Kinetics and Mechanism of Thiophene Hydrodesulfurization over Carbon-Supported Transition Metal Sulfides

E. J. M. Hensen, M. J. Vissenberg, V. H. J. de Beer, J. A. R. van Veen, and R. A. van Santen

Schuit Institute of Catalysis, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands

Results of a detailed kinetic study on the thiophene hydrodesulfurization reaction at atmospheric pressure over a set of carbon-supported transition metal sulfides, i.e., the sulfides of Co, Mo, Rh, and the mixed CoMo sulfide, are presented. It is found that (partially) hydrogenated thiophenes, i.e., 2,3-dihydrothiophene, 2,5-dihydrothiophene, and tetrahydrothiophene, are important intermediates in the reaction mechanism. The reaction orders of thiophene suggest that carbon–sulfur bond cleavage is rate limiting for most of the catalysts. The CoMo catalyst may have hydrogenative sulfur removal as the rate limiting step. This catalyst shows a strong decrease in apparent activation energy with temperature to be ascribed to a large change in steady state surface coverage by thiophene (or H$_2$S) as a function of temperature. This is consistent with a strong interaction between catalyst and thiophene. The Rh catalyst most probably shows a phase transition leading to different kinetic parameters. A strong interaction between the metal sulfide and thiophene is important for a high HDS activity. © 1996 Academic Press, Inc.

1. INTRODUCTION

Hydrotreatment applications for removal of heteroatoms such as sulfur from oil feedstock are one of the largest processes in the petroleum refining industry. In spite of the wide application of hydrotreating catalysts based on transition metal sulfides (TMS) and extensive research over the past decades, a variety of topics concerning hydrodesulfurization (HDS) are still not fully understood.

For instance, the reaction mechanism for the hydrodesulfurization of the widely used model compound thiophene is a matter of great debate. In the earliest proposal (1) it was suggested that thiophene desulfurization proceeds through a double β-hydride elimination followed by a fast hydrogenation of adsorbed diacetylene to 1,3-butadiene. Alternatively, hydrogenolysis of the carbon–sulfur bonds may yield 1,3-butadiene directly as was proposed by Lipsch and Schuit (2). However, Kraus and Zdrazil (3) pointed out that based on the chemistry of thiophene it is likely that the aromatic ring is hydrogenated to tetrahydrothiophene and that this compound should be considered as an intermediate. Mostly, this compound is only reported in high pressure thiophene HDS studies (4). Also, partially hydro-

genated thiophenes, i.e., 2,3-dihydrothiophene (2,3-DHT) and 2,5-dihydrothiophene (2,5-DHT), have been proposed as possible intermediates (5), although they were not detected in the gas phase. Markel *et al.* determined the HDS activity of these thiophenes and found that the dihydrothiophenes are much more reactive than tetrahydrothiophene which in turn is more reactive than thiophene (6).

Another un-resolved issue is the origin of the periodic trends of the hydrodesulfurization activity for the various TMS. Besides the industrially important Co- and Ni-promoted MoS$_2$ and WS$_2$ catalysts, many TMS show a high hydrodesulfurization activity. Generally, Balandin volcano-type activity curves for these sulfides were found with maxima in thiophene HDS for the sulfides of Ir, Rh, and Co (7–9). Harris and Chianelli (10) interpreted this in terms of the Sabatier principle. In contrast, Nørskov *et al.* (11) state that the activity is related to the ability of the TMS to generate a sulfur vacancy. The TMS with the lowest metal–sulfur bond energy will have the largest number of sulfur vacancies and the highest activity. Wiegand and Friend (12) suggested that the most active materials are the ones which activate the carbon–sulfur bond. Thus, strong interactions between thiophene and the TMS should result in a high activity. Interestingly, a recent theoretical study (13) showed that the interactions between the sulfur of thiophene and the various TMS is a good parameter for the HDS activity across the periodic table.

Intensive research aimed at elucidating the nature of the active phase and the role of Co- or Ni-promoters has resulted in different views concerning the synergetic effect in sulfided Co(Ni)–Mo(W) catalysts. Amongst others, the Co–Mo–S model (14, 15), the remote control model (16), and the rim-edge model (17) are the most used descriptions of the active phase for these catalysts. De Beer *et al.* proposed that MoS$_2$ merely acts as a stabilizing carrier for highly dispersed Co– or Ni–sulfide particles (18, 19). This view is supported by combined EXAFS and Mössbauer emission spectroscopy measurements (20, 21) showing that small CoS$_x$ ensembles are present at the MoS$_2$ crystallite edges, which suggests that small Co– or Ni–sulfide particles have a high HDS activity. This is consistent with the

high thiophene HDS activity found for sulfide clusters dispersed on a carbon support (7, 9) and occluded in zeolite micropores (22). Other authors ascribe the increase in HDS activity by promoter ions to an electronic effect. For instance, Harris and Chianelli (23) proposed on the basis of theoretical calculations that the promoter ion increases the electron density on Mo-sites, thus increasing their activity. Also on the basis of theoretical calculations, Topsøe *et al.* (24) suggested that the metal–sulfur interaction energy is decreased in the Co−Mo−S phase, resulting in an increase of the number of sulfur vacancies.

In the present study an effort is made to clarify some of the issues mentioned above. For this purpose, a set of carbon-supported TMS was prepared. Inert carbon was used as the support because it enables the determination of intrinsic activities of metal sulfides. Furthermore, it has been shown before that on carbon supports small metal sulfide particles can be formed which exhibit high thiophene HDS activities (7). Cobalt, molybdenum, and a mixed cobalt–molybdenum catalyst were prepared. A rhodium catalyst was also prepared because rhodium sulfide has been reported to have a high thiophene HDS activity (7). Kinetic parameters such as the reaction order of thiophene, apparent activation energy, and preexponential factor were determined for these systems. Furthermore, the effluent products were studied in great detail to clarify some aspects of the reaction mechanism.

2. METHODS

2.1. Preparation of Catalysts

For the preparation of carbon-supported TMS, NORIT RX-3 Extra was used. The surface area was found to be 1190 m^2/g, and the pore volume 1.0 ml/g. The carbon was ground and the sieve fraction of 125–250 μm was used. Monometallic catalysts were prepared via aqueous impregnation of the metal salts according to the procedure of Vissers *et al.* (7). For details, the reader is referred to Table 1. The bimetallic cobalt–molybdenum catalyst was prepared by one-step aqueous impregnation of cobalt nitrate and ammonium heptamolybdate using nitrilotriacetic acid as the complexing agent as described by Van Veen *et al.* (25). The atomic ratio of cobalt over molybdenum was 1/3 and 1.2 mol NTA was used per mol Mo.

The metal contents of the cobalt- and/or molybdenum-containing catalysts were determined by AAS, while the noble metal content of the rhodium catalyst was checked by UV–VIS analysis after color complex formation with SnCl$_2$. The results are shown in Table 1.

2.2. Reactor Setup

Kinetic measurements were carried out in an atmospheric single-pass microflow reactor with an internal diameter of 4 mm. Gasified thiophene (Janssen Chimica,

TABLE 1

Prepared Catalysts

Catalyst	Precursor metal salt	Supplier	Metal content (wt%)
Mo/C	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	Merck, >99%	8.8
Co/C	$Co(NO_3)_2 \cdot 6H_2O$	Merck, >99%	5.6
Rh/C	$RhCl_3 \cdot xH_2O$	Johnson Matthey (40 wt% Rh)	5.2
CoMo/C	$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	Merck, >99%	8.0
	$Co(NO_3)_2 \cdot 6H_2O$	Merck, >99%	1.6
	$N(C_3H_7O)$ (NTA)	Janssen Chimica, >97%	

>99%) was obtained by passing hydrogen through the liquid in a saturator equipped with a cooler. The required thiophene concentration was obtained by diluting this flow with pure hydrogen (Hoekloos, purity 99.95% additionally led through a gas-clean filter system to remove traces of oxygen, water, and hydrocarbons). The catalyst bed consisted of an amount of catalyst diluted with inert carbon of the same sieve fraction to achieve plug flow conditions. The amount of catalyst was chosen in such a way that during kinetic measurements the reactor was operated differentially, i.e. at conversions below 10%.

2.3. Kinetic Measurements

Catalysts were sulfided *in situ* in a H$_2$S/H$_2$ mixture (Hoekloos, 10% H$_2$S). The gas flow was kept at 60 ml/min (STP), while heating the catalyst at a rate of 6 K/min (in the case of CoMo/C 2 K/min) to 673 K. The temperature was then kept at 673 K for 2 h. After sulfidation, the catalyst was exposed to a mixture of 6×10^3 Pa thiophene and 1×10^3 Pa H$_2$S in hydrogen at 673 K. The total gas flow was increased to 100 ml/min (STP). Kinetic measurements were started after a stabilization period of 24 h.

The reaction order of thiophene was determined by measuring the reaction rate as a function of the thiophene partial pressure which was varied between 1.25×10^3 and 6×10^3 Pa at 573 and 623 K. The reaction order n was calculated by fitting the reaction rate R (mol/kg · h) to the thiophene concentration (p) using the power-rate law equation $R = k \cdot p^n$. The apparent activation energy and preexponential factor (ν_{pre}) were determined by evaluation of the reaction rate as a function of temperature. Furthermore, the amount of hydrothiophenes was determined as a function of the conversion for both Mo/C and CoMo/C at 623 K. During these measurements the total gas flow was changed while the partial pressure of the different components was kept constant.

Samples were analyzed by a gas chromatograph (Hewlett–Packard 5890 Series II equipped with a Chrompack CP-SIL 5 CB column). Besides 1-butene, *n*-butane,

trans-2-butene, and cis-2-butene, small amounts of C_1–C_3 products and traces of *n*-octane were detected. GC–MS (gas chromatography/mass spectrometry) analysis of some gas samples revealed no 1,3-butadiene which suggests that it is either not formed or formed only in small amounts. At lower reaction temperatures, three extra peaks appeared in the chromatogram, one of which could easily be identified as THT. In an effort to identify the other unknown peaks 2,3-DHT and 2,5-DHT were prepared because they are not available commercially.

2.4. Preparation of 2,3-dihydrothiophene and 2,5-dihydrothiophene

As 2,3-DHT and 2,5-DHT were needed only to identify the unknown peaks, it was not necessary to produce them separately which is a laborious task. A convenient way to prepare a mixture of these dihydrothiophenes was described by Gianturco *et al.* (26). This method yields 2,3-DHT and 2,5-DHT in a ratio of 2 : 1. After dissolving the resulting mixture in *n*-hexane, 2,3-DHT and 2,5-DHT were successfully identified by GC-MS. Samples of this mixture were then injected with a 1-μl syringe into the GC-column. The two remaining unknown peaks in the chromatograms could be identified as 2,3-DHT and 2,5-DHT.

3. RESULTS AND DISCUSSION

3.1. Activities and Selectivities

The initial activities of the carbon-supported TMS are presented in Table 2. The reaction rate at 673 K after 30 min reaction is given on a per mol total metal basis. Amongst the single TMS Rh/C is the most active catalyst while Mo/C clearly has the lowest activity. The activity trends correspond well with the activities reported in other studies (7–9). CoMo/C is the most active catalyst at the reaction conditions applied. Since it has been shown that for the Co–Mo–S phase the reaction rate is linear with the amount of cobalt (15), we also expressed the reaction rate for this catalyst per mol cobalt. The activity per cobalt site is found to be almost eight times higher than for Co/C.

TABLE 2

Activities of Carbon-Supported Metal Sulfides: $T = 673$ K, $P_{H_2S} = 1 \times 10^3$ Pa, $P_{thiophene} = 4.43 \times 10^3$ Pa

Catalyst	Reaction rate after 30 min at 673 K mol thiophene/mol metal · h
Mo/C	23
Co/C	62
CoMo/C	150
	465[a]
Rh/C	122

[a] Reaction rate per mol cobalt.

TABLE 3

Selectivities for the Hydrogenated Thiophenes: $P_{H_2S} = 1 \times 10^3$ Pa, $P_{thiophene} = 4.43 \times 10^3$ Pa

Catalyst	Temperature	sel. 2,3-DHT	sel. 2,3-DHT	sel. THT (%)
Mo/C	573	4%	—[a]	50
Co/C	573	1%	—	7
CoMo/C	573	2%	—	14
Rh/C	573	0.05%	—	0.10
Rh/C	623	0.10%	—	0.05
Eq. amount[b]	573	—[c]	—[c]	>90

[a] Denotes below detection limit.
[b] Data taken from Stull *et al.* (27).
[c] No thermodynamic data available.

The selectivities to the different hydrothiophene product molecules at a reaction temperature of 573 K and a conversion of approximately 5% are summarized in Table 3. For all catalysts the selectivity to THT is much higher compared to the partially hydrogenated thiophenes. At these low conversions minor amounts of 2,3-DHT and no 2,5-DHT were detected. Since the selectivity to THT is well below its thermodynamic equilibrium value (27) and THT is known to desulfurize more easily than thiophene (28), THT can be considered an intermediate for the thiophene hydrodesulfurization reaction. Although no thermodynamic data have been determined for the partially hydrogenated thiophenes, the low abundance of 2,3-DHT suggests that this compound is either quickly desulfurized or hydrogenated to THT. These findings are in accordance with those reported by Markel *et al.* (6) who found that 2,3-DHT is much more reactive than THT over alumina-supported MoS$_2$. In Table 4 calculated enthalpy differences for the gas phase hydrogenation of thiophene to 2,3-DHT and 2,5-DHT and their further hydrogenation to THT are presented. Clearly, all hydrogenation reactions are exothermic. The second hydrogenation step to THT is most favorable. These results also indicate that, after hydrogenation to THT, dehydrogenation to 2,3-DHT or 2,5-DHT is unlikely. This is consistent with the study of Markel *et al.* (6) who indeed found that (partially) hydrogenated thiophenes are both desulfurized and hydrogenated to THT while the interconversion of THT to 2,3-DHT was not detected.

TABLE 4

Calculated Enthalpies of Gas Phase Hydrogenation Reactions of the Different Thiophenes[a]

Thiophene + H_2 → 2,3-DHT	$\Delta E = -95.76$ kJ/mol
Thiophene + H_2 → 2,5-DHT	$\Delta E = -103.41$ kJ/mol
2,3-DHT + H_2 → THT	$\Delta E = -137.40$ kJ/mol
2,5-DHT + H_2 → THT	$\Delta E = -129.75$ kJ/mol

[a] Calculations were performed by Dr. S. P. Bates using the quantum-chemical ADF program.

The catalyst with the lowest desulfurization activity, i.e., Mo/C, shows the highest selectivity to THT, while the most active monometallic catalyst Rh/C shows a very low selectivity. This suggests that for the Mo/C the carbon–sulfur bond cleavage reactions are slow and desulfurization mainly occurs via THT. The reaction rate of Rh/C is so high that desulfurization probably occurs mainly via 2,3-DHT, 2,5-DHT, and THT. As can be seen from Table 3, the selectivity to 2,3-DHT becomes higher than the selectivity to THT at a reaction temperature of 623 K for Rh/C. Hence, the route via 2,3-DHT becomes most favorable. Surprisingly, Co/C has a lower selectivity for THT than does CoMo/C. A reason could be that the relative rate of hydrogenation of thiophene is smallest on Co/C.

Figure 1 displays the yields of the (partially) hydrogenated thiophenes as a function of the conversion for CoMo/C at 623 K. The yields for the (partially) hydrogenated thiophenes are very low and so is the accuracy. However, it seems that 2,3-DHT is initially formed together with THT. Furthermore, at higher conversions the yield of 2,5-DHT increases at the expense of 2,3-DHT. This appears to be support for the thought that 2,5-DHT is formed by isomerization of 2,3-DHT. Organometallic studies (29, 30) suggest that a nucleophilic attack at the 2-position of thiophene by hydride species followed by protonation of the 3-position can give 2,3-dihydrothiophene. The adsorption mode of thiophene would then be η_2-C,C' or η_3-S,C,C'. In Fig. 2 the results are shown for Mo/C. A much higher selectivity to THT is observed for this catalyst. Also, the amount of 2,5-DHT is much higher, while the amount of 2,3-DHT is nearly constant. This is consistent with the lower desulfurization rate of Mo/C compared to that of the promoted system.
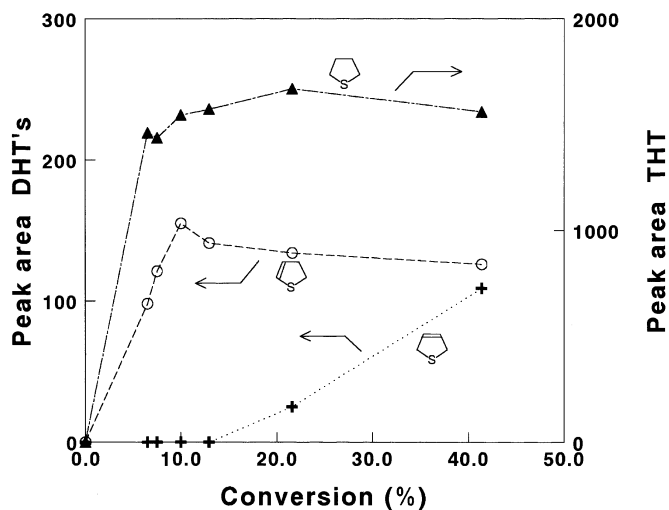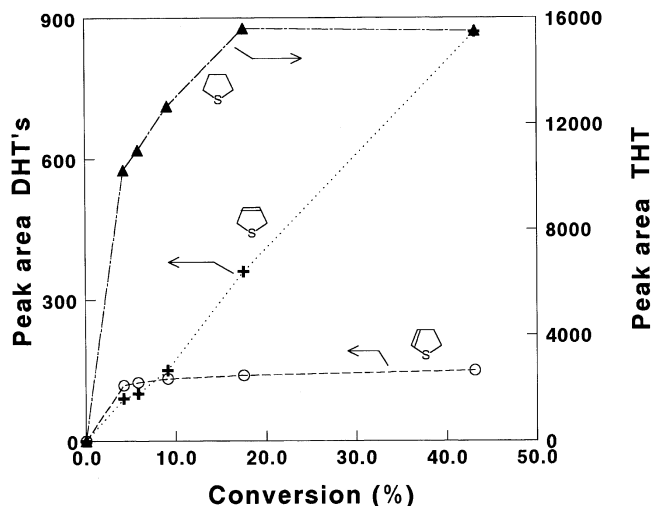

FIG. 2. Yields of hydrothiophene product molecules for Mo/C (623 K; $P_T = 4.43 \times 10^3$ Pa; $P_{H_2S} = 1 \times 10^3$ Pa): (–▲–) tetrahydrothiophene, (–⊖–) 2,3-dihydrothiophene, (–+–) 2,5-dihydrothiophene.

The reason why the presence of these partially hydrogenated thiophenes is not reported by others (4, 7, 9) may relate to the particular conditions applied here. Most low-pressure experiments were carried out at high temperatures, close to 673 K, whereas hydrogenation reactions are thermodynamically favored at low temperatures. In addition, 1 vol% H_2S was added to the reactor inlet to reduce H_2S partial pressure fluctuations. H_2S is known to inhibit hydrodesulfurization reactions by competitive adsorption on sulfur vacancies (31). At low H_2S partial pressures 2,3-DHT formed by hydrogenation of thiophene is quickly desulfurized or hydrogenated to THT, which keeps the gas phase concentration below detection limit. Increasing the H_2S partial pressure (up to 1×10^3 Pa in our experiments) retards desulfurization reactions, hence the gas phase concentration of these (partially) hydrogenated thiophenes increases.

3.2. Kinetic Measurements

The reaction orders of thiophene, the apparent activation energies, and the pre-exponential factors for the different catalysts are presented in Table 5. The apparent activation energy for Mo/C corresponds well with the value reported by Ledoux et al. (9) (84 kJ/mol) who also determined activation energies for carbon-supported metal sulfides. In that study no (partially) hydrogenated thiophenes were reported. Our value for Co/C is some 25 kJ/mole higher, while the activation energy for Rh/C is 20 kJ/mole lower. These discrepancies can be explained by the fact that in our experiments H_2S has been added to the reactor feed. In the study of Ledoux et al. no H_2S was added. Hence, rhodium is probably less sulfided. Furthermore, Rh/C shows interesting behavior (Fig. 3): below 613 K the apparent activation

FIG. 1. Yields of hydrothiophene product molecules for CoMo/C (623 K; $P_T = 4.43 \times 10^3$ Pa; $P_{H_2S} = 1 \times 10^3$ Pa): (–▲–) tetrahydrothiophene, (–⊖–) 2,3-dihydrothiophene, (–+–) 2,5-dihydrothiophene.

TABLE 5

Kinetic Parameters for Carbon-Supported TMS

Catalyst	Temp. trajectory (K)	E_{act} (kJ/mol)[a]	ν_{pre}[b]	$n_{573 K}$	$n_{623 K}$
Mo/C	523–653	82	4×10^8	0.39	0.51
Co/C	523–653	87	2×10^{10}	0.50	0.60
CoMo/C	523–590	106	5×10^{12}	0.06	
	643–673	47	6×10^7		0.28
Rh/C	523–613	100	6×10^{11}	0.35	
	613–673	70	7×10^8		0.50

[a] Accuracy in activation energy: ± 2 kJ/mol.

[b] Unit of pre-exponential factor: (m^3/kg · h).

energy is found to be much higher than between 613 K and 673 K. Most likely, this is due to a phase transition between Rh_2S_3 (<613 K) and $Rh_{17}S_{15}$ (>613 K) (32). Mangnus (33) calculated from thermodynamic data that this phase transition should occur at 613 K at a H_2S/H_2 ratio of 0.01 which is approximately the ratio at our reactor inlet.

While Co/C and Mo/C show a temperature independent activation energy, CoMo/C shows also a different behavior (Fig. 4). Up to temperatures of 590 K the apparent activation energy is constant, i.e., 106 kJ/mole. At higher temperatures the apparent activation energy starts to decrease. From Fig. 4 one can see that around 673 K the apparent activation energy has become 47 kJ/mole. This may suggest that at these high temperatures pore-diffusion limitations occur. However, experiments with different catalyst particle sizes revealed that no such limitations are present for our catalysts. The decrease in activation energy for CoMo catalysts with temperature has been reported earlier. For instance, Van Gestel (34) found similar behavior for an alumina-supported CoMo catalyst, while Startsev *et al.* (35) found an inflection point around 573 K, above which the apparent activation energy is constant at a value of 60 kJ/mole. Pore
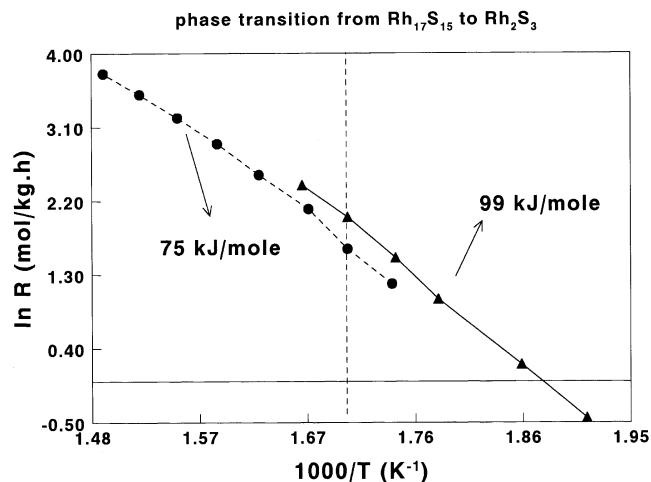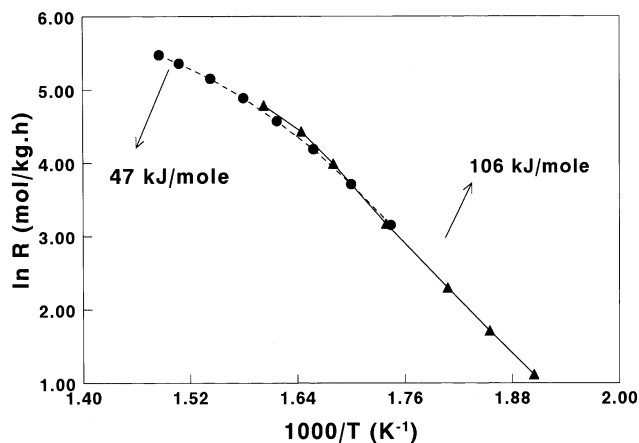

FIG. 4. Arrhenius plot for CoMo/C (two experiments with different amounts of catalyst).

diffusion limitations were also ruled out by experiments with different grain sizes.

The measured reaction orders of thiophene between zero and unity suggest that a surface reaction is rate limiting. On the basis of quantum-mechanical calculations Neurock and Van Santen (36) showed that both carbon–sulfur bond cleavage reactions (surface reaction) and hydrogenative sulfur removal that creates the sulfur vacancy (desorption reaction) are potential rate limiting steps for thiophene HDS. Hence, the reaction orders lead us to believe that carbon–sulfur bond cleavage is rate limiting for most of our catalysts. CoMo/C shows at low temperatures a higher activation energy than Mo/C and Co/C. The low reaction order of thiophene at 573 K and the relatively large change of the reaction order as a function of temperature for CoMo/C point to a strong TMS–thiophene interaction. Therefore, desorption of strongly bonded H_2S may be rate limiting for this catalyst at low temperatures. The high pre-exponential factor for this catalyst supports such a reaction step being rate limiting, since desorption of products into the gas phase leads to a large gain in entropy as compared to surface reactions (37). However, differences in the number of sulfur vacancies can also lead to large changes in the pre-exponential factor.

The high HDS activity of CoMo/C can be explained by the strong TMS–thiophene interaction. The most active single TMS, i.e., Rh/C, also shows a lower reaction order of thiophene when compared to Mo/C and Co/C. The two Rh sulfide phases show different kinetic parameters. Differences in Rh sulfide–thiophene interaction energy may explain this behavior. This emphasizes that the TMS structure is an important parameter in explaining HDS activities.

The peculiar behavior of CoMo/C at temperatures above 613 K can be explained by a gradual change in surface coverage. The relatively large change in reaction order of thiophene is consistent with this proposal. When a simplified

FIG. 3. Arrhenius plot for Rh/C (two experiments with different amounts of catalyst).

Langmuir–Hinshelwood model for the reaction of thiophene at the TMS surface is considered, one can derive for the reaction rate r:

$$r = k \cdot \Theta_{\text{thiophene}}$$

$$r = k \cdot \frac{K_{\text{ads}} \cdot P_{\text{thiophene}}}{1 + K_{\text{ads}} \cdot P_{\text{thiophene}}} \qquad [1]$$

In Eq. [1], k is the rate that corresponds to the rate limiting step (rls) of the reaction. It will depend on H_2 and H_2S partial pressures. When k has an Arrhenius-type behavior and can be considered independent of surface coverage, one finds the exact result (38)

$$E_{\text{act}}^{\text{app}} = -R_g \frac{\partial \ln r}{\partial T^{-1}} = E_{\text{act}}^{\text{rls}} + (1 - \Theta) \cdot \Delta H_{\text{ads}}, \qquad [2]$$

with $\Theta_{\text{thiophene}}$ denoting the surface coverage by thiophene; $E_{\text{act}}^{\text{app}}$ the apparent activation energy; $E_{\text{act}}^{\text{rls}}$ the activation energy rate of the limiting step; K_{ads} the adsorption constant thiophene; $P_{\text{thiophene}}$ the partial pressure thiophene; and ΔH_{ads} the heat of adsorption of thiophene. Below 590 K the surface coverage is high which follows from the low reaction order of thiophene (0.06) measured for CoMo/C at 573 K. Then the apparent activation energy is equal to the activation energy of the rate limiting surface reaction step. At higher temperatures the surface coverage decreases due to desorption of thiophene. The apparent activation energy then decreases with an amount linear to the heat of adsorption of thiophene. From a similar analysis one can derive that also the apparent activation entropy decreases with decreasing surface coverage, which is observed experimentally for the pre-exponential factor. The some applies to the effect of H_2S desorption. This phenomenon is not observed for Mo/C and Co/C which is probably due to the much lower TMS–thiophene (or H_2S) interaction energy. Their surface coverage does not change much with temperature, as can be concluded from the measured reaction orders as a function of temperature.

On the basis of the kinetic results one cannot assign the high activity of CoMo/C simply to a cobalt or molybdenum site. One reason can be the difference between small cobalt sulfide particles located at the edges of MoS_2 in CoMo/C compared to Co_9S_8-like particles in Co/C as observed by Mössbauer spectroscopy (20, 21). Only at very low sulfidation temperatures, i.e., below 473 K, was it found that Co/C has the same Mössbauer parameters as CoMo/C (21). Upon heating, the highly dispersed CoS_x phase is converted to Co_9S_8-like particles.

The foregoing shows that carbon–sulfur bond cleavage is most probably rate limiting for all catalysts. Interestingly, we have concluded that the catalyst with the highest thiophene HDS activity has the strongest TMS–thiophene interaction. This is in contrast to the theory of Nørskov et al. (11) who suggest that a weak interaction leads to a high HDS activity. The observation of low metal–sulfur bond energy for active bulk TMS (11, 37) still holds. However, we conclude that the reaction rate is not controlled by the number of sulfur vacancies but rather by the strength of the TMS–thiophene interaction.

4. CONCLUSIONS

It has been established that the partially hydrogenated thiophenes 2,3-DHT and 2,5-DHT as well as THT should be considered as intermediates for thiophene hydrodesulfurization. Thiophene is hydrogenated to 2,3-DHT. This intermediate can desulfurize, isomerize to 2,5-DHT, or be hydrogenated to THT. The yield of the (partially) hydrogenated thiophenes depends on the catalyst used: catalysts with low HDS activities such as Mo/C give rise to large amounts of these intermediate compounds, while a very active catalyst such as Rh/C produces very small amounts.

Based on the kinetic parameters the carbon–sulfur bond cleavage appears rate limiting for all catalysts. However, the low reaction order of thiophene for CoMo/C at 573 K can also point to hydrogenative sulfur removal being rate limiting for this catalyst. Whereas Mo/C and Co/C have temperature independent activation energies, Rh/C and CoMo/C both show temperature dependent behavior. In the case of Rh/C, there is most likely a phase transition at 613 K between Rh_2S_3 (<613 K) and $Rh_{17}S_{15}$ (>613 K). The decrease in apparent activation energy with temperature for CoMo/C is ascribed to a decrease in surface coverage by thiophene (or H_2S). This is consistent with the observation that the TMS–thiophene interaction is strongest for this catalyst. It is concluded that high thiophene HDS activity is linked to strong TMS–thiophene interaction.

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