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Intrinsic thiophene hydrodesulfurization kinetics of a sulfided NiMo/SiO_2 model catalyst: volcano-type behavior

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A realistic planar model of a silica-supported NiMo sulfide hydrotreating catalyst was used to study the intrinsic kinetics of thiophene hydrodesulfurization over a broad temperature range at atmospheric pressure. The specific nonporous nature of the model catalysts excludes possible diffusion limitations, which are commonly encountered in kinetic studies of their industrial porous analogues. The unique possibility to measure the intrinsic chemical kinetics over a large temperature range allowed us to observe a Volcano-type behavior for thiophene hydrodesulfurization. The specific kinetic parameters are discussed in terms of possible mechanisms.

KEY WORDS: model catalysts; hydrodesulfurization; intrinsic kinetics; NiMo/SiO_2 catalyst.

1. Introduction

Hydrotreatment is one of the key processes in oil refineries to produce clean motor fuels. Especially, the removal of sulfur from hydrocarbon feedstock, hydrodesulfurization (HDS), has gained importance due to more stringent legislations for vehicular emissions and fuel quality and an increasing need to process low-quality feedstocks. CoMo- and NiMo-mixed sulfides are the most important catalytic materials effective in the removal of sulfur, nitrogen, oxygen, and metals. While the active state of such catalysts has been studied in great detail [1–3], essential aspects of the reaction mechanisms need further clarification. The hydrodesulfurization of thiophene is one of the most used test reactions for this type of catalysts. Despite its simplicity, both in operation and interpretation, there is still much debate on the underlying mechanism. For example, both the surface reaction of adsorbed thiophene and hydrogenative sulfur removal have been identified as possible rate-determining steps [4]. Next to the direct extraction of sulfur from thiophene, prehydrogenation to dihydrothiophenes and tetrahydrothiophene appears to play a role [5].

From a mechanistic point of view, there is an interest in measuring the activation energy over a large temperature range. For instance, several authors [5–7] have reported that the decrease in apparent activation energy with increasing temperature is due to changes in surface coverage. However, often such a decrease can also be attributed to internal pore diffusion limitations. Moreover, Leliveld *et al.* [8] reported the intriguing observation that after a decrease in activity with temperature, the reaction rate increases again around temperatures of 773 K. This was taken as an indication that different active sites are available. Taking into account these peculiarities, there is a clear need to study the kinetics of thiophene HDS over a large temperature range in the absence of diffusion limitations.

Earlier work has demonstrated that realistic planar models for high-surface area HDS catalysts can be prepared. These catalysts exhibit realistic HDS activities and have been shown to be extremely useful for structure–activity correlations [9–12]. An additional advantage of the flat model approach is the absence of pores. This excludes the influence of limitations of internal mass transfer on the chemical kinetics. In this contribution, we report on a kinetic study of thiophene HDS over silica-supported NiMo model catalysts over a broad temperature range. The kinetic results indicate that our model catalyst approach is suitable for studying intrinsic chemical kinetics of heterogeneous catalytic reactions.

2. Experimental

The details of the preparation and the characterization of the NiMo model catalysts have been described in [9–12]. Summarizing, the model catalysts consist of planar SiO_2 supports prepared by calcination of a Si(100) single crystal wafer. Subsequently, these model supports were spincoated at 2800 rpm with aqueous solutions of the required metal salts $Co(NO_3)_2 \cdot 6H_2O$ (Merck, p.a.), $Ni(NO_3)_2 \cdot 6H_2O$ (Merck, p.a.), $(NH_4)_6$,

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$Mo_7O_{24} \cdot 4H_2O$ (Merck, purity $>97\%$) and $(NH_4)_6 W_{12}O_{39} \cdot xH_2O$ (Aldrich, p.a.) in nitrogen atmosphere. The concentrations of the precursor solutions were adjusted to result in the required metal loadings (2 Co(Ni) at/nm^2 and 6 Mo(W) at/nm^2).

Thiophene and tetrahydrothiophene (THT) HDS activity measurements were carried out at atmospheric pressure in a mixture of 4 vol% thiophene (Acros, purity $>99\%$) or 2 vol% tetrahydrothiophene (Aldrich, purity 99%) in hydrogen (Hoekloos, purity $>99.99\%$). The catalysts were presulfided in a flow (60 mL/min) of a mixture of 10 vol% H_2S in H_2 (Scott Chemicals) by heating at a rate of 5 K/min to the desired sulfidation temperature and keeping the sample at this temperature for 1 h. The catalyst temperature was then adjusted to the desired reaction temperature. Subsequently, the reactor was flushed with the reactant mixture for 5 min at the reaction temperature. The reaction was then carried out in batch mode by closing the reactor inlet and outlet. This was marked as zero reaction time. After a reaction time of 1 h, a gas-phase sample was taken from the reactor using a precision sampling gas syringe, which was injected on a DB-1 column to analyze the following main products: C1–C3 hydrocarbons, 1-butene, *n*-butane, *trans*-2-butene, *cis*-2-butene, thiophene, tetrahydrothiophene. The HDS activities are expressed as thiophene (tetrahydrothiophene) conversion after 1 h of reaction time and per 5 cm^2 of model catalyst. These values were corrected for blank thiophene (tetrahydrothiophene) conversion measured using an empty reactor, which were typically lower than 5% of the catalytic activity measured on model catalysts. A next experiment was performed after the catalyst was resulfided at 673 K for 1 h.

3. Results and discussion

3.1. Mass transfer limitations

In porous catalysts, both internal and external mass transfer limitations complicate the determination of intrinsic chemical kinetics. In our model system, internal mass transfer limitations are essentially absent due to the nonporous nature of the catalyst. A further point of concern relates to the rate of mass transfer from the bulk gas-phase to the catalytic surface. The relative effect of the external mass transfer limitation on the catalytic activity can be evaluated using the Damköhler number. The Damköhler number [13] is given by

$$Da^I = \frac{k_r \cdot L}{D_e} \tag{1}$$

where k_r is the reaction rate constant (m/s), L the maximum thickness of the boundary layer (m) and D_e the diffusion coefficient of the reactant (m^2/s). Typical values for these constants are $k_r = 2.4 \cdot 10^{-6}$ m/s (corresponding to the highest thiophene conversion after 1 h reaction for the most active catalyst), $L = 1.5 \cdot 10^{-1}$ m and $D_e = 9 \cdot 10^{-5}$ m^2/s (the diffusion coefficient of thiophene in hydrogen at 673 K) results in a value for Da^I of $4.1 \cdot 10^{-3}$. This low value implies that diffusion rates to the catalyst surface are much higher than reaction rates. The reaction rate parameters and diffusion coefficients were used to model the concentration profile of thiophene around the wafer model catalyst in our batch reactor. Obviously, the concentration differences are more pronounced in the axial than in the radial direction. Nevertheless, the largest decrease in thiophene concentration was smaller than 0.5% in line with the low value of the Damköhler number. This essentially means that no diffusion boundary layers are formed. In conclusion, both internal and external mass transfer limitations do not play a role and therefore intrinsic kinetics can be derived from our activity measurements.

3.2. Intrinsic kinetic measurements

As outlined in the experimental section, the catalytic measurements were carried out performing a resulfidation step between each experiment. This procedure was developed in order to obtain reproducible and reliable kinetic data, minimizing any deactivation process. Figure 1 indeed shows that the HDS activity remains nearly constant when applying this procedure. On the contrary, the catalyst deactivates when no resulfidation step was performed. This is most probably related to partial sulfur removal or minor coke formation during the desulfurization reaction.

Figure 2(a) shows the thiophene HDS activities of a NiMo/SiO$_2$ model catalyst as a function of temperature for two sulfidation temperatures. The conversion for the catalyst sulfided at 773 K is close to zero, around 473 K, and increases strongly with temperature. Clearly, there is a maximum in activity around 673 K. Decreasing the reaction temperature from 773 K stepwise to 473 K (descending branch) shows that the activity trend is reversible. This activity trend has the characteristics of a Volcano curve and can be explained by Sabatier's principle. At low temperatures, the surface is completely covered with adsorbed species, i.e., reaction intermediates, resulting in a low reaction rate. With increasing temperature, the intrinsic rate constant increases and the coverages decrease. Finally, this results in a situation in which the surface is almost completely empty and a low activity is observed. When the adsorption energy is higher than the activation energy, an activity maximum can be found at intermediate temperature where there is an optimum between surface coverage and rate constant, as will be demonstrated later.

On the other hand, a hysteresis is observed on the catalyst sulfided at 673 K, most probably due to

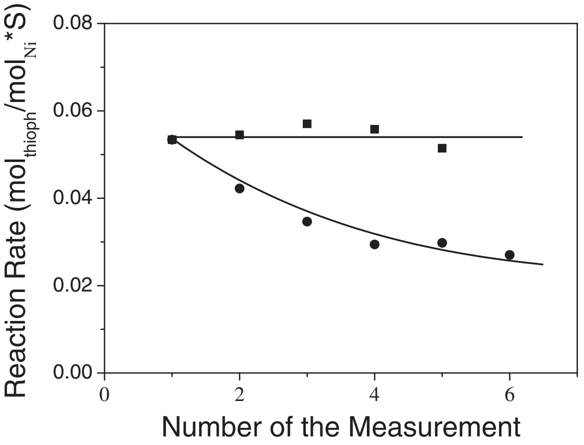

Figure 1. Thiophene reaction rate over a NiMo/SiO_2 model catalyst (sulfided at 673 K) at a reaction temperature of 673 K. Between the experiments the catalyst was (a) resulfided at 673 K for 1 h (squares) and (b) not resulfided (circles).

sintering of the active phase. After a first cycle, the activity trend becomes, however, reversible and the descending branch, which represents the stable behavior of the catalyst, still exhibits a maximum around 673 K.

Figure 2(b) shows that similar trends are observed for model catalysts, which are made up of the CoMo and NiW combinations. The activity decreases in the order NiW > NiMo > CoMo in correspondence with our earlier reports [9–12]. Note that all these measurements were performed after sulfidation at 773 K and then performing thiophene HDS activity measurements upon decreasing temperature. All three catalysts exhibit a maximum around 673 K.

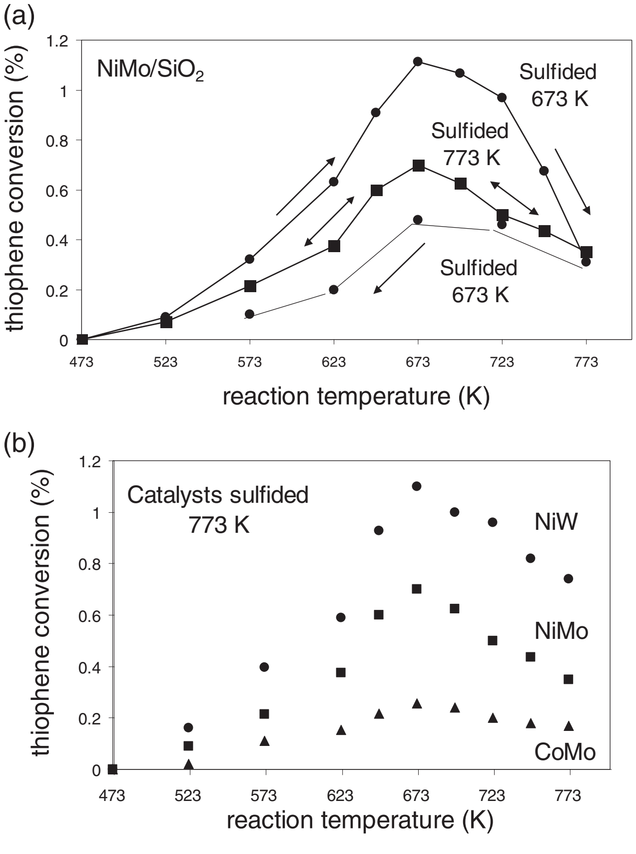

Figure 2. Thiophene HDS activities as a function of reaction temperature for (a) NiMo/SiO_2 sulfided at 673 K and 773 K and (b) CoMo/SiO_2, NiMo/SiO_2 and NiW/SiO_2 sulfided at 773 K.

Although the results point to the overriding importance of chemical kinetics to explain the Volcano-type behavior, a thermodynamic limitation of the hydrogenation of thiophene to tetrahydrothiophene has to be considered. Despite much research effort, the exact mechanism of thiophene HDS is not clear. Amongst others, direct sulfur removal [14,15], prehydrogenation to dihydrothiophenes [7,16,17] and tetrahydrothiophene [7,18] have been considered. Here, we confine ourselves to note that we did not observe any of these intermediates during the present thiophene HDS experiments. A further argument in favor of the importance of the direct route is the absence of dehydrogenation to thiophene at high temperatures when using tetrahydrothiophene (THT) as reactant. This implies that the equilibrium between thiophene and tetrahydrothiophene does not establish itself very fast. As soon as THT is formed, it is desulfurized because of the much higher reactivity of the hydrogenated compound. This suggests that there is no limitation due to the equilibrium between thiophene and THT. The THT HDS reaction was carried out in a similar manner as the thiophene HDS experiments. Figure 3 shows that there is a strong decrease in overall THT HDS activity at elevated temperatures to be attributed to structural rearrangements. However, the decreasing branch does not provide evidence for an activity maximum. It is important to mention that, after the first cycle, the activity trend, as for thiophene HDS, becomes reversible and the descending branch represents, therefore, the stable behavior of the catalysts.

Leliveld *et al.* [8] studied thiophene HDS over a typical high-surface-area alumina-supported CoMo catalyst over a wide temperature range. These authors also found a Volcano-type behavior, the difference being

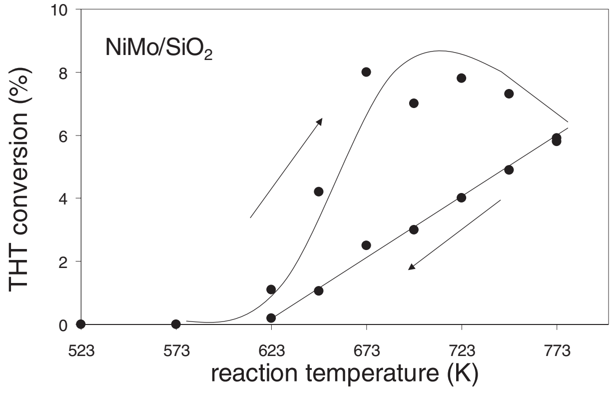

Figure 3. Tetrahydrothiophene HDS activity as a function of reaction temperature for a NiMo/SiO_2 model catalyst sulfided at 673 K.

that after an initial decrease up to 700 K an activity increase was observed. Descending temperatures showed a hysteresis and no maximum was observed. The increase in HDS activity at high temperatures was explained by a second type of active site. Although the activity maximum is reproduced, our activity measurements do not show a further increase of activity at higher temperatures.

Figure 4 displays an Arrhenius plot for NiMo/SiO$_2$ sulfided at 773 K. The indicated values for the apparent activation energy clearly decrease from a value of 145 kJ/mol at low temperature, which decrease to values lower than 50 kJ/mol in the temperature range 523–673 K. Finally, above 673 K, a negative apparent activation energy is found. We stress here that the values relate to a certain temperature range while in fact the activation energy continually decreases with increasing temperature [5–7]. Note that E_{act}^{app} represents the apparent activation energy and not the activation energy of the rate-determining step (E_{act}^{rds}). Similar values for E_{act}^{app} could be derived for the other model catalysts in figure 3(b). These values are summarized in table 1.

Table 1
Apparent activation energies for the various model catalysts in two different temperature ranges (sulfidation temperature: 773 K)

Catalyst	E_{act}^{app} (kJ/mol) (523–673 K)	E_{act}^{app} (kJ/mol) (673–773 K)
NiW/SiO$_2$	38	−17
NiMo/SiO$_2$	45	−36
CoMo/SiO$_2$	50	−19

Figure 5 shows the Arrhenius plot for hydrodesulfurization of THT over NiMo/SiO$_2$ sulfided at 673 K. These catalytic data correspond to the descending branch displayed in figure 4, i.e., when the catalytic data were obtained by decreasing the reaction temperature from 773 K stepwise to 623 K. The apparent activation energy decreases from 154 kJ/mol in the temperature range 623–673 K to 42 kJ/mol above 673 K. Thus, in contrast to the thiophene HDS experiments, no negative apparent activation energies are found when tetrahydrothiophene is the reactant, even at temperatures above 673 K. The apparent activation energies are significantly higher than the corresponding values for thiophene HDS. Sullivan and Ekerdt [19] have recently reported similar apparent activation energies for MoS$_2$/SiO$_2$ model catalysts in the same temperature range: 48 kJ/mol for thiophene HDS and 174 kJ/mol for tetrahydrothiophene HDS respectively.

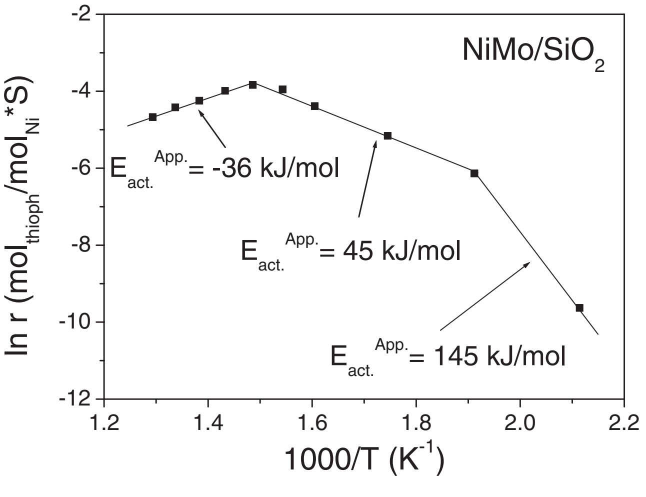

Figure 4. Arrhenius plot for thiophene HDS on NiMo/SiO$_2$ model catalysts sulfided at 773 K.

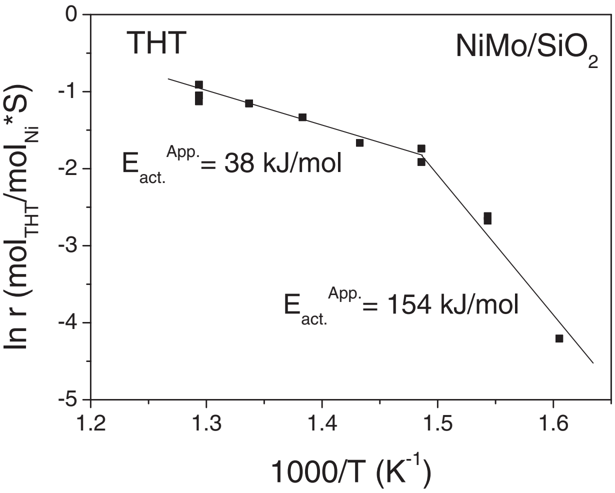

Figure 5. Arrhenius plot for THT HDS on NiMo/SiO$_2$ model catalysts sulfided at 673 K.

It is interesting to note that the activation energies for thiophene HDS reported in this contribution seem to be underestimated in the temperature range 523–673 K. However, this fact cannot be ascribed to mass-transfer limitations. An essential advantage of the planar model catalyst approach is that intrinsic kinetics can be derived over a much wider temperature range than normally possible. In contrast, thiophene HDS experiments at high temperatures may be carried out under mass-transfer-limiting conditions in the case of porous catalysts. Our approach thus gives insight into some fundamental aspects of this important test reaction.

While the reaction mechanism of thiophene HDS is not totally clear, most proposals stress the importance of the reaction between adsorbed thiophene and some hydrogen species, competitive adsorption of hydrogen sulfide and a weak adsorption of hydrogen. Here, we assume a simple mechanism made up of the reaction between adsorbed thiophene and an adsorbed hydrogen atom (assuming two different adsorption sites), neglecting the inhibiting effect of H$_2$S (due to the low conversion), the reaction rate (r) can be expressed as

$$r = k\frac{K_T p_T K_{H_2} p_{H_2}}{(1 + K_T p_T)(1 + K_{H_2}^{1/2} p_{H_2}^{1/2})^2} \qquad (2)$$

with k being the reaction rate constant, K_T and K_{H_2} the adsorption constants for thiophene and hydrogen, and p_T and p_{H_2} the partial pressures of thiophene and hydrogen. When k has Arrhenius-type behavior and can be considered independent of surface coverage, one can calculate the apparent activation energy by

$$\begin{aligned} E_{\mathrm{act}}^{\mathrm{app}} &= -R_g \cdot \frac{\partial \ln r}{\partial T^{-1}} \\ &= E_{\mathrm{act}}^{\mathrm{rds}} + (1 - \Theta_{\mathrm{T}}^{\#}) \cdot \Delta H_{\mathrm{ads}}^{\mathrm{T}} + (1 - \Theta_{\mathrm{H}}^{*}) \\ &\quad \cdot \Delta H_{\mathrm{ads}}^{H_2} \end{aligned} \tag{3}$$

with $E_{\mathrm{act}}^{\mathrm{app}}$ being the apparent activation energy, R_g the gas constant, T the temperature, $E_{\mathrm{act}}^{\mathrm{rds}}$ the activation energy of the rate-determining step, Θ_{T} the surface coverage by thiophene on sites of type #, $\Delta H_{\mathrm{ads}}^{\mathrm{T}}$ the heat of adsorption of thiophene, Θ_{H} the surface coverage by hydrogen atoms on sites of type * and $\Delta H_{\mathrm{ads}}^{\mathrm{H_2}}$, the heat of dissociative adsorption of hydrogen.

At low temperatures, the coverages of both thiophene and hydrogen are close to unity and the apparent activation energy ($E_{\mathrm{act}}^{\mathrm{app}}$) equals the activation energy of the rate-determining step ($E_{\mathrm{act}}^{\mathrm{rds}}$). However, at higher temperatures, the coverages become lower and in the limit of an empty surface, we find

$$E_{\mathrm{act}}^{\mathrm{app}} = E_{\mathrm{act}}^{\mathrm{rds}} + \Delta H_{\mathrm{ads}}^{\mathrm{T}} + \Delta H_{\mathrm{ads}}^{\mathrm{H_2}} \tag{4}$$

In this limit, the apparent activation energy is lowered by an amount equal to the sum of the adsorption energies of thiophene and hydrogen. As such, a negative apparent activation energy is found when this sum exceeds the activation barrier of the rate-determining step. Moreover, expression (3) explains the gradual decrease of the activation energy with increasing temperature due to a decrease surface coverage with reacting species. We stress here that the adsorption energy of hydrogen is most probably quite low compared to that of thiophene [e.g., reference 4]. In this case, equations (2)–(4) still hold and a negative apparent activation energy can be found if the adsorption energy of thiophene exceeds the activation barrier [7].

For THT HDS, the apparent activation energy is significantly higher. However, it is important to mention that the conversion levels for THT were higher than for thiophene HDS. Consequently, the inhibiting effect of H$_2$S could play a role and equation (3) becomes

$$\begin{aligned} E_{\mathrm{act}}^{\mathrm{app}} &= E_{\mathrm{act}}^{\mathrm{rds}} + (1 - \Theta_{\mathrm{T}}^{\#}) \cdot \Delta H_{\mathrm{ads}}^{\mathrm{T}} + (1 - \Theta_{\mathrm{H}}^{*}) \cdot \Delta H_{\mathrm{ads}}^{\mathrm{H_2}} \\ &\quad - \Theta_{\mathrm{H_2S}}^{\#} \cdot \Delta H_{\mathrm{ads}}^{\mathrm{H_sS}} \end{aligned} \tag{5}$$

At low temperature, i.e., high reactant coverages, the above equation can be simplified to

$$E_{\mathrm{act}}^{\mathrm{app}} = E_{\mathrm{act}}^{\mathrm{rds}} - \Theta_{\mathrm{H_2S}}^{\#} \cdot \Delta H_{\mathrm{ads}}^{\mathrm{H_sS}} \tag{6}$$

Thus, the apparent activation energy is increased by an amount equal to the adsorption energy of H$_2$S times its coverage.

Moreover, one does not observe a maximum in activity in the temperature range investigated in the present study. This ties in with the strong bond energy between the catalytic surface and tetrahydrothiophene. Consequently, one expects the maximum in activity to occur at much higher temperatures. Although no maximum is observed in the analyzed temperature range, the apparent activation energy strongly decreased as temperature increases. As in the case of thiophene HDS, the decrease in the apparent activation energy can be explained by a coverage decrease as temperature increases, indicating that the volcano-like behavior is most likely related to a coverage effect. The large difference in the activation energy—which relates to the apparent activation energy at low temperature—for thiophene and tetrahydrothiophene HDS points to a large difference in the complexes involved in the rate-limiting step. This further underpins our surmise that direct sulfur elimination is the main pathway in the case of thiophene desulfurization.

4. Conclusions

In this contribution, we have shown that planar nonporous model catalysts can be applied to obtain intrinsic kinetic parameters for the relatively simple thiophene HDS test reaction. Kinetic experiments were carried out over a broad temperature range, i.e., $T = 473$–773 K. Volcano-type curves were observed for the HDS activity as function of the reaction temperature, with an optimum activity around 648–673 K. It is essential to exclude structural changes of the active phase by stabilizing the catalyst in high-temperature sulfidation at 773 K. The Volcano-type behavior is observed for typical hydrotreating catalysts but depends strongly on the pretreatment conditions. The observed temperature dependency results in a negative apparent activation energy for thiophene HDS at high temperatures. This relates to intrinsic kinetic phenomena on the catalyst surface. Such behavior can be explained on the basis of a relatively simple kinetic model for the thiophene HDS reaction. The described approach allows one to obtain intrinsic kinetic parameters over a wide range of temperatures for hydrotreating catalysts.

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