

## Correlation between Low-Pressure Thiophene HDS and High-Pressure Dibenzothiophene HDS

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It is shown that if the kinetics of the reaction is carefully applied, the HDS of thiophene under atmospheric pressure of  $H_2$  is an excellent predictive test of the HDS of dibenzothiophene under industrial conditions of reaction. In addition to kinetics the main precaution is to not mix catalysts of different families, i.e., CoMo or NiMo. © 1990 Academic Press, Inc.

### INTRODUCTION

CoMo and NiMo catalysts are used extensively for the hydrodesulphurization (HDS) of different oil fractions by high-pressure hydrogen treatment. The improvement of this family of catalysts or their replacement by more active new catalysts requires time-consuming and very expensive tests on the pilot plant scale because most of the literature denies the possibility of using lab scale reactors under atmospheric pressure and thiophene as a test molecule to predict industrial activity. Betteridge and Burch (1) have recently published a series of tests on CoMo and NiMo catalysts where thiophene HDS, under normal pressure, is compared to high-pressure tests (4.2 MPa) on a light gas-oil containing 116 ppm of sulphur (2); the discrepancy between the two tests is obvious. However, Qusro and Massoth found a good correlation when testing support effect on pure Mo catalysts (3). Other rapid and cheap tests have also been proposed, based mainly on chemisorption:  $H_2$  uptake (2) and  $O_2$ , CO, and  $H_2S$  uptakes, which do not correlate with HDS activity for Burch and Collins (4), and  $O_2$  uptake alone which correlates with HDS activity only on small ranges of activity (DOC technique) for the Shell group (5). Much of the literature deals

with these attempts to correlate chemisorption and activity (6-8), but none is convincing or efficient.

The aim of this article is to show that the HDS of thiophene under atmospheric pressure of  $H_2$  can correlate very accurately with the HDS of dibenzothiophene under industrial operating conditions as long as the lab test is performed under perfect kinetic conditions and as long as CoMo's are compared with CoMo's, NiMo's with NiMo's, NiW's with NiW's . . . without mixing these different families.

### EXPERIMENTAL

#### *Apparatus*

An all-glass system was equipped with greaseless valves and ball-joint connections, except for the metallic katharometer (TCD) and its connections.

High-purity  $H_2$  and 2% vol  $H_2S/H_2$  from Air Liquide were used, without further purification for  $H_2S/H_2$ , and with double purification through silicagel and zeolites at 90 K for  $H_2$ . All off-gas  $H_2S$  was destroyed by contact with solid or liquid KOH.

The gas flow rate was measured by a ball flowmeter and adjusted with a needle valve located just before the pump. The total pressure was kept at atmospheric level by using both a bubbler and a slow gas flow to

avoid any pressure drop through the reactor.

Distilled thiophene (Purum Fluka) (generally 25  $\mu$ l) was injected by means of a high-precision syringe ( $\pm 0.1$   $\mu$ l) through a vaccine cap located above the saturator; the reaction products were also collected with syringes after the reactor.

The first katharometer (TCD) measured the partial pressure of the feed and the second enabled the mass balance after reaction to be checked. The temperature of the saturator is selected according to the required thiophene partial pressure (273 K, 18.8 Torr for the test). The signal corresponding to the thiophene was perfectly rectangular on the recorder and showed a constant partial pressure of thiophene.

The mixture thiophene-H<sub>2</sub> was preheated before the catalyst bed through quartz balls, in the same zone of the oven where the temperature was kept constant ( $\pm 0.5$  K) on 7 cm. One thermocouple piloted the regulation of the oven while a second thermocouple on the wall of the reactor measured the temperature of the catalyst bed (generally 500 K for the tests). The reactor was made of quartz and was designed to work under differential conditions.

The products were injected into two columns for gas chromatography (silicon SE30,  $\frac{1}{4}$  in., 5 m and OV101, capillary, thick film, 50 m) and analysed after separation by a FID detector. The double analysis improved the accuracy. The products found after reaction were the three *n*-butenes, butane, and thiophene; neither tetrahydrothiophene nor butadienes were observed and only small traces of C<sub>2</sub> hydrocarbons were overlooked.

The standard procedure consisted of an *in situ* presulphurization at 723 K for 2 h with 2% vol H<sub>2</sub>S/H<sub>2</sub> of 5 to 10 mg ( $\pm 0.02$  mg) of catalyst, followed by a decrease in temperature to 500 K under H<sub>2</sub>S/H<sub>2</sub> flow; after stabilization the flow was switched to pure H<sub>2</sub> (25 cm<sup>3</sup>/min) and thiophene was injected as soon as the TCD signal showed

the disappearance of H<sub>2</sub>S in the flow. The products were collected after 5 min of parallel signal between the two TCD signals. The catalysts were always kept under H<sub>2</sub>S/H<sub>2</sub> flow in absence of thiophene in order to keep their sulphidation state unchanged. A batch of a single catalyst was tested three or four times during 1 day (1.5 h between each test) at different flow rates to evaluate the rate of the reaction and to check that no deactivation was occurring. The same catalyst was tested a second day on another batch by following the same procedure. The conversion was always kept below 1.5%.

The high-pressure HDS of dibenzothiophene (DBT) was carried out in a fixed-bed, upflow automated bench scale pilot unit. A catalyst charge of 20 ml was supported in the center section of the tubular reactor (17 mm internal diameter), heated by a three-zone electrical heater. An axial thermowell (5 mm outside diameter) extending upward through the reactor measured the internal temperature.

The catalysts were presulphided *in situ* at 673 K and atmospheric pressure in a stream of 10% vol H<sub>2</sub>S/H<sub>2</sub> flowing at 40 liters/h for 4 h. The temperature was then lowered to 563 K, the reactor pressurized with hydrogen, and the feed flow started. The following conditions were applied to all runs: temperature 563 K for 24 h, then 583 K for 24 h before the collection of the products; liquid hourly space velocity = 2 h<sup>-1</sup>; total pressure = 4.5 MPa. The synthetic feed (under N<sub>2</sub> blanket) was delivered precisely at 40 cm<sup>3</sup>/h by a metering pump. The cocurrent gas flow rate of 40 liters/h (STP) was controlled by a mass flow controller. The feed solution contained diphenylmethane (DPM) as solvent, to which 0.80 mol/liter of DBT was added, corresponding to 2.6 wt% of sulphur. Liquid products were separated from the effluent stream at reactor pressure. Gases were first scrubbed with NaOH solution, measured with a wet test meter, and then vented. Liquid level within the separator was controlled by sensing differ-

ential pressure to provide a continuous flow of liquid to the product receiver. Liquid samples were automatically collected and analysed on a Packard Model 437 GC equipped with a column packed with 10% XE60 on Chromosorb T, a FID, and a microprocessor. The components were identified by GC-MS and use of authentic standards. Products of reaction were biphenyl (major product), cyclohexylbenzene, and trace amounts of bicyclohexyl and tetra- and hexahydrodibenzothiophene.

### Kinetics of HDS

Many authors have shown the complex system of equations which can explain the kinetics of the HDS reaction. The different models have been reviewed by Vrinat (9). Recently, Radomyski *et al.* (10) proposed a new equation

$$r_T = k \cdot \frac{K_T P_T \cdot K_H P_H}{(1 + K_T P_T)(1 + K_H P_H + K_S P_S)}$$

very close to the equation proposed by Satterfield and Roberts (11), both based on the Langmuir-Hinshelwood model,

$$r_T = k \cdot \frac{K_T P_T \cdot K_H P_H}{(1 + K_T P_T + K_S P_S)^2}$$

where  $r_T$  = rate of thiophene hydrogenolysis;  $k$  = rate constant;  $K_T$ ,  $K_H$ ,  $K_S$  = adsorption equilibrium constants of thiophene, hydrogen, and  $H_2S$ ; and  $P_T$ ,  $P_H$ ,  $P_S$  = partial pressure of thiophene, hydrogen, and  $H_2S$ .

Most of the studies published in the literature confirm these equations; we shall report in this article our own results; if one accepts these equations, some important consequences must be underlined.

*First consequence.* At low pressure (i.e., 1 atm), if the conversion  $\alpha$  becomes too high,  $K_S P_S$  becomes nonnegligible and diminishes the apparent rate whatever the chosen equation. In addition, if a differential reactor must be used, it is fundamental to work at low conversion.

*Second consequence.* At low hydrogen pressure, the partial pressure of thiophene

must be kept very low versus the hydrogen pressure if one wishes to approximate the kinetics of thiophene HDS reaction to a first-order rate. If  $K_T P_T$  is small versus 1 and if the conversion is kept low ( $K_S P_S$  small versus 1),  $K_H P_H$  being constant and agglomerated in  $k$ , the two equations become

$$r_T = k' \cdot K_T P_T.$$

While these two consequences seem obvious, neither of them is generally respected by the huge number of HDS reactions performed under atmospheric pressure and reported in the literature. We believe that it is the main reason for the discrepancy between high-pressure and low-pressure tests.

*Third consequence.* (This consequence is only valid for the equation of Radomyski *et al.*) At high conversion the adsorption of  $H_2S$  competes with  $H_2$  and not with the thiophene. This point is the original finding of Radomyski *et al.*, while in all the other models a competition between the two sulphided molecules was always intuitively proposed. Thus if  $K_H P_H$  becomes very high in front of  $K_S P_S$ ,  $K_S P_S$  can be neglected and the poisoning effect due to the high conversion (high  $H_2S$  partial pressure) is no longer an obstacle to measuring the activity of the catalysts.

### Kinetics Verifications on the Low-Pressure Pilot

The same NiMo/Al<sub>2</sub>O<sub>3</sub> HR346 from Procatalyse has been used for all the verifications.

A first-order reaction in a differential volume of an ideal integral isothermal reactor, without axial mixing and radial gradients of concentration or fluid velocity is described by,

$$F \cdot c \cdot d\alpha = k_0 \cdot c(1 - \alpha) \cdot dV \quad (1)$$

$$F \cdot \frac{d\alpha}{1 - \alpha} = k \cdot dV \Rightarrow \ln \frac{1}{1 - \alpha} = k \cdot \frac{V}{F},$$

where  $F$  = molar flow of the heterocycle,  $\alpha$  = conversion,  $k$  = rate constant containing

TABLE I

Rate of HDS under Pure H <sub>2</sub> and under 2% H <sub>2</sub> S/H <sub>2</sub> at 513 K versus Thiophene Partial Pressure						
Thiophene partial pressure <i>P</i> (Torr)	6	9	19	27	55	93
Rate <i>r</i> of HDS under H <sub>2</sub> in mol/g(cat.) · s × 10 <sup>-6</sup>	1.35	1.98	3.33	3.72	4.32	4.30
-ln <i>r</i>	13.51	13.13	12.61	12.50	12.35	12.36
Conversion in %	9.50	9.05	6.23	4.98	3.18	2.80
Rate <i>r</i> of HDS under H <sub>2</sub> S in mol/g(cat.) · s × 10 <sup>-6</sup>	0.276	0.390	0.773	1.000	1.440	1.210
-ln <i>r</i>	15.10	14.76	14.07	13.82	13.45	12.62
Conversion in %	2.03	1.83	1.48	1.35	1.07	0.80

the initial concentration  $c_0$  for simplification, and  $dV =$  element of volume of the reactor. If  $V_{\text{cat.}} = V(1 - \varepsilon)$  and if  $M_{\text{cat.}} = \rho_c \cdot V$ , with  $\varepsilon$  void volume and  $\rho_c$  density of the catalyst bed, then

$$\ln \frac{1}{1 - \alpha} = k' \cdot \frac{M}{F} \quad (2)$$

As the reaction is first order with respect to the heterocycle,

$$r = k' \cdot (1 - \alpha) \quad (3)$$

$$\Rightarrow r = (1 - \alpha) \cdot \ln \frac{1}{1 - \alpha} \cdot \frac{F}{M} \quad (4)$$

( $k'$  also contains  $c_0$ ).

If the reactor works under differential conditions, at very low conversion, Eq. (4) becomes

$$r = \alpha \cdot \frac{F}{M} \quad (5)$$

The results reported in Table 1 and in Fig. 1 demonstrate that the reaction is first order only at low partial pressure of thiophene (below 25 Torr) with respect to thiophene and that a partial pressure of H<sub>2</sub>S dramatically decreases the rate of the reaction. The data obtained in pure H<sub>2</sub> typically fit equations of the form

$$r = K \cdot \frac{K_T P_T}{1 + K_T P_T}$$

and are consistent with both the Satterfield and Roberts equation and the Radomyski *et al.* equation ( $K_S P_S$  is neglected because of the low conversion). When the feed contains H<sub>2</sub>S the same equation fits the Radomyski model because  $K_S P_S$  is constant; but for Satterfield's model, the denominator must have a square form.

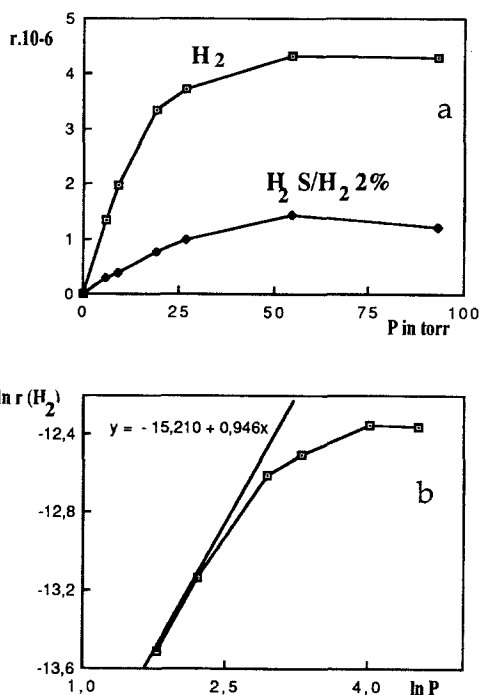


FIG. 1. Rate and order of reaction (see Table I).

TABLE 2  
Characteristics of the Catalysts

Catalysts	Preparation	Specific surface (m <sup>2</sup> /g)	Concentration MoO <sub>3</sub> (% wt)	Concentration CoO(% wt)	Concentration NiO(% wt)
CoMo HT15	Impregnation	168	13.5	3.1	—
CoMo HT17	Impregnation	—	13	2.8	—
CoMo 54MK	Impregnation	175	14	2.8	—
CoMo 69MK	Impregnation	150	13	2.8	—
CoMo 75MK	Impregnation	150	13	2.8	—
CoMo IN6	Impregnation	200	12	2.9	—
CoMo HT18	Kneading	238	17.5	5	—
NiMo HT21	Kneading	300	17.5	—	3.8
NiMo HT23	Kneading	246	17.5	—	3.8
NiMo HT27	Kneading	286	17.5	—	3.1
NiMo IN6	Impregnation	198	14.4	—	3.4

### Kinetics on the High-Pressure Pilot

Equation (2) is valid for the reactions carried out at high hydrogen pressure but because of the high conversion (50–90%) the low-pressure development cannot be made and only the rate constant has been evaluated:

$$k = \ln \frac{1}{1 - \alpha} \cdot \frac{V}{F_v} \Rightarrow$$

$$k = \ln \frac{1}{1 - \alpha} \cdot (\text{LHSV})$$

per gram of catalyst

$$k = \ln \frac{1}{1 - \alpha} \cdot \frac{(\text{LHSV})}{M} \quad (k \text{ in } \text{h}^{-1} \cdot \text{g}^{-1})$$

$F_v$  = volume flow.

Because of the fact that the density of the different catalysts was not constant and in order to be homogeneous with the low-pressure test rates measured per gram of catalyst, the rate constant at high pressure was divided by the catalyst mass.

The linearity of  $k$  was checked by varying the LHSV; this indicates that under high pressure first order appears to be reasonably valid, even at high conversions, confirming the Radomyski equation (see above) or possibly due to low concentration of DBT in the feed (consistent in this

case with the equation of Satterfield and Roberts), so that inhibition terms become negligible. All the measures reported later were obtained for LHSV = 2 h<sup>-1</sup>.

### Catalysts

The characteristics and preparation procedures for the different catalysts are reported in Table 2. Different  $\gamma$ -aluminas prepared by Rhône-Poulenc have been used. Mo was impregnated from a water solution of ammonium paramolybdate while Co was obtained from either nitrate or sulphate salts. The two IN6 catalysts are commercial NiMo and CoMo from Procatalyse. The kneading preparation has already been reported (12).

## RESULTS AND DISCUSSION

The rate of thiophene HDS reaction at normal H<sub>2</sub> pressure,  $r$ , and the rate constant  $k$  for the dibenzothiophene HDS reaction both per gram of catalyst are reported in Table 3. (The rate  $r$  is expressed in mol · g(cat.)<sup>-1</sup> · s<sup>-1</sup> and  $k$  in h<sup>-1</sup> · g(cat.)<sup>-1</sup>).

Figure 2a shows the linear correlation between  $r$  and  $k$  for all the tested CoMo. The regression factor  $R$ , equal to 1.00, shows that on a wide range of activity, specific surface, alumina support, shape of support, and impregnation conditions, a

TABLE 3  
Comparative HDS Activities

Catalysts	Low pressure			High pressure		
	Mass (mg)	Conversion (%) (average)	$r \times 10^{-10}$	Mass (g)	Conversion (%)	$k$
CoMo/alumina						
HT17	5.40	0.33	3750	17.69	50	0.080
75MK	7.50	0.81	6720	17.85	69	0.130
69MK	5.43	0.65	8750	17.05	77	0.173
54MK	4.72	0.82	11100	11.02	62.5	0.244
HT15	8.74	1.55	12120	13.63	81	0.245
IN6	4.50	0.90	12680	15.27	88	0.275
HT18	8.95	1.30	8200	17.27	83	0.205
NiMo/alumina						
HT23	6.20	0.63	5900	16.48	49	0.091
HT21	7.90	1.06	8350	14.50	55	0.111
HT27	6.60	1.28	13340	14.59	78	0.209
IN6	5.80	1.37	14040	15.25	67	0.170

perfect correspondence exists between the two measurements. One of the catalysts, HT18, is not taken into account for the calculation of the regression factor because it is a very exotic catalyst made by kneading preparation instead of impregnation (12). However, although these differences in preparation and concentration are very important, the point representing this catalyst HT18 is still very close to the perfect line ( $R = 0.99$ ).

In order to check whether this correlation exists for catalysts not prepared by impregnation, we have studied a series of NiMo prepared by kneading. In Fig. 2b, the same excellent correlation between high- and low-pressure reactions is observed ( $R = 0.99$ ). Even when adding the NiMo IN6 prepared by coimpregnation, the correlation remains good ( $R = 0.97$ ).

Finally, in Fig. 2c the activities of CoMo and NiMo catalysts are reported together and it is easy to observe that it is not possible to mix the two families on the same correlation line although the slopes of the two regression lines are not so different.

It remains to explain this difference. Many speculations can be proposed:

—higher rate of poisoning of NiMo versus CoMo at high pressure while no poisoning occurs at low pressure both because of the very high purity of the reactants and because of the low reaction temperature retarding any formation of coke or cracked molecules;

—different reaction mechanisms at high pressure between NiMo and CoMo;

—different stability of the catalyst under high pressure, etc.

In fact, we have strong evidence that even at high partial pressure of  $H_2S$ , some nonsulphided nickel metal atoms remain on NiMo catalysts while no cobalt metal atom remains unsulphided on CoMo catalysts (13). The result is the presence of more hydrogenated products on NiMo than on CoMo and also the presence of cracked products which are not observed on CoMo (these metallic atoms can also be responsible for the better HDN properties of NiMo when compared to those of CoMo). The

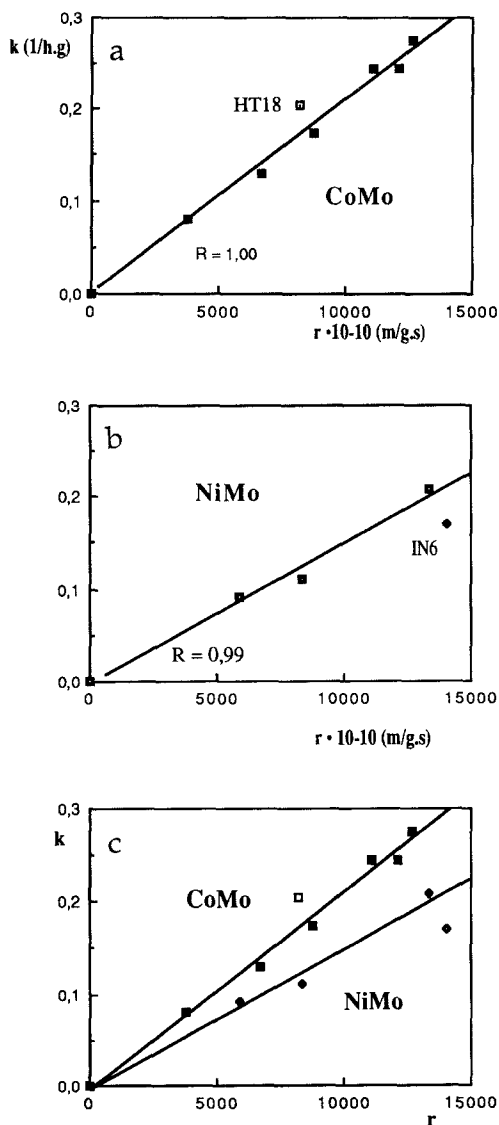


FIG. 2. Correlation between high- and low-pressure HDS reactions.

presence of these cracked molecules is sometime associated with a higher rate of poisoning (14) and the first speculation will be the explanation.

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