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Kinetics of sulfur model molecules competing with H_2S as a tool for evaluating the HDS activities of commercial $CoMo/Al_2O_3$ catalysts

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Abstract

The relative-volume activities (RVAs) for real feedstocks HDS of four commercial $CoMo/Al_2O_3$ catalysts have been compared to the rates for thiophene and dibenzothiophene conversion. The reaction of thiophene competing with H_2S was studied in flow microreactors under a wide range of conditions: 300–400°C, overall pressure 0.1 or 3 MPa, thiophene pressure 8–125 kPa, H_2S content 0–15 mol%. The reaction of dibenzothiophene (DBT, 2 wt% in decaline) was carried out in a batch reactor at 335°C and 4 MPa.

The conversion of the two model molecules proceeds through the same mechanism with a preliminary dearomatization step followed by parallel hydrogenolysis and hydrogenation. From kinetic modeling, the global rates and the contribution of the hydrogenation and hydrogenolysis routes to HDS were determined. Under pressure, hydrogenolysis was predominant. In that case, thiophene and DBT behaved similarly and their initial relative rates did not correlate the RVA. Industrial HDS is controlled by hydrogenation as evidenced by the good correlation between RVA and the rates of dearomatization of thiophene at atmospheric pressure and hydrogenation of the product biphenyl from DBT under pressure. It is concluded that the reaction of model molecules under selected conditions can appraise rapidly industrial HDS. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Hydrosulfurization; Reactivity relationships; Model reactions; Industrial HDS; $CoMo/Al_2O_3$ catalysts

1. Introduction

The increasing need for low-sulfur fuels requires to improve drastically the efficiency of hydrotreating processes [1]. Many efforts are devoted to the development of newer active catalysts. But, there is not yet a recognized alternative to the conventional $Co(Ni)Mo/Al_2O_3$ catalysts. Although the $CoMo/Al_2O_3$ catalysts have been largely improved for hydrodesulfurization (HDS) during the past decades [2,3], they are still not able to satisfy the stringent present regulations for a very long period of time. Consequently, their lifetime is short. It results in a growing interest in evaluating fresh and regenerated catalysts.

In industry, the catalysts are tested under real conditions in bench-scale units, which is rather expensive and time-consuming. Conversely, in academic laboratories, the catalytic properties are more rapidly appraised by using numerous spectroscopic,

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chemisorption, or microreactor activity techniques [4–12]. Among all of them, the reaction of representative molecules seems more appropriate. However, none of the tests is universally accepted because of the choice of the model molecule and reaction conditions [10,12].

The aim of this study is to examine in detail the influence of conditions on the reaction pathways of thiophene and dibenzothiophene. The rates were determined from kinetic modeling and compared to industrial HDS of several CoMo/Al_2O_3 catalysts. We show that the HDS activity of industrial CoMo catalysts can be rapidly anticipated.

2. Experimental

Four commercial CoMo/Al_2O_3 catalysts (named A to D) have been used. Their activities for industrial HDS have been measured in bench-scale units with various feedstocks including straight-run and vacuum gas oils. The activities were calculated on a reactor-volume basis and averaged. The relative-volume activities (RVAs) reported in this study referred to catalyst A. The RVA values were 100, 135, 140 and 180 for catalysts A to D, respectively.

The thiophene (T) conversion was carried out at 300–400°C in two different microflow systems. In the first one, the rate for thiophene HDS was measured under differential conditions at 0.1 MPa with a fixed pressure of thiophene (8 kPa). The second system was operated at 3 MPa under a wider range of conditions: thiophene pressure 8–125 kPa, space time 2–12 gh/mol, H_2/T 20–350 mol/mol. Thiophene diluted in a mixture of hexane, heptane, and xylene, was metered by a HPLC pump. The liquid feed was totally vaporized in the hydrogen flow. The diluting hydrocarbons were not converted up to 380°C. Thiophene and its products, thiolane (THT), butenes and butanes (lumped as C_4), were analyzed by on-line GC. In both systems, H_2S (0–15 mol%) could be added independently of the thiophene flow.

The oxidic catalysts were crushed and sieved between 0.2 and 0.5 mm. They were sulfided in the reactor at 400°C by H_2S (15 mol%)–H_2 (85) for the atmospheric runs, or H_2S (10 mol%)–CH_4 (10)–H_2 (80) for the pressure runs. In the latter case, H_2S and CH_4 were produced quantitatively from dimethyldisulfide before entering the reactor.

The conversion of dibenzothiophene (DBT) was carried out in a batch reactor (50 cm^3). A mass of 0.55 g of catalyst was ex situ sulfided at 400°C and 0.1 MPa with a H_2S (15 mol%)–H_2 mixture. The sulfided catalyst was then poured into the reactor containing 30 cm^3 of a solution of DBT (2 wt%, C^o_{DBT}=0.094 mol/l), decalin (*cis* 53.5%, *trans* 42.9%), and decane (1.6%). All transfers were realized under argon to prevent oxygen contamination. The reactor was closed and heated to 330°C. Then, hydrogen was introduced and the pressure adjusted to 4 MPa and the temperature to 335°C. The reaction began when the agitation started (500 rpm). Liquid samples were removed periodically and analyzed by GC. The liquid remaining in the sampling line was flushed back to the reactor by hydrogen so that the hydrogen concentration was constant throughout the run. From vapor–liquid equilibrium calculation [13], the initial H_2-to-sulfur molar ratio was about 34.

3. Results and discussion

3.1. Thiophene conversion

Fig. 1 shows a typical variation of the conversion of thiophene upon addition of H_2S over catalyst C at 340°C and 3 MPa. The conversion is progressively

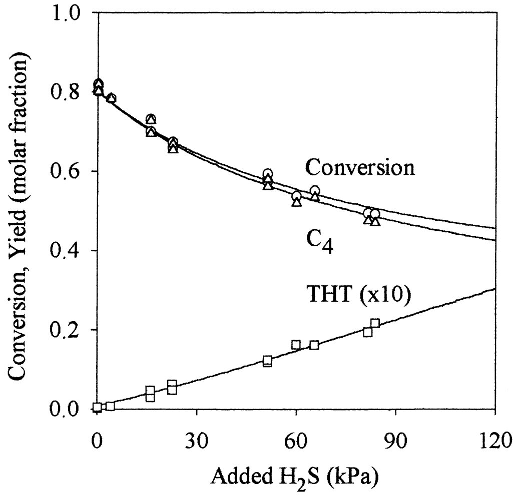
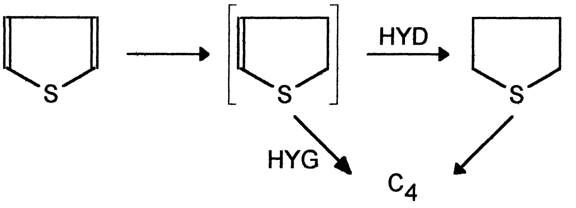


Fig. 1. Influence of added H_2S on the conversion of thiophene (○), and on the yields of THT (□) and C_4 (Δ). Catalyst C – 340°C, 3 MPa, P^o_T=8 kPa, W/F^o_T=5.4 gh/mol.



Scheme 1. Thiophene reaction network.

inhibited. But, a complete inhibition could never be obtained at all temperatures even with higher amounts of added H_2S. This suggests that H_2S plays a particular role in the conversion [14].

Catalysts A to D were very selective into C_4 hydrocarbons. The yield of C_4, which measures the HDS, decreased upon addition of H_2S (Fig. 1). On the other hand, the yield of THT almost linearly increased showing that H_2S was able to favor hydrogenation. Similar behavior was already observed at 280°C [15]. With the four catalysts examined here, it holds at 300–380°C.

The product distribution agrees with the reaction network (Scheme 1) previously reported [16]: C_4 and THT are produced via hydrogenolysis (HYG) and hydrogenation (HYD) after preliminary dearomatization of thiophene. The curves in Fig. 1 were drawn after kinetic modeling with the hypothesis formerly considered [16,17]:

1. hydrogenation occurs after attack of T by electrophilic $H^{\delta+}$ surface species issued from the dissociation of H_2 and H_2S, while C–S hydrogenolysis requires nucleophilic species, essentially $H^{\delta-}$ provided by H_2;
2. two kinds of active sites, i.e. sulfur vacancies and sulfur-saturated vacancies were postulated. The former sites prevail at low amounts of H_2S.

Hence, pressures of H_2 and H_2S govern the amount of active species. T and its competitor H_2S control the distribution of active sites.

This model allows to determine the contribution of the hydrogenation and hydrogenolysis pathways to the global rate. Fig. 2 shows a typical variation of the initial rate upon addition of H_2S for catalyst C at 340°C and with a thiophene pressure of 8 kPa. The hydrogenation route through THT is negligible at very low H_2S; it amounts only to 25% of the global rate at 120 kPa of H_2S.

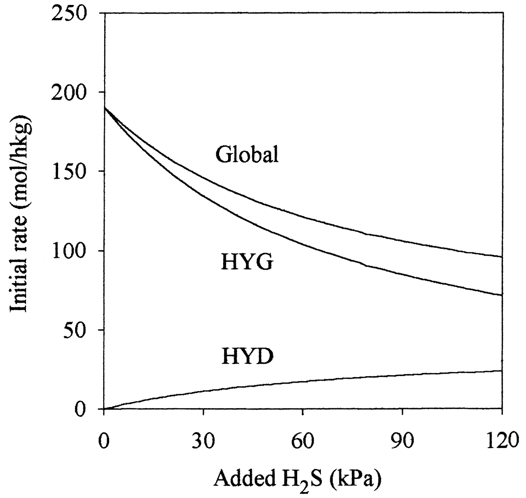


Fig. 2. Modeling of the influence of H_2S pressure on the initial rates for the conversion of thiophene, hydrogenation (HYD) and hydrogenolysis (HYG). Catalyst C – 340°C, 3 MPa, P^{o}_{T}=8 kPa.

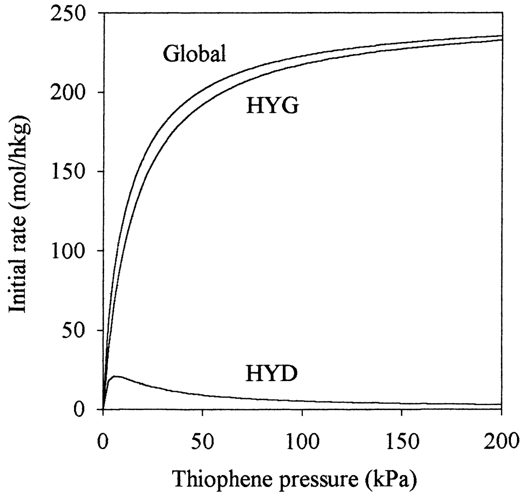


Fig. 3. Modeling of the influence of thiophene pressure on the initial rates for the conversion of thiophene, hydrogenation (HYD) and hydrogenolysis (HYG). Catalyst C – 340°C, 3 MPa, $P^{o}_{H_2S}$=85 kPa.

Increasing the thiophene pressure at constant H_2S (85 kPa), the hydrogenolysis route was almost exclusive for thiophene pressures higher than ca. 50 kPa (Fig. 3). In that case, the thiophene test represents a unique function of the catalyst, i.e. its ability to break a C–S bond. At lower pressures of thiophene, hydrogenation contributes significantly to the global rate.

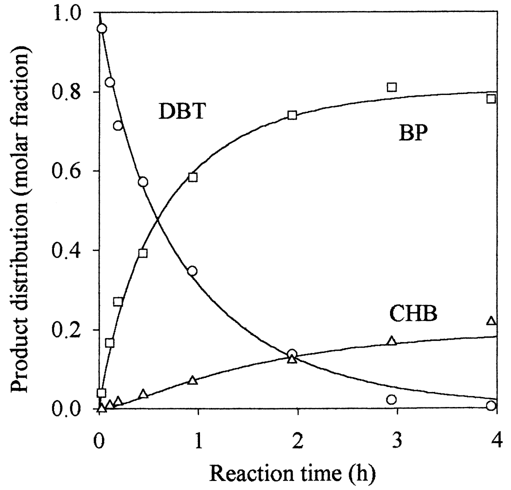


Fig. 4. Evolution of the molar fraction of DBT (○), BP (□) and CHB (△) with reaction time. Catalyst C – 335°C, 4 MPa.

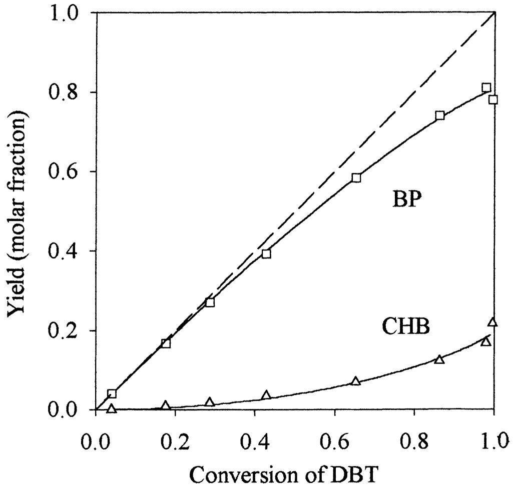


Fig. 5. Selectivity diagram. Same symbols as in Fig. 4. Catalyst C – 335°C, 4 MPa.

However, hydrogenolysis stayed predominant even at the highest applied pressures of H_2S.

These features hold at all temperatures in the range 300–380°C. A slight lowering of the contribution of the hydrogenation route was noticed by increasing the temperature as a consequence of a lower activation energy than that of the C–S breakage [17].

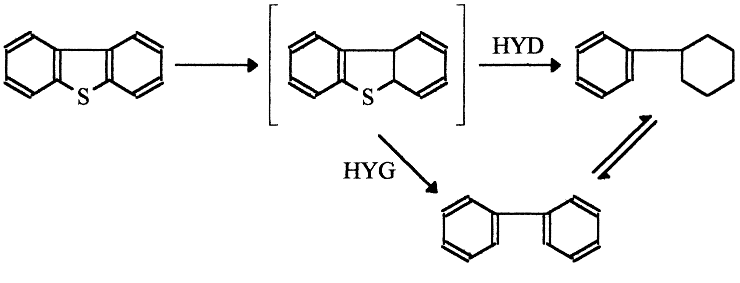
3.2. Dibenzothiophene conversion

Fig. 4 displays a typical product distribution versus reaction time for catalyst C at 335°C and 4 MPa. DBT was converted into biphenyl (BP) and cyclohexylbenzene (CHB); they accounted for more than 95% of the mass balance.

From the selectivity diagram (Fig. 5), BP appears to be formed primarily and CHB secondary, suggesting a consecutive network. This however, is misleading because the H_2S concentration continuously increases with DBT conversion. Referring to the thiophene reaction where H_2S favored hydrogenation, CHB should become also a primary product as soon as DBT was desulfurized. Indeed, primary CHB has been evidenced by many authors [18–23].

Furthermore, interconversion between BP and CHB was reported [24]. It probably occurred here since we observed a catalytic dehydrogenation of decalin up to 5% into tetralin and naphthalene.

The reaction network we considered is shown in Scheme 2. The formation of BP and CHB occurs after dearomatization of DBT into a dihydro compound, in agreement with Singhal et al. [18,19]. Removal of H_2S will then yield BP. Its rate of formation measures the hydrogenolysis route to global HDS. CHB is formed after additional hydrogenation steps of the dihydro intermediate [18,19,21–23]. The formation of CHB



Scheme 2. Dibenzothiophene reaction network.

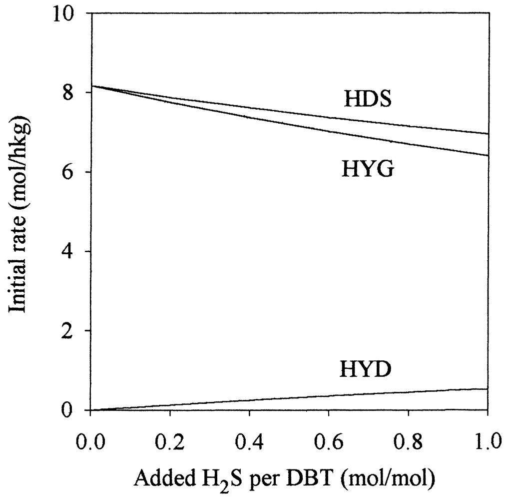


Fig. 6. Simulated effect of added H_2S on the initial rates for DBT conversion, hydrogenation (HYD) and hydrogenolysis (HYG). Catalyst C – 335°C, 4 MPa.

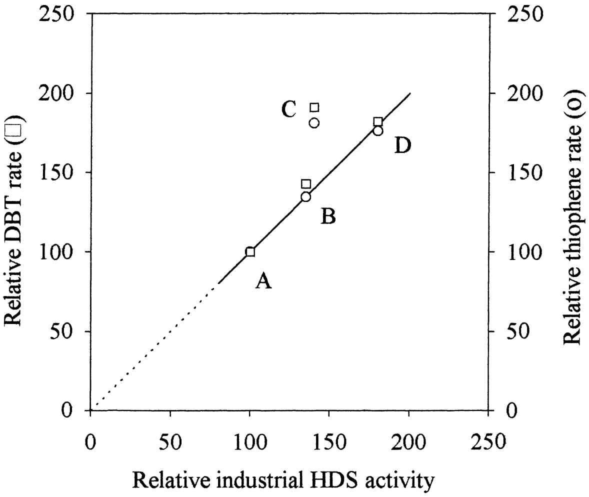


Fig. 7. Correlation between relative rate for hydrogenolysis and industrial RVA. Catalysts A to D; initial HDS of DBT (□), 335°C, 4 MPa; HDS of thiophene (○), 380°C, 3 MPa, $P^{\mathrm{o}}_{\mathrm{T}}$=125 kPa, $P^{\mathrm{o}}_{\mathrm{H_2S}}$=85 kPa.

measures the hydrogenation capacity of the catalyst. Similarity with the thiophene network is obvious. The rate equations used for thiophene were transposed to DBT. Kinetics modeling was satisfactory as shown by the curves in Figs. 4 and 5.

We used these equations to simulate the distinct effect of H_2S on initial rates (Fig. 6). The simulation was applied up to 1 mol of added H_2S per mole of DBT. The trends were rather similar as found with thiophene when very low amounts of H_2S were added (Fig. 2). This well illustrates the minor contribution of the hydrogenation route to global HDS of DBT.

3.3. Correlation with industrial activity

From kinetics of thiophene and dibenzothiophene, we determined both hydrogenation and hydrogenolysis rates over the CoMo catalysts. It is thus worthwhile to ascertain which function is the most relevant with respect to industrial HDS. This was sought for by comparing the relative rates for model molecules and industrial feeds (RVA).

Firstly, we focus on the reaction of DBT since it was extremely selective towards hydrogenolysis. In that case, the relative initial rates poorly correlate the industrial RVA (Fig. 7). Catalyst C was found equivalent to catalyst D, and departs from the ideal correlation line with a slope unity joining catalysts A, B and D. With thiophene, hydrogenolysis was also predominant at pressures of thiophene higher than 50 kPa (Fig. 3) whatever, the pressure of H_2S. Under these conditions, the relative rates were very close to those of DBT (Fig. 7). We can therefore conclude that C–S hydrogenolysis is not the key factor limiting the HDS of real feeds.

We now turn to the relation between rates for hydrogenation and industrial activities. The major difficulty is that under pressure the contribution of the hydrogenation route to global HDS was always minor (Figs. 2 and 6). Hence, with DBT, hydrogenation was better evaluated by the conversion of biphenyl into cyclohexylbenzene. Kinetic modeling gave access to this rate. A very good correlation was then obtained with the RVA values (Fig. 8). Nevertheless, one should prefer to correlate HDS with a molecule bearing a sulfur atom.

With thiophene, the hydrogenation rate under pressure was inaccurate because of the low yield of THT. However, under the best conditions, i.e. a pressure of thiophene equal to 8 kPa (Fig. 3), catalysts C and D were now distinguished and ranked satisfactorily with the RVA. Going further, we carried out the thiophene conversion under conditions where hydrogenation is rate-limiting. This was easily realized at atmospheric

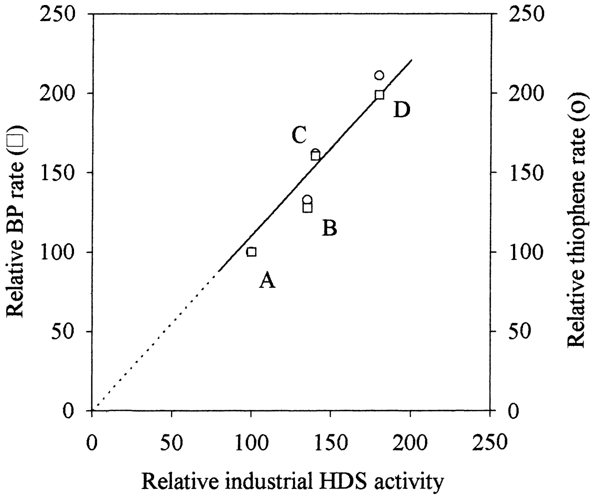


Fig. 8. Correlation between relative rate for hydrogenation and industrial RVA. Catalysts A to D; HYD of BP at 10% conversion of DBT (□), 335°C, 4 MPa; HDS of thiophene (○), 400°C, 0.1 MPa, P^{o}_{T}=8 kPa, $P^{o}_{H_2S}$=2 kPa.

pressure. In that case, HDS is fully controlled by dearomatization [15]. Measurements of initial rates affords as expected a very good correlation with RVA (Fig. 8). On that account, the thiophene test fully validates the correlation obtained with biphenyl. Conclusively, hydrogenation is the main function to develop in order to achieve industrial HDS.

4. Conclusion

This work stresses the importance of experimental conditions in the conversion of model molecules for ranking industrial catalysts. Indeed, depending on the conditions, thiophene ranks the CoMo/Al_2O_3 catalysts either as dibenzothiophene hydrogenolysis or as biphenyl hydrogenation.

As inferred with thiophene and dibenzothiophene, any model molecule which reacts following a complex scheme should be representative of industrial HDS once the conditions favor hydrogenation over hydrogenolysis. A poor correlation with industrial activities is obtained with thiophene or dibenzothiophene under pressure because the hydrogenolysis route to global HDS is predominant. Hydrogenation of biphenyl perfectly correlates industrial HDS as does the dearomatization of thiophene at atmospheric pressure. We therefore, recommend the thiophene test at atmospheric pressure because of its rapidity and easiness.

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