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Hydrodesulfurization of Thiophene Using Rhodium(III) Zeolites: 13X and ZSM-5

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The hydrodesulfurization of thiophene using rhodium(III)-13X and -ZSM-5 zeolites has been studied in a pulsed microreactor as a function of temperature. Hydrodesulfurization catalysts were prepared by sulfidation with thiophene and with H_2S/H_2. The C_4 products included butene and butane. Neither tetrahydrothiophene nor butadiene was identified in the product gas stream. Thiophene conversion over Rh(III)-ZSM-5 sulfided at 400°C with a 10 vol% H_2S/90 vol % H_2 mixture was at least as effective as a commercial cobalt–molybdate catalyst under similar reaction conditions. The effectiveness of the Rh(III)-ZSM-5 catalyst sulfided with the H_2S/H_2 mixture at 250°C and with thiophene at 100°C was less than the cobalt–molybdate catalyst. The conversion percentage to C_4 hydrocarbons was greater on the Rh(III)–13X than on Co–Mo/Al_2O_3. Analysis by X-ray photoelectron spectroscopy (XPS) of the Rh-zeolite catalysts before and after use indicated that the active species is Rh(I). A mechanism for reaction on the Rh-zeolite is proposed where oxidative addition-reductive elimination reactions of Rh(I)/Rh(III) are involved in the hydrodesulfurization process.

INTRODUCTION

The proposed increase in the use of petroleum and coal-derived materials with high concentration of sulfur-containing compounds demands efficient catalytic processes for the removal of sulfur (*1*, *2*). Akhtar and co-workers (*3*) identified a number of thiophene derivatives in the liquid products from the hydrogenation of a Kentucky coal sample. Schemes and strategies for the desulfurization of coal and coal-derived products have suggested catalytic upgrading of soluble components (*4*, *5*). The most widely used desulfurization catalyst is cobalt–molybdate/alumina (*6* ,*7*). In studies of model thiophene systems the activity has been related to surface concentrations of anion vacancies where sulfide adsorption occurs and of sulfide-oxide sites where hydrogen adsorption and transfer proceed (*8*). An alternative mechanism for activity invokes π-bonding of the aromatic portion of thiophene to the catalyst surface (*2*, *9*, *10*). Hydrodesulfurization using rhodium, rhenium, iridium, and osmium sulfides is more effective than processes using cobalt or molybdenum sulfides (*1*). Pecoraro and Chianelli (*1*) observed that the catalyst activity could be related to the percentage of *d* character in the metal.

Rhodium zeolites have been used for carbonylation reactions (*11*), in the reduction of NO by CO (*12*), and for hydrodesulfurization of heterocyclic compounds (*13*). In the latter study (*13*) no investigation of the rhodium surface chemistry was carried out. Rhodium surface chemistry has been examined by infrared and X-ray photoelectron spectroscopic methods (*12*). The appearance of new infrared spectral bands upon adsorption of NO (*12*) and CO (*12*, *14*) led to the suggestion that Rh(I) species were active intermediates in the catalytic reactions. Andersson and Scurrell (*11*) have carried out an extensive study of the XPS spectra of rhodium zeolites in an attempt to identify the active species in carbonylation processes. XPS binding energy data were used to confirm the presence of Rh(I), however, unique binding energy results for Rh(I) were not obtained in all cases (*11*, *14*). The

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results of XPS studies on Rh(III) zeolite Y have been interpreted to suggest that Rh(0) is the active species for catalytic processes (*15*) Stepwise reduction of Rh(III) according to the sequence

$$\mathrm{Rh(III)} \xrightarrow[\mathrm{H_2}]{55^\circ\mathrm{C}} \mathrm{Rh(II)} \xrightarrow[\mathrm{H_2}]{150^\circ\mathrm{C}} \mathrm{Rh(I)} \xrightarrow[\mathrm{H_2}]{500^\circ\mathrm{C}} \mathrm{Rh(0)}$$

has been reported for the alteration of the surface chemistry of Rh(III) on SiO_2 (*16*) A Rh(I) carbonyl cluster species is offered as the intermediate in the Fischer–Tropsch production of hydrocarbons (*16*) Clearly rhodium in treated zeolites has been effective for a number of catalytic processes The ability of Rh(I) to bond to sulfur and to olefin functional groups is well recognized (*17*) The possibility of the formation of coordinatively unsaturated low valent metal ions in the zeolite is particularly attractive for activating heterocyclic compounds

Brooks (*13*) investigated the use of transition metal zeolite catalysts for the hydrodesulfurization of thiophene Maximum catalytic activity was found for nickel-, copper-, and rhodium-treated zeolites It was suggested that the excellent catalytic activity was due to (a) enhanced adsorption of reactant on the high surface area zeolite, (b) hydrocracking due to the high acidity of the zeolite, and (c) enhanced hydrogenolysis due to the transition metal No detailed surface characterization of the catalysts was carried out and the mechanism of catalyst interaction was not investigated

In this study the hydrodesulfurization of thiophene using rhodium zeolites has been investigated Rhodium(III) zeolites 13X and ZSM-5 were activated by reaction with thiophene and with H_2S/H_2 at several temperatures and their conversion ability for hydrodesulfurization of thiophene compared The evidence presented suggests that Rh(I) is the active species for the hydrodesulfurization process

EXPERIMENTAL SECTION

Zeolite 13X powder was obtained from Linde Division, Union Carbide The rhodium(III)-13X was prepared by ion exchange A sample of 0 235 g of $RhCl_3$ $3H_2O$ was dissolved in 15 ml of 6 *N* NH_4OH, and to this solution was added 2 0 g of zeolite 13X The suspension was stirred for 3 days The suspension was centrifuged and the Rh(III)-13X was washed with 1 liter of H_2O and dried overnight in air at 80°C A Rh(II)-13X sample was prepared by interacting a methanol solution of $Rh_2(CO_2CH_3)_4$ with zeolite 13X To a solution of 0 11 g of $Rh_2(CO_2CH_3)_4$ in 25 ml of methanol, was added 2 g of zeolite 13X The suspension was stirred 3 days The Rh(II)-13X sample was dried overnight in air at 80°C The $RhCl_3$ $3H_2O$ material was obtained from Engelhard Industries and $Rh_2(CO_2CH_3)_4$ was prepared by the method of Rempel (*18*)

The ZSM-5 zeolite was prepared according to the procedure outlined by Argauer and Landolt (*19*) Fifteen milliliters of 1 34 *N* tetrapropylammonium hydroxide was added to 3 11 g SiO_2 The mixture was heated to 100°C until dissolution of SiO_2 occurred To this solution was added 0 20 g $Na_2Al_2O_4$ $3H_2O$ in 5 ml of distilled deionized H_2O This mixture was allowed to stir for 10 min and then was placed in a thick-wall Pyrex tube The tube was sealed and placed in an oven at 165°C for 6 days The resulting white solid (ZSM-5-G2) was collected by centrifugation, washed with 1 liter of distilled water, and calcined at 500°C for 12 h to remove the amine The zeolite was sodium-saturated Characterization of the ZSM-5 zeolite was accomplished by X-ray diffraction, infrared spectroscopy, and X-ray photoelectron spectroscopy The results were compared with similar measurements on an authentic sample of Mobil ZSM-5 (ZSM-5-M) kindly provided by Mr C S Cheng of Mobil Research and Development Corporation The results of these analyses are collected in Table 1 A comparison of the characterization measurements indicates that the synthesized ZSM-5 designated ZSM-5-G2 is structurally equivalent to ZSM-5-M Rhodium(III) was ad-

TABLE 1

Characterization of ZSM-5 Catalyst

X-Ray diffraction

ZSM-5-M		ZSM-5-G2	
$d \pm 0$ 1 Å	Intensity[a]	$d \pm 0$ 1 Å	Intensity[a]
11 9	vs	11 9	vs
3 9	vs	3 9	s
10 5	s	10 7	s
3 8	vs	3 8	s

Infrared bands (cm^{-1})

ZSM-5-M	ZSM-5-G2
1098	1092
790	788
612	627
548	549
446	445
379	350

X-Ray photoelectron spectroscopy binding energies

	Si 2*p* (±0 1 eV)	Al 2*p* (±0 1 eV)	Si/Al (atomic ratio)
ZSM-5-M	103 4	73 9	26 9
ZSM-5-G2	103 4	74 3	31 6

[a] vs, very strong, s, strong

sorbed onto ZSM-5-G2, by the method of ion exchange described above for the preparation of Rh(III)-13X

The cobalt–molybdenum/alumina catalyst was purchased from Alpha Products The Co–Mo/Al_2O_3 catalyst was composed of 12% MoO_3 and 3% CoO (manufacturer's analysis data) Thiophene was obtained from Aldrich Chemical Company (99+ % purity) and was used without further purification Gas chromatographic analysis of thiophene revealed no impurities that would interfere with the catalytic studies

The thiophene hydrodesulfurization reactions were carried out in a pulsed microreactor/gas chromatograph system Compound separations were accomplished using a $\frac{1}{8}$-in diameter, 8-foot column packed with Supelco 3% SP-2250 on 100/120 mesh Supelcoport substrate The column was operated at 70°C and the thermocouple detector at 200°C The chromatographic response was calibrated by injecting known volumes of thiophene, C_4 hydrocarbons, and H_2S into the chromatograph The reactions were studied at a flow rate of 40 ml/min H_2 The hydrogen carrier gas was purified before entering the reactor/gas chromatograph by passing the gas over a molecular sieve trap and an oxygen trap

The microreactor was a 1-mm-diameter stainless-steel tube mounted up stream from the analytical column and directly behind the injection port Injections were made directly into the reaction cell A 5-mg sample of Rh zeolite or Co–Mo/Al_2O_3 catalyst was loaded in the reactor and was sandwiched by quartz wool plugs The hydrodesulfurization (HDS) reactions were carried out at 350, 400, 450, and 600°C The temperature of the reactor was measured with a calibrated chromel–alumel thermocouple The conversion percentage was evaluated from the integrated chromatographic peak intensities by using

$$\% \text{ conversion} = \frac{\frac{1}{2}(I_{C_4} + I_{H_2S})}{\frac{1}{2}(I_{C_4} + I_{H_2S}) + I_{C_4H_4S}} \times 10^2$$

where I_{C_4} = total quantity C_4 hydrocarbons, I_{H_2S} = quantity of H_2S, and $I_{C_4H_4S}$ = quantity of thiophene

Products were trapped after exit from the analytical column in a glass U-trap maintained at liquid-nitrogen temperature The products were analyzed using a UTI 100 C quadrupole mass spectrometer Spectra were measured at 70 eV and the mass spectrometer sensitivity was determined for C_4 hydrocarbons by measuring spectra for butane, *cis*-2-butene, and 1,3-butadiene The precision of the intensity measurements, ±5%, made it impossible to distinguish between 1-butene and *cis*- and *trans*-2-butene The quantity of butene includes all isomers of butene Only butane and butene hydrocarbons and H_2S were detected in the product gas stream The overall reaction investigated is

$$C_4H_4S + H_2 \rightarrow H_2S + [C_4H_{10} + C_4H_8]$$

where H_2S makes up 50% (mol) of the product composition The limit of detection for thiophene conversion is 0 10% The precision in the measurements for the thiophene conversion percentage results is ± 0 10% The precision for the butane/butene ratio determination is ± 20%

Since the sulfided form of catalysts appears to be the active species for hydrodesulfurization (*1*), two methods were investigated for sulfiding the Rh(III) zeolites One method involved making 0 5 μl injections of thiophene into the system with the Rh(III) zeolite at 100°C until the peak shapes and the ratio of peak heights of products to unreacted thiophene were reproducible to within ±0 5% The conditioning process was usually complete after about 10 injections The second method of sulfiding was to contact the Rh(III)-ZSM-5-G2 catalyst with a flowing stream of a 10 vol% H_2S/90 vol% H_2 gas mixture at atmospheric pressure for 2 h at temperatures 22, 150, 200, 350, and 400°C The Rh(III)-13X and the cobalt–molybdate/alumina catalysts were sulfided for 2 h at 250 and 400°C in a stream of 10 vol% H_2S/90 vol% H_2 at atmospheric pressure Following sulfidation the samples were cooled in a helium gas flow The Co–Mo/Al_2O_3 catalyst could not be sulfided with thiophene at 100°C so no comparison of activity with the Rh(III) zeolite catalysts can be made

XPS spectra were measured using a DuPont 650 spectrometer Samples were mounted with Scotch brand double-stick tape Rhodium zeolite samples were transported and introduced into the XPS spectrometer under a dry Ar atmosphere and in air No differences in the XPS results were noted for the two transportation/introduction procedures A magnesium anode, $h\nu$ = 1253 6 eV was used as the X-ray source Spectra were calibrated by reference to the binding energy for the C 1*s* photoelectron peak at 284 6 eV It was found that while acquiring the XPS spectra, rhodium on the zeolite undergoes radiation-induced reduction Evidence for the change in rhodium oxidation state included a decrease in binding energy and broadening of the Rh $3d_{3/2}$ and Rh $3d_{5/2}$ photoelectron peaks This process was complete after about 2 h in the spectrometer All rhodium spectra were obtained within the first 5 or 10 min of collecting spectra before significant reduction had occurred At least four different measurements of the XPS spectra were made for the zeolites, Co–Mo/Al_2O_3, rhodium compounds, and rhodium-treated zeolites Elemental atomic ratios were calculated from integrated photopeak intensities for Rh $3d_{5/2}$, S $2p_{1/2\ 3/2}$, Si $2p_{1/2\ 3/2}$, and Al $2p_{1/2\ 3/2}$ which were corrected for the photoionization cross section (*20*) and an instrumental sensitivity factor Curve resolution of photoelectron peaks was performed using the GASCAP program (*21*)

Electrophoretic mobility studies for ZSM-5 were made using a Rank Brothers Mark II Particle Microelectrophoresis instrument The suspension was prepared by mixing 0 1 g of ZSM-5 in 500 ml of 10^{-2} *M* $NaClO_4$ The mobility measurements were made using a constant applied voltage of 60 V Ten measurements were made at both the front and back stationary planes The pH_{IEP} for ZSM-5-M was 2 6 while the value for ZSM-5-G2 was 2 4 The error in the mobility measurements is ±0 5 μm/s/V/cm

A Norelco X-ray diffractometer employing nickel-filtered Cu$K\alpha$ radiation was used A Perkin–Elmer 283B spectrophotometer was used to collect infrared data The samples were run as a KBr pellets

RESULTS AND DISCUSSION

Surface Characterization of Zeolites

Rhodium(III) zeolites were characterized using XPS before and after ion exchange, after sulfidation, and after use in the HDS reactor The XPS results are summarized in Table 2 for the various samples and rhodium compounds

TABLE 2

XPS Characterization of Rh Zeolite Samples

Sample	Binding energy (eV)				Atomic ratio	
	Rh $3d_{5/2}$	S $2p$	Si $2p$	Al $2p$	S/Rh	Rh/(Al + Si)
Zeolite 13-X	—	—	101 7	73 8	—	—
Rh(III)-13X[a]	309 5	—	101 7	73 7	—	0 18
$Rh_2(CO_2CH_3)_4$-13X (Rh(II))	308 4		101 8	73 8	—	0 031
(Rh(I)/(0))	307 4					
Rh(III)-13X	309 4	162 5	—	—	0 63	0 16
Thiophene-sulfided 100°C	307 2					
H_2S/H_2-sulfided						
250°C	307 5	162 2	—	—	1 67	0 15
400°C	308 0	162 4	—	—	2 06	0 16
ZSM-5-G2	—	—	103 4	74 3	—	—
Rh(III)-ZSM-5-G2[a]	309 8	—	102 8	74 3	—	0 11
Thiophene-sulfided 100°C	307 4	163 1	—	—	0 22	0 08
H_2S/H_2 sulfided						
250°C	308 2	162 2	—	—	2 50	0 10
400°C	307 6	162 2	—	—	1 01	0 09
Rh_2S_3 (This work)	308 6	162 3			1 47	

Literature values

	Rh $3d_{5/2}$		Rh $3d_{5/2}$
$RhCl_3$/zeolite X *(11a)*	310 2	$Rh(PPh_3)_3Cl$ *(24)*	309 4
		(14, 26)	308 2
$Rh(NH_3)_5Cl$/zeolite X *(11b)*	310 2	*(29)*	307 8
		(28)	307 6
$RhBr_3$/zeolite Y *(15)*	309 5	*(25)*	307 2
$RhCl_3$ $3H_2O$ *(11a, 27)*	310 2	Rh(DOC)[b](CO)Cl *(23)*	308 7
(26)	309 4		
(This work)	309 6	$RhCl(CO)(PPh_3)_2$ *(26)*	308 7
		(29)	309 0
Rh_2O_3 *(22)*	308 4	*(28)*	308 5
(23)	309 1		
		Rh(0) *(36)*	307 4
$Rh_2(CO_2CH_3)_4$ (This work)	308 6	*(29)*	307 2
(35)	308 8	*(22, 26, 12)*	307 1
		(23)	307 0
$HRh(CO)(PPh_3)_2$ *(11a)*	309 5		
(29)	308 7		

[a] $RhCl_3$ $3H_2O$ + 6 *M* NH_4OH + zeolite

[b] Cyclooctadiene-1,5

Rh(III) Zeolites

The Rh $3d_{5/2}$ binding energy for Rh(III)-13X is equal to that for $RhCl_3$ $3H_2O$, a finding which is interpreted to indicate that Rh(III) is adsorbed on the surface The Rh $3d_{5/2}$ photopeak for $Rh_2(CO_2CH_3)_4$ adsorbed on 13X is broad with a binding energy which is lower than the value for pure $Rh_2(CO_2CH_3)_4$ The Rh $3d_{5/2}$ peaks for Rh(II)-13X could be curve resolved to yield photopeaks with binding energies centered at 308 4 and 307 4 eV The higher binding energy is only slightly lower than the value for the parent Rh(II) compound and this photopeak is assigned to Rh(II) The lower binding energy is in the range of binding energies for Rh(I) or Rh(0) It was not possible to make a unique assignment for the lower energy photopeak

The Rh $3d_{5/2}$ binding energy for Rh(III)-ZSM-5-G2 is in good agreement with the value measured for $RhCl_3$ $3H_2O$, for Rh(III) zeolite Y (15) and for Rh(III) zeolite X (11b) The equivalent binding energies of the Rh $3d_{5/2}$ photopeaks for rhodium on ZSM-5-G2, in $RhCl_3$, and on other zeolites indicates that rhodium exists as Rh(III) on the ZSM-5-G2 surface

Sulfided Rh(III) Zeolites

The Rh(III) zeolites samples were reacted with thiophene and with H_2S/H_2 at several temperatures in order to obtain a variety of sulfided catalysts The sulfiding of Rh(III) zeolites leads to an alteration in the rhodium surface chemistry, which is indicated by the decrease in the Rh $3d_{5/2}$ binding energies The elucidation of a specific rhodium oxidation state from binding energy measurements is complicated by the fact that Rh $3d_{5/2}$ binding energies are severely dependent on the nature of the coordinating environment (*11, 14, 15, 22–27*) The identification of Rh(I) and Rh(0) is particularly difficult since the reported Rh $3d_{5/2}$ binding energies for Rh(0) and for Rh(I) overlap (Table 2)

The Rh $3d_{5/2}$ binding energies for the thiophene-sulfided Rh(III)-13X samples are lower than the values for the starting Rh(III)-13X zeolite The Rh XPS spectrum exhibited two photopeaks with $3d_{5/2}$ binding energies centered at 309 4 and 307 2 eV The higher binding energy is little changed from that of the starting Rh(III)-13X zeolite The Rh $3d_{5/2}$ binding energy at 307 2 eV is near that reported for Rh(0) and also for Rh(I) compounds (Table 2) It appears that thiophene sulfidation leads to a mixture of Rh(III) and Rh(I)/Rh(0) oxidation states

The Rh $3d_{5/2}$ PWHM's (peak width at half maxima) for the H_2S/H_2-sulfided Rh(III)-13X samples were 1 8 eV When compared with the Rh $3d_{5/2}$ PWHM for $RhCl_3$ (1 8 eV) and $Rh_2(CO_2CH_3)_4$ (1 9 eV), the Rh(III)-13X PWHM value is indicative of only one rhodium species The Rh $3d_{5/2}$ binding energies for the H_2S/H_2-sulfided 13X are lower than the presulfided value The value for the sample sulfided at 250°C is in the region for Rh(I) or Rh(0) and thus the XPS binding energy data are not definitive in identifying the rhodium chemical state The Rh $3d_{5/2}$ binding energy, 308 0 eV, for the catalyst sulfided at 400°C is near the values reported for Rh(I) compounds (*11a, 14, 23–29*) None of the sulfided Rh(III)-13X samples yields a Rh $3d_{5/2}$ binding energy equal to the value measured for Rh_2S_3 This latter result suggests that Rh_2S_3 is not formed on the surface in the sulfidation of Rh(III)-13X under the experimental conditions used in this study The sulfur $2p$ binding energies are equal to the value measured for metal sulfides, but the absence of a Rh $3d_{5/2}$ photopeak attributable to Rh(III) argues against the formation of Rh_2S_3

The rhodium $3d_{5/2}$ binding energy for thiophene-sulfided Rh(III)-ZSM-5-G2 is near the value for Rh(I) or Rh(0) The PWHM for the sample (1 8 eV) is consistent with the presence of only one rhodium oxidation state The XPS results demonstrate that sulfur is present as sulfide on the surface and the S/Rh ratio was 0 22 The low S/Rh ratio may indicate that sulfidation did not produce a well-defined stoichiometric rhodium sulfide The sulfur $2p$ binding energy for the thiophene-sulfided Rh-zeolite, 163 1 eV, is between the values of thiophene, 164 5 (*30*) Na_2S, 162 0 (*30*), and Rh_2S_3, 162 3 The PWHM for sulfur in a single oxidation state is 2 2 eV, while the value for thiophene Rh zeolite is 2 5 eV This result suggests that sulfur may be present as adsorbed thiophene (*31*) and as an inorganic sulfide

The XPS characterization results for H_2S/H_2-sulfided Rh(III)-ZSM-5-G2 are pre-

TABLE 3

XPS Results for Sulfidation of Rh(III)-ZSM-5-G2 with 10 vol% H_2S/90 vol% H_2 at Selected Temperatures for 2 h

Temperature (°C)	Binding energy (±0 1 eV)		Atomic ratios	
	Rh $3d_{5/2}$	S $2p$	S/Rh	Rh/(Al + Si)
22	309 2	162 4	0 36	0 11
150	308 4	162 3	2 30	0 10
250	308 2	162 2	2 50	0 10
350	307 7	162 3	0 90	0 10
400	307 6	162 2	1 01	0 09
Rh(III) ZSM 5 G2	309 8	—	—	0 11

sented in Table 3, and the Rh $3d$ XPS spectra for Rh(III)- and H_2S/H_2-sulfided Rh(III)-ZSM-5-G2 samples are presented in Fig 1 Sulfidation yields three groups of sulfided Rh(III)-ZSM-5-G2 samples as indicated by the Rh $3d_{5/2}$ binding energies and the S/Rh atomic ratios The three groups correspond to samples sulfided at 22, at 150 and 250, and at 350 and 400°C The sample obtained by sulfidation at 22°C yields the lowest S/Rh ratio and a Rh $3d_{5/2}$ binding energy only slightly lower than the value for the starting Rh(III)-ZSM-5-G2 However, the PWHM for the Rh $3d_{5/2}$ photopeak for the 22°C sulfided sample is wider than for the starting Rh(III)-ZSM-5-G2 It is reasonable that Rh(III) and Rh(II) species are present on this sample For Rh(III)-ZSM-5-G2 sulfided at 150 and 250°C the Rh $3d_{5/2}$ binding energies, at 308 4 and 308 2 eV, respectively, are suggestive of a reduced rhodium species The rhodium binding energies are lower than the value measured for Rh(II) in $Rh_2(CO_2CH_3)_4$, but greater than for Rh(I) or Rh(0) The S/Rh atomic ratios were 2 30 and 2 50 for the 150 and 250°C sulfided samples, respectively This ratio is greater than the value expected for a rhodium sulfide The sulfur $2p$ photopeaks have peak widths and binding energies characteristic of a single sulfide species The high S/Rh ratio could arise if polysulfides (*32*) or other metal sulfides are formed or if H_2S is strongly adsorbed on the catalyst

The rhodium binding energies for samples sulfided at 350 and 400°C are in the range of values reported for Rh(I) and Rh(0) It is likely that a single rhodium species is present since the Rh $3d_{5/2}$ PWHM's, 1 8 eV (Fig 1) are equal to the values for simple rhodium-containing species (*11*) The S/Rh ratio, 1 0, is lower than the ratio measured at 150 and 250°C This ratio is between the ratios for Rh(III) and Rh(I) sulfides and could indicate that a mixture of the two is present However, the presence of Rh(III) is not supported by the XPS binding energy results since no Rh $3d_{5/2}$ photopeak characteristic of Rh(III) is recorded in the 309 6-eV region for these samples

The sulfur $2p$ binding energies for Rh(III)-ZSM-5-G2 sulfided with H_2S/H_2 are equal and the PWHM values, 2 2 eV, suggest the presence of only one sulfur, the sulfide The sulfur $2p$ binding energy in Rh_2S_3 is 162 3 eV, a value which is equal to the binding energy for the H_2S/H_2-sulfided

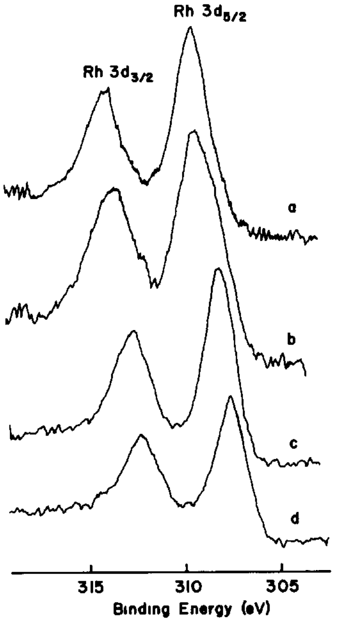


FIG 1 XPS Rh $3d$ spectra for Rh(III)-ZSM-5 catalysts (a) Rh(III)-ZSM-5 before sulfidation (b) Rh(III)-ZSM-5 sulfided H_2S/H_2 (22°C) (c) Rh(III)-ZSM-5 sulfided H_2S/H_2 (250°C) (d) Rh(III)-ZSM-5 sulfided H_2S/H_2 (400°C)

Rh(III)-ZSM-5-G2. However, the rhodium binding energies indicate that rhodium in the zeolite is not similar to Rh(III) in Rh_2S_3. Thus, the XPS results suggest that reduced rhodium is formed on the Rh(III)-ZSM-5-G2 sulfided catalysts, but the rhodium oxidation state cannot be identified unequivocally from the binding energy results.

Hydrodesulfurization of Thiophene

Hydrodesulfurization reactions were carried out using quartz wool, Na^+-13X and Na^+-ZSM-5-G2 zeolites, at 350, 400, 450, and 600°C to discover whether these materials contributed to the desulfurization of thiophene. Thiophene conversion ($\leq$0.10%) was not observed on either quartz wool or on Na^+-13X or Na^+-ZSM-5-G2. Hydrodesulfurization of thiophene was observed on rhodium(III) zeolites and it is concluded that the activity is due to rhodium or to a combined effect of rhodium and the zeolite support.

Rh(III)-13X

Thiophene conversion studies were conducted on Rh(III)-13X sulfided at 100°C with thiophene and on H_2S/H_2 sulfided Rh(III)-13X and Co–Mo/Al_2O_3 as a function of temperature. The conversion results are presented in Table 4. The conversion ability for the 13X zeolite catalysts sulfided at 250°C with H_2S/H_2 is similar to that for Co–Mo/Al_2O_3. At a reaction temperature of 600°C Co–Mo/Al_2O_3 exhibits maximum conversion ability (5.57%). Rh(III)-13X sulfided at 400°C shows higher conversion at 400, 450, and 600°C than Co–Mo/Al_2O_3. For thiophene-sulfided samples the results indicate that Rh(III)-13X has excellent activity and converts 13.4% of the thiophene at 600°C. This conversion percentage is greater than that for any other catalyst studied.

The C_4 products detected with the mass spectrometer were butene and butane. No tetrahydrothiophene or butadiene were detected under any experimental conditions. Within the precision of the measurements, the butane/butene ratio decreases with increasing temperature for desulfurization with Rh(III)-13X and with Co–Mo/Al_2O_3 (Table 4). The decrease in the ratio is related to the greater activation energy for HDS compared to hydrogenation of butene. With increasing temperature the HDS process increases more rapidly than the hydrogenation of butene and thus the production of butene is greater. Further discussion of the variation in product ratios is beyond the scope of the present study.

The catalysts were characterized by XPS after use in conversion reactions up to 600°C and after use at each temperature for thiophene-sulfided Rh(III)-13X in an attempt to identify the active rhodium species and to uncover any features that might be related to the high activity for thiophene conversion on Rh(III)-13X. The XPS binding energy and atomic ratio results for this

TABLE 4

Thiophene Conversion Percentage and Product Distribution for Sulfided Rh(III)-13X, Rh(III)-ZSM-5-G2, and Co–Mo/Al_2O_3 (40 ml/min H_2 flow rate, 5 mg catalyst)

Reactor temperature (°C)	Rh(III) 13X						Rh(III) ZSM 5 G2						Co–Mo/Al_2O_3			
	Th[a]	A/E[b]	250°C[a]	A/E[b]	400°C[a]	A/E[b]	Th[a]	A/E[b]	250°C[a]	A/E[b]	400°C[a]	A/E[b]	250°C[a]	A/E[b]	400°C[a]	A/E[b]
350	0.76	0.45	0.48	0.41	0.34	1.56	0.34	0.91	0.44	1.0	0.49	1.11	0.52	1.23	0.40	4.55
400	2.01	0.34	0.53	0.56	0.91	0.49	0.60	0.63	0.49	0.53	0.57	0.63	0.63	0.58	0.51	0.61
450	4.23	0.28	0.72	0.60	1.76	0.30	0.96	0.48	1.09	0.43	0.70	0.63	1.09	0.40	0.60	0.48
600	13.42	0.36	3.81	0.29	4.28	0.26	3.13	0.42	4.73	0.29	3.32	0.31	5.57	0.15	2.82	0.25

[a] Conversion percentage. Th = thiophene sulfided. 250 400°C H_2S/H_2 sulfided at 250 and 450°C respectively.

[b] Butane/butene ratio.

TABLE 5

XPS Results for Sulfided Rh(III)-Zeolites after Hydrodesulfurization Reactions

After hydrodesulfurization from 350° to 600°C	Rh(III)-13X Binding energy (eV)		Atomic ratio	
	Rh $3d_{5/2}$	S $2p$		
10% H_2S/90% H_2 (250°C)	307.0	162.2	0.11	0.14
10% H_2S/90% H_2 (400°C)	307.4	162.6	0.21	0.10
Thiophene (100°C)	307.0	162.4	0.25	0.15
After hydrodesulfurization and removed at the temperature (°C), thiophene-sulfided Rh(III)-13X				
350	307.2	162.3	0.89	0.18
400	307.2	162.4	0.80	0.15
450	307.1	162.1	0.54	0.13
600	307.1	162.3	0.25	0.12
	Rh(III)-ZSM-5-G2			
After hydrodesulfurization from 350 to 600°C				
10% H_2S/90% H_2 (250°C)	307.6	162.1	0.13	0.06
10% H_2S/90% H_2 (400°C)	307.6	162.4	0.43	0.10
Thiophene (100°C)	307.6	162.1	0.07	0.05

characterization are given in Table 5. The Rh $3d_{5/2}$ binding energies are approximately equal and the PWHM for the $3d_{5/2}$ photopeaks is 1.8 eV. The PWHM results suggest that only one rhodium species is present or if more than one species is present, the binding energies are equal. The Rh $3d_{5/2}$ results for thiophene-sulfided Rh(III)-13X are unlike the results for the initially prepared catalyst where a mixture of Rh(III) and Rh(I)/Rh(0) was found. The binding energy for the used catalyst is also slightly lower than for the 400°C H_2S/H_2-sulfided Rh(III)-13X starting catalyst (Table 2). The Rh $3d_{5/2}$ binding energy is in the region attributed to Rh(I) and Rh(0). The XPS results alone do not identify the active species as Rh(I) or Rh(0), but do suggest that Rh(III) and Rh(II) are not present on active Rh-13X. The sulfur $2p$ binding energy corresponds to that for sulfide and is equivalent to the value measured for the H_2S/H_2-treated catalyst.

The atomic Rh/(Al + Si) ratios are not altered significantly from the values determined for the ion-exchanged and sulfided catalysts. With increasing temperature of hydrodesulfurization it is noted that the Rh/(Al + Si) ratio decreases from a value of 0.18 to 0.12. Whether this decrease is due to loss of rhodium, to migration of rhodium into the zeolite cage, or to sintering of rhodium-13X (*11b*) cannot be established from the present results. The S/Rh atomic ratio is significantly less in the used catalysts when compared to the prepared sulfided materials. The S/Rh ratio changes from values in the range of 0.6 to 2.0 for sulfided Rh(III)-13X to values near 0.2 ± 0.1 after use in the HDS reactor for thiophene conversion up to 600°C. The S/Rh ratios for thiophene-sulfided Rh(III)-13X catalysts that were removed from the reactor after use up to the designated temperatures, 350, 400, 450, and 600°C, decrease from 0 89 to 0 25 with increasing temperature The ratios are not indicative of Rh_2S_3 or Rh_2S formation, although the S/Rh ratio, 0 54, for the sample removed at 450°C corresponds to the ratio for Rh_2S The presence of Rh_2S_3 can be eliminated since no Rh(III) photopeak is recorded in the spectra for the used catalyst An alternative explanation of the S/Rh ratio would include the presence of a rhodium sulfide and rhodium metal Because of the near equality of Rh(I) and Rh(0) binding energies the XPS results do not permit identification of rhodium metal along with a rhodium sulfide species on the zeolite surfaces

To inquire whether Rh(0) could be the active species, a sample of Rh(III)-13X was reduced in H_2 at 600°C for 2 h The Rh $3d_{5/2}$ binding energy for the sample is 307 2 eV which is in the range for Rh(0) and for our sulfided Rh(III)-13X samples This Rh(0)-13X sample was sulfided with thiophene at 100°C using the procedure for sulfiding Rh(III)-13X Thiophene conversion reactions were carried out at selected temperatures using this catalyst The conversion percentages were 350°C, 0 39, 400°C, 0 36, 450°C, 0 28, and 600°C, 0 77 These conversion values are significantly below the values found for thiophene-sulfided Rh(III)-13X and suggest that Rh(0)-13X is not an effective catalyst Taking the Rh(0)-13X conversion results and considering the XPS Rh $3d_{3/2}$ data we suggest that the zeolite surface species is Rh(I) and that the active species in the hydrodesulfurization reaction is Rh(I)

Rh(III)-ZSM-5-G2

Hydrodesulfurization reactions were carried out using Rh(III)-ZSM-5-G2 sulfided with thiophene at 100°C and with H_2S/H_2 at 250 and 400°C These samples were selected since the presence of mixed rhodium oxidation states was suggested by the XPS results and because the S/Rh ratios were dissimilar

The conversion percentage results for thiophene and the butane/butene product ratio are summarized in Table 4 for sulfided Rh(III)-ZSM-5-G2 and are compared with the results for sulfided Co–Mo/Al_2O_3 An increase in the conversion percentage with increasing temperature is found At the temperatures investigated, the thiophene conversion percentage for each catalyst sulfided with H_2S/H_2 at 250 and at 400°C is similar For Rh(III)-ZSM-5-G2 sulfided with thiophene the conversion percentage is equivalent to the result found for H_2S/H_2-sulfided zeolite Thus the sulfided Rh(III)-ZSM-5-G2 material is no more effective than the commercial sulfided Co–Mo/Al_2O_3 catalyst when employed for HDS under similar experimental conditions

The butane/butene product ratio decreases with increasing temperature for Rh(III)-ZSM-5-G2 for all sulfiding treatments The butane/butene ratio for Co–Mo/Al_2O_3 is lower than that for the Rh-ZSM-5-G2 at 600 and 450°C However, at 400°C the product ratios are similar The variation in product ratios is like the result discussed above for Rh(III)-13X It is suggested that the ratios are influenced by the relative magnitude of the activation energies for HDS and for butene hydrogenation The decrease in the formation of butane at high temperatures may be related also to the lower adsorption of butene on the zeolite However, in this study no experiments were carried out to examine the adsorption characteristics of Rh(III)-ZSM-5-G2

The surfaces of the catalysts were characterized after the hydrodesulfurization reactions to correlate surface characteristics with thiophene conversion activity and to determine the active rhodium hydrodesulfurization species The XPS results are summarized in Table 5 The Rh $3d_{5/2}$ binding energies are equal, 307 6 eV, for the three Rh(III)-ZSM-5-G2 samples The alteration in Rh $3d_{5/2}$ binding energy after the HDS reaction for the sample sulfided at

250°C with H_2S/H_2 and the value of the PWHM, 1 8 eV, indicate that a single reduced rhodium species is present The equivalence of the rhodium binding energies is indicative of the same rhodium oxidation state in each catalyst and the magnitude of the binding energy suggests the presence of Rh(I) or Rh(0) The sulfur 2*p* binding energies are near the value determined for sulfur in Rh_2S_3 and in the catalyst sulfided with H_2S/H_2 at 250 and 400°C These results are consistent with a formulation of sulfur as sulfide in the catalyst

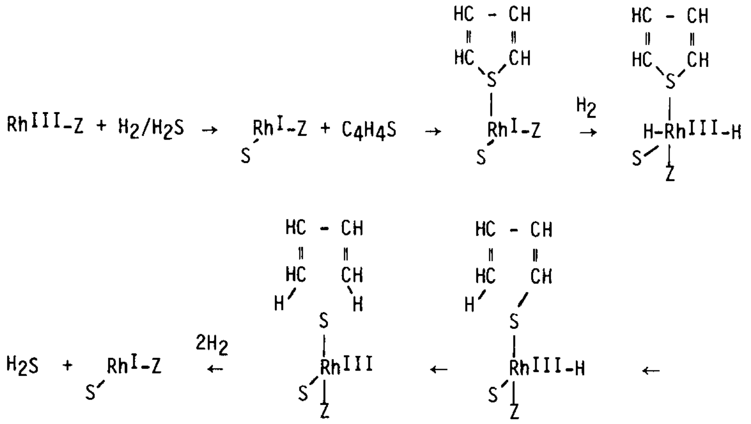
The rhodium surface concentration, as measured by the Rh/(Si + Al) ratio, is less after use to 600°C in the reactor for the samples sulfided with thiophene and with H_2S/H_2 at 250°C while the ratio for the sample sulfided at 400°C with H_2S/H_2 has increased slightly The magnitude of the increase for the latter sample is not significant and is within the precision of the measurements The decrease in rhodium ratio for the thiophene- and H_2S/H_2-(250°C) Rh zeolite may be the result of sintering (*11b*) or of migration of rhodium into the zeolite Alterations in rhodium for the thiophene-and H_2S/H_2-(250°C) sulfided Rh(III)-ZSM-5-G2 might be expected since the initially prepared catalyst contained a mixture of rhodium oxidation states [H_2S/H_2-(250°C)Rh-ZSM-5-G2] and/or incomplete reaction of sulfur surface species (thiophene–Rh-ZSM-5-G2) Further evidence for alteration in the catalysts after use is noted from the S/Rh ratios For each catalyst the ratio is lower and the ratios for the thiophene and H_2S/H_2 (250°C) Rh-ZSM-5 samples are less than would be anticipated for a stoichiometric rhodium sulfur compound On the other hand, the ratio for the H_2S/H_2-(400°C) Rh-ZSM-5-G2 sample after reaction is approximately that expected for a Rh(I) sulfide This correspondence may be fortuitous No evidence (except for XPS results) was gathered to support the formation of a rhodium(I) sulfide

The absence of interpretable S/Rh ratios and the determination of Rh $3d_{5/2}$ binding energies equivalent to the value for Rh(0) could be used to argue for Rh(0) as the active species in these hydrodesulfurization experiments To test this hypothesis a sample of Rh(III)-ZSM-5-G2 was reduced in pure H_2 at 600°C for 4 h The XPS surface analysis of this sample yielded a Rh $3d_{5/2}$ binding energy of 307 4 eV which is equivalent to values measured for Rh(0) and for H_2S/H_2-sulfided Rh(III)-ZSM-5-G2 materials However, the Rh(0)-ZSM-5-G2 catalyst was used in the reactor at 350, 400, 450, and 600°C, the conversion of thiophene was <0 10% In addition, XPS analysis of the sample following use in the reactor indicated that the Rh $3d_{5/2}$ binding energy was unaltered and that sulfur could not be detected The absence of sulfur on the Rh(0)-ZSM-5-G2 catalyst after repeated reactions with thiophene indicates that the Rh(0) catalyst is unable to form a sulfide species Further, it is known that Rh(0) is an excellent hydrogenation catalyst for reduction of olefins to alkanes (*33*) The product ratio for desulfurization on the sulfided Rh(III)-ZSM-5-G2 samples revealed that the butane/butene ratio decreased with increasing temperature This result would not be expected if Rh(0) was the active species The findings herein point to Rh(I) as the important species for hydrodesulfurization of thiophene on sulfided Rh(III)-ZSM-5-G2

This conclusion may be compared with the findings of others where attempts have been made to identify the active rhodium species Kuznicki and Eyring (*15*) presented XPS data in support of Rh(0) as the active species in "so-called" Rh(III) zeolite catalysts This conclusion (*15*) has been called premature by Andersson and Scurrell (*11b*) who have carried out an extensive XPS characterization study of Rh(III) zeolites for methanol carbonylation Andersson and Scurrell (*11b*) reported that treatment of $Rh(NH_3)_5Cl$ zeolite with CO or a mixture of CO and CH_3I does not alter the Rh $3d_{5/2}$ binding energy even though infrared studies demonstrate that Rh(I) is present. Binding energies at 308.6 and 308.2 eV for $RhCl_3/SiO_2$ and $RhCl_3/SnO_2$, respectively, are assigned to Rh(I) species (*11b*). The binding energies reported in the present study are lower than the values assigned for Rh(I) species (*11b*) but it is noted for these Rh(I) species (*11b*) there is a difference of 0.4 eV for Rh(I) on SiO_2 and on SnO_2. Furthermore, a difference of 0.5 eV in the Rh $3d_{5/2}$ binding energies for Rh_2O_3 and Rh_2S_3 is noted in Table 2. A lowering of the Rh $3d_{5/2}$ binding energy upon sulfidation could lead to a Rh(I)-sulfided species with a binding energy in the region 307.5 eV.

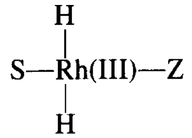
Proposed HDS Mechanism

In the present study chemical and surface analysis (XPS) results are consistent with the notion that Rh(I) is the active species. With this information a proposed mechanism similar to that suggested (*29*) for the hydrogenation of olefins involving a Rh(III)/Rh(I) couple is suggested as a basis from which further testing can be initiated (Scheme I).



In this scheme Rh(III) zeolite, RhIII-Z, is reduced by H_2/H_2S to yield sulfided Rh(I) zeolite. Thiophene adsorbs via coordination of sulfur to Rh(I) in a one-point attachment process (*34*). Alternate bonding modes could occur via a Rh(I)–olefin-π bond interaction or by a sulfur and olefin-π-bond attachment. The specific mode of attachment was not elucidated in this work. Hydrogen addition occurs via oxidative addition to Rh(I) to provide hydrogen for rupturing the carbon–sulfur bonds. Hydride transfer from Rh(III) produces the diolefin (butadiene) which can be hydrogenated subsequently. The proposed hydride transfer yields Rh(III) with a coordinated sulfur which is removed as H_2S with H_2. Reformation of Rh(I) is accomplished by reaction with a second mole of H_2.

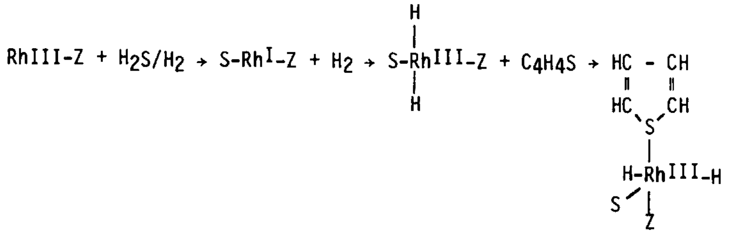
As an alternative it is also possible that the initial interaction of thiophene and Rh zeolite could occur by thiophene adsorption on a species such as



$$S\text{—}\overset{\displaystyle H}{\underset{\displaystyle H}{Rh(III)}}\text{—}Z$$

formed in an oxidative-addition reaction with H_2 and Rh(I) zeolite as shown in Scheme II. The Rh(III)–thiophene species is the same as that shown in Scheme I.

The experiments in the present study do not favor Schemes I or II for representing the initial interaction of thiophene with sulfided Rh zeolite. However, based on the knowledge that Rh(I) coordination to sulfur and π-olefin ligands is favorable (*17*), the interaction represented by Scheme I is probably preferred.



$$\mathrm{Rh^{III}\text{-}Z + H_2S/H_2 \rightarrow S\text{-}Rh^{I}\text{-}Z + H_2 \rightarrow S\text{-}Rh^{III}H_2\text{-}Z + C_4H_4S \rightarrow}$$

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