immediately upon heating, suggesting that it forms from thiophene-derived fragments that remain after ring opening and desulfurization (Fig. 6b). Benzene molecules have a higher H : C ratio than thiophene molecules desulfurized via intramolecular hydrogen transfer, suggesting that hydrogen transfer from co-adsorbed species must occur, leaving behind highly unsaturated and strongly-bound organic fragments. Benzene (Fig. 6b), toluene, methylthiophene, benzothiophene, and light alkenes (ethene and propene) also desorb at somewhat higher temperatures. Interestingly, only small amounts of H_2S desorb at these high temperatures, indicating that most of the sulfur removal had already occurred at lower temperatures and that the hydrocarbons desorbed at higher temperatures were formed at lower temperatures. With He as the carrier, H_2S (Fig. 6a), benzene (Fig. 6b), and benzothiophene desorb at similar temperatures on H-ZSM5 and Co/H-ZSM5, while toluene and methylthiophene desorb at slightly higher temperatures on Co/H-ZSM5 than on H-ZSM5. This is consistent with the infrared results, which showed that adsorbed species are retained to higher temperatures on Co/H-ZSM5 than on H-ZSM5 (Fig. 3). The presence of Co cations appears to lead to more unsaturated intermediates by providing sites for the removal of hydrogen as H_2.[11,30] Cations do not appear to influence desulfurization pathways or to provide active sites for desulfurization of pre-adsorbed thiophene.

With H_2 as the carrier gas, reaction pathways were similar to those with He on H-ZSM5, except that larger amounts of benzene evolved in a single peak at the same temperature as the second peak observed when He was used as the carrier gas. H_2S evolution curves were identical with H_2 and He (not shown). Benzene and toluene (Fig. 6c) evolved at higher temperatures on Co/H-ZSM5 than on H-ZSM5 when H_2 is used as the carrier and the amount of benzene formed is much higher on Co/H-ZSM5 than on H-ZSM5. This appears to reflect a role of Co cations in dissociating H_2 and leading to the hydrogenation of unsaturated organic residues, which become stranded in the absence of such hydrogenation reactions. Co cations influence product evolution temperatures, but not the identity of the products formed or the thiophene reaction pathways. Previous mechanistic studies have also shown that Co cations influence the rate but not the pathways of desulfurization reactions using propane or H_2 as a hydrogen source.[3]

The total amounts of hydrocarbon products desorbed from H-ZSM5 and Co/H-ZSM5 in He and in H_2 are reported in Table 1. Reactions of adsorbed thiophene using He as the carrier gas led to a larger number of products, because the absence of H_2 favors reactions among thiophene-derived adsorbed intermediates, and to the formation of a wide range of larger organosulfur compounds (Table 1). In contrast, the use of Co cations as H_2 activation sites led to larger amounts of hydrocarbons and to the more prevalent removal of sulfur as H_2S (Table 1). The amount of thiophene desorbed as hydrocarbons and organosulfur compounds is smaller than the total amount of thiophene initially adsorbed; it is also smaller than the amount of thiophene that desorbs unreacted (Table 1). The stranded thiophene appears to consist of oligomers or dehydrogenated debris from ring opening reactions, which cannot desorb and become sources of hydrogen for hydrogenation and desorption of thiophene-derived species.

After thermal treatments in He (Fig. 6a and 6b) or H_2 (Fig. 6c), the samples were cooled to ambient temperature and heated in H_2 to 873 K at 1.67 K s^{-1}. Samples were cooled again to ambient temperature and heated in air to 873 K at 1.67 K s^{-1}. During both treatments, the evolution of products was monitored by mass spectrometry. During H_2 treatment, benzene and toluene were detected as major products and methane, ethene, ethane, propene, and propane in trace amounts. The amounts of products formed were much smaller than those formed during the initial desorption experiments (Table 1, Fig. 6a–c). During the subsequent air treatment, CO_2 and SO_2 were detected, but their concentrations could not be measured because of their small amounts and unavailable calibrations. No H_2O was detected, suggesting the absence of hydrogen atoms in the residual organic species. However, the sensitivity for H_2O was low because of a ubiquitous water background signal in the mass spectrometer.

In situ infrared spectroscopic studies

The previous infrared and temperature programmed desorption studies focused on adsorption and reactions of preadsorbed thiophene. Here, we show infrared spectra collected during steady-state thiophene reactions at 773 K on H-ZSM5 and Co/H-ZSM5 using He or propane as additional gas phase components. Fig. 7 shows infrared spectra for H-ZSM5 during catalytic decomposition of thiophene–He mixtures at 773 K as a function of time on stream; an initial spectrum of the H-ZSM5 sample before exposure to thiophene is also shown. Only free acidic OH bands (3610 cm^{-1}) are detected during reactions of thiophene–He mixtures on H-ZSM5 at 773 K and the intensities of these bands are identical to those in the fresh H-ZSM5 sample before contact with thiophene. The absence of new bands and the unchanged intensity and frequency of the OH infrared band at 3610 cm^{-1} show that the amount of thiophene and of its reaction products adsorbed on acidic OH groups is very low during steady-state thiophene decomposition at 773 K.

Fig. 8 shows the corresponding infrared spectra for H-ZSM5 during steady-state reactions of thiophene–propane mixtures at 773 K as a function of time on stream. Several poorly resolved bands appear at ~2980 cm^{-1} upon contact of the sample with the reactant mixture at 773 K. These bands correspond to propane molecules present in the gas phase within the beam path. The OH band intensities during steady-state catalysis were identical to those in the fresh sample. As in the case of reactions of pure thiophene, catalytic surfaces appear to remain largely uncovered by adsorbed species derived from propane and thiophene during these catalytic reactions on H-ZSM5.

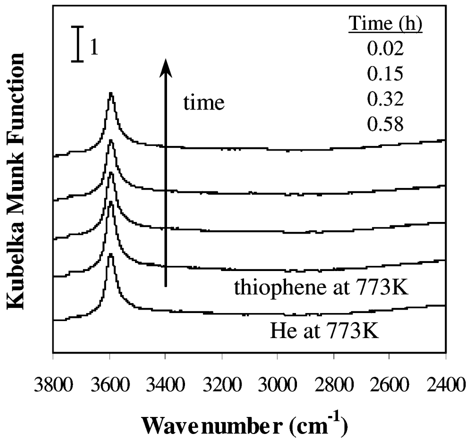


Fig. 7 Infrared spectra of OH region of H-ZSM5 (Si/Al = 14.5) in contact with thiophene/He at 773 K with increasing time compared to spectrum of dehydrated sample in He at 773K.

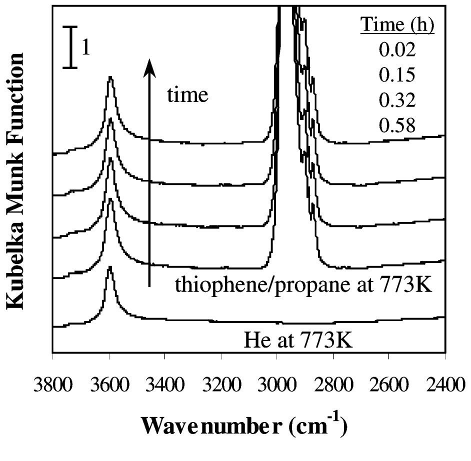


Fig. 8 Infrared spectra of OH region of H-ZSM5 (Si/Al = 14.5) in contact with thiophene–propane–He at 773 K with increasing time compared to spectrum of dehydrated sample in He at 773 K.

Infared spectra were also measured on Co/H-ZSM5 samples during reactions of thiophene and thiophene–propane mixtures at 773 K. These spectra also failed to show any detectable adsorbed species or any changes in the number of free acidic OH groups during steady-state catalysis. Co cations do not appear to introduce binding sites capable of stabilizing infrared-active adsorbed thiophene or thiophene-derived intermediates during these catalytic reactions.

In summary, acidic OH groups remain predominantly unoccupied during catalytic reactions at 773 K and no infrared-active adsorbed species are introduced by Co cations. Thiophene has been shown to inhibit propane reactions on Co/H-ZSM5 through a decrease in the availability or the reactivity of Co or OH sites.[3] Inhibition effects caused by blockage of acidic OH groups would have been detected as a perturbation of the OH stretching modes, while interactions between Co cations and thiophene-derived intermediates would have led to new absorption infrared bands, unless such deactivating residues have very low absorption cross-sections or no residual C–H bonds. The observed inhibition effects on bifunctional dehydrocyclodimerization reactions[3] are not caused by blockage of acidic OH sites. Cations were previously shown to increase the rate of thiophene desulfurization using propane as co-reactants.[1,2] Here, we show that interactions between thiophene and Co sites do not lead to any adsorbed species detectable by infrared.

In situ Co K-edge XANES

In situ Co K-edge X-ray absorption near-edge spectroscopy was used to probe the local structure of the Co cations in Co/H-ZSM5 and to detect any changes in coordination or adsorbate coverage caused by thiophene–propane reactions. The local structure of Co cations in fresh and dehydrated Co/H-ZSM5 samples was previously examined using X-ray absorption spectroscopy.[13] These studies showed that Co cations are present at cation exchange sites as well dispersed divalent cations with tetrahedral coordination after dehydration and during reactions in H_2 or C_3H_8 at 773 K.[13] D_2-OH and infrared measurements showed that one Co^{2+} cation replaces 1.1–1.3 OH groups, suggesting the presence of Co dimers and some monomers, each interacting with two next nearest neighbor Al framework sites.[13]

The near-edge spectrum of Co/H-ZSM5 during reaction at 773 K is shown in Fig. 9a; the corresponding spectra for Co/H-ZSM5 after dehydration, for Co metal, and for Co sulfide are also shown. The spectra for Co/H-ZSM5 during reaction resemble that of the dehydrated sample. Difference spectra between the sample during reaction and the dehydrated sample, and the Co and Co sulfide standards are shown in Fig. 9b. The difference between the spectra during reaction and the dehydrated fresh sample suggests a slight distortion of the Co^{2+} structure, possibly as a result of adsorbed species interacting with these cations. These differences appear to reverse partially some of the changes in the near-edge spectra observed during thermal treatment of fresh samples exposed to ambient air. These thermal treatments remove water molecules coordinated to Co^{2+} cations. Thus, it appears that some species adsorb on these cations during propane–thiophene reactions at 773 K. The large near-edge spectrum differences between the sample during thiophene–propane reactions and Co metal or Co sulfide show that the oxidation state and local coordination of Co cations during reaction differ markedly from those in Co metal and Co sulfide structures (Fig. 9b).

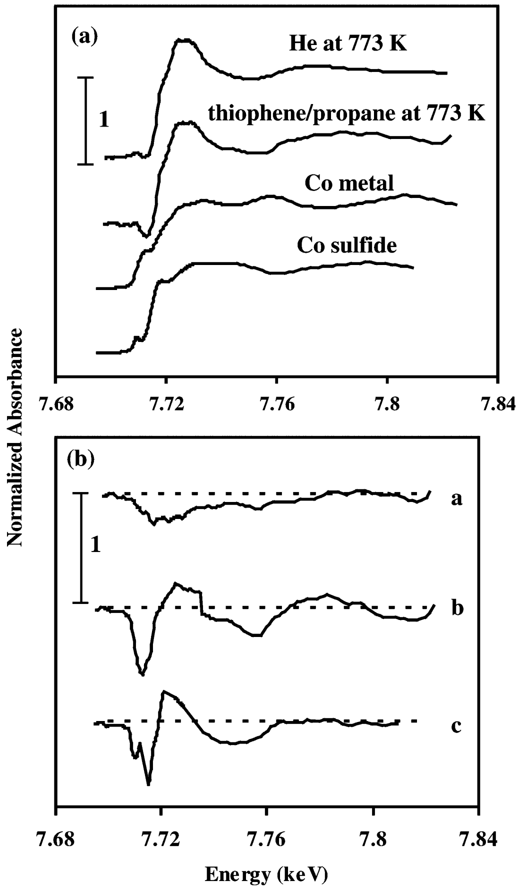


Fig. 9 (a) Co K-edge XANES of Co/H-ZSM5 dehydrated in He at 773 K, Co/H-ZSM5 during thiophene–propane reaction at 773 K, Co metal, and Co sulfide. (b) Difference spectra of: a, Co K-edge XANES of Co/H-ZSM5 during thiophene-propane reaction at 773 K and of Co/H-ZSM5 dehydrated in He at 773 K; b, Co K-edge XANES of Co/H-ZSM5 during thiophene-propane reaction at 773 K and of Co metal; and c, Co K-edge XANES of Co/H-ZSM5 during thiophene-propane reaction at 773 K and of Co sulfide.

In summary, slight changes in the structure of Co cations were detected by X-ray absorption spectroscopy during thiophene–propane reactions, possibly due to adsorbed species, but Co^{2+} cations remain at exchange sites in the presence of thiophene–propane mixtures at 773 K. Co cations in Co/H-ZSM5 also do not reduce in H_2 or propane at 773 K, and their local coordination remains unchanged during these treatments.[13] Temperature programmed reduction studies confirmed that Co^{2+} cations remain as divalent cations in H_2 even at 1273 K.[13]

Sulfur K-edge XANES

Sulfur K-edge X-ray absorption near-edge spectra (XANES) can discern the type of sulfur compounds present in a sample, because these spectra are very sensitive to the oxidation state and chemical environment of sulfur atoms.[31–33] Here, sulfur K-edge X-ray absorption spectra were measured for samples used in thiophene, thiophene–H_2, and thiophene–propane reactions at 773 K for several hours. These spectra were used to estimate the type and concentration of sulfur compounds remaining on samples after reaction. The sulfur K-edge position is sensitive to the sulfur oxidation state and to the type of sulfur species present. The edge height of the absorption edge before normalization is proportional to the concentration of sulfur absorbers in the sample.

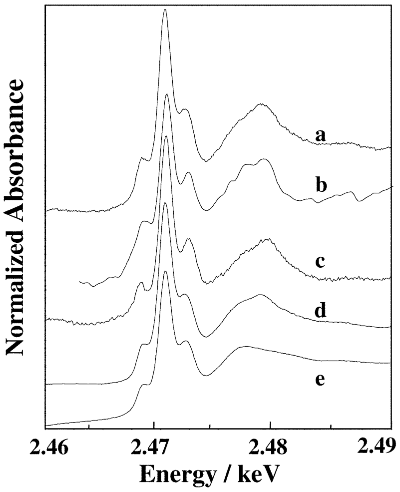


Fig. 10 Sulfur K-edge XANES of H-ZSM5 after reactions of (a) 1 kPa C_4H_4S, 20 kPa C_3H_8, balance He (b) 3 kPa C_4H_4S, balance He (c) 3 kPa C_4H_4S, 1–5 kPa H_2, balance He (d) 3 kPa C_4H_4S, 150 kPa H_2, balance He (e) 3 kPa C_4H_4S, 20 kPa C_3H_8, balance He [Si/Al = 14.5, 773 K].

Fig. 10 shows normalized sulfur K-edge near-edge spectra for H-ZSM5 samples after reactions of thiophene, thiophene–H_2, and thiophene–propane mixtures. The spectra for these three samples are very similar, indicating that similar types of sulfur species remain after each of these reactions. The edge energies (2468–2477 eV) correspond to sulfur atoms in organic compounds and the concentrations of these species are reported in Table 2 as [S : Al] atomic ratios. The amount of residual sulfur increased with increasing thiophene concentration in thiophene–propane mixtures. The presence of H_2 (150 kPa) or propane (20 kPa) leads to lower residual sulfur contents, because these co-reactants provide hydrogen species that hydrogenate and desorb organosulfur compounds.

The near-edge spectra for several cation-exchanged H-ZSM5 samples after thiophene–propane reactions at 773 K are shown in Fig. 11. These spectra show that the adsorbed sulfur compounds are similar on Zn/H-ZSM5, Co/H-ZSM5, and H-ZSM5. Thus, cations do not appear to influence the type of organosulfur species retained by these samples during thiophene–propane reactions. This seems to confirm that cations do not influence the pathways involved in thiophene–

Table 2 Sulfur content and sulfur/Al (S : Al) ratio of H-ZSM5 after thiophene, thiophene–H_2, and thiophene–propane reactions [Si/Al = 14.5, 773 K]

	Pressure/kPa				
	Thiophene	H_2	Propane	Sulfur wt.%	S : Al ratio
A	1	0	20	0.11	0.032
B	3	0	0	0.92	0.27
C	3	1–5	0	1.3	0.38
D	3	150	0	0.53	0.15
E	3	0	20	0.14	0.041

Table 3 Sulfur content, sulfur : Al (S : Al) ratio, and sulfur : metal (S : M) ratio of H-ZSM5, Zn/H-ZSM5, and Co/H-ZSM5 after thiophene–propane reactions [773 K, 1 kPa C_4H_4S, 20 kPa C_3H_8]. Preparation and characterization details of the Zn/H-ZSM5 sample were reported previously[1]

Catalyst	M : Al ratio	Sulfur wt.%	S : Al ratio	S : M ratio
H-ZSM5	—	0.11	0.032	—
Zn/ H-ZSM5	0.15	0.09	0.026	0.17
Co/ H-ZSM5	0.07	0.06	0.017	0.25

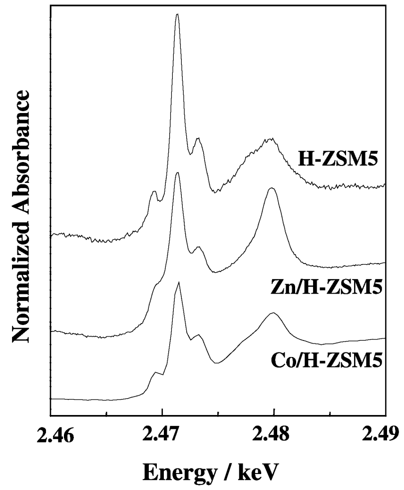


Fig. 11 Sulfur K-edge XANES of H-ZSM5, Zn/H-ZSM5, and Co/H-ZSM5 after thiophene–propane reactions [773 K, 1 kPa C_4H_4S, 20 kPa C_3H_8, balance He]. Preparation and characterization details of the Zn/H–ZSM5 sample were reported previously.[1]

propane reactions.[3] No inorganic sulfides were apparent in any of the samples, as also concluded from the nearly unchanged structure of Co cations during reaction. Co cations are stable against sulfidation and reduction during thiophene–propane reactions in which H_2S is formed and present.

The sulfur to aluminum (S : Al) and sulfur to cation (S : M) atomic ratios in these samples are reported in Table 3. The amounts of sulfur remaining after thiophene–propane reactions on H-ZSM5, Co/H-ZSM5, and Zn/H-ZSM5 account for less than 1% of the amount of sulfur removed from thiophene as H_2S, confirming that these materials act as catalysts and not as sulfur traps that merely bind thiophene-derived sulfur species.

Conclusions

Infrared spectroscopic studies showed that thiophene interacts with acidic OH groups of H-ZSM5 and Co/H-ZSM5 and that ring opening and oligomerization occur near ambient temperature. No bands corresponding to thiophene interactions with Co cations were detected, but they may have been obscured by broad bands for condensed thiophene. Temperature programmed desorption studies did not detect any thiophene interactions with Co cations. Some unreacted thiophene desorbs during temperature ramping. These arise from thiophene physisorbed on channel walls or interacting with residual Na cations. Most of the thiophene adsorbed at ambient temperature did not desorb unreacted, but reactions products, such as H_2S and benzene, were detected at relatively low temperatures by mass spectrometry and thiophene oligomers were apparent from the color changes in the samples during thiophene adsorption. Infared spectra during propane–thiophene reactions at 773 K did not detect significant coverages of adsorbed species interacting with acidic OH groups or any bands associated with organic species interacting with Co cations. Sulfur K-edge X-ray absorption spectra showed that organic sulfur species remain on samples after thiophene–propane reactions, but inorganic sulfides were not detected. The amount of retained organic sulfur is less than 1% of that removed from thiophene as H_2S. Co cations at exchange sites do not sulfide or reduce during reactions. X-ray absorption at the Co K-edge confirmed that Co cations are stable against sulfidation and reduction in the presence of thiophene–propane mixtures at 773 K. The local structure of the Co cations is slightly different, however, from that in fresh samples, apparently as a result of strongly adsorbed species interacting with the exchanged Co^{2+} cations.

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