

Effect of H₂S on hydrodesulphurization of dibenzothiophene, 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene on CoMo/Al₂O₃ catalyst

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The effect of H₂S on the activity of the novel CoMo/Al₂O₃ catalyst, prepared using citric acid, in HDS of DBT, 4-MDBT and 4,6-DMDBT in the model mixture as well as in straight-run gas oil was studied. It was shown, that DBT and 4-MDBT conversion depends on the H₂S pressure, while 4,6-DMDBT conversion was practically independent on H₂S. The results obtained let us to conclude, that the effect of H₂S on the deep HDS of real feedstock depends strongly on the individual sulphur compounds contents and their ability to react through DDS or HYD route.

Introduction

The main difficulty arising during the production of low sulphur diesel fuels (<50 ppm S) is the conversion of sterically hindered alkyl substituted dibenzothiophenes [Babich, 2003]. It was shown that supporting of active components from solutions containing chelating agents allows to prepare the catalyst with the type II Co–Mo–S phase, revealed an increased activity in desulphurization of such molecules [Van Dillen, 2003]. To predict the catalyst performance in real feed stocks it is necessary to elucidate the inhibiting effects of different poisons, such as H₂S, N-containing and aromatic molecules, on reactivity of sulfur species in the deep desulphurization conditions. The aim of the present study is to investigate the effect of H₂S on the activity of novel CoMo/Al₂O₃ catalysts prepared using citric acid [Klimov, 2008] in hydrodesulphurization of DBT, 4-MDBT and 4,6-DMDBT in the model mixture as well as in the real feedstock – straight-run gas oil (SRGO).

Experimental

1.1 Catalyst and sulfidation

The CoMo/Al₂O₃ catalyst has been prepared with pore volume impregnation method using bimetallic CoMo complexes with citric acid with the subsequent drying at 110 °C for 8–10 hours [Klimov, 2008]. γ -Al₂O₃ granulated in the form of trilobe extrudates with diameter of 1.4 mm and length/diameter ratio equal to 3–5 was used as the support. Prior to reaction, catalysts were sulfided in situ by a straight-run gas oil enriched by dimethyldisulfide (0.6 wt.%), the preparation and sulfidation procedures have been described earlier [Pashigreva, 2008].

1.2 . HDS reaction

The HDS reaction of DBT, 4-MDBT and 4,6-DMDBT in model mixture and in SRGO was performed in a high-pressure three-phase down-flow lab reactor (internal diameter 16 mm, isothermal zone 300 mm in length) using 10 ml of catalyst in the form of trilobe extrudates mixed with fine carborundum particles (fraction 0.25–0.5 mm). The HDS of DBT's in the model mixture (500, 247, and 77 wt ppm S for DMDBT, 4-MDBT and 4,6-DMDBT) was carried out at hydrogen pressure 3.5 MPa, oil flow rate 4 h⁻¹, hydrogen/oil = 200 and temperature 320, 335 and 350°C. The model mixture was prepared by dilution of DBT, 4-MDBT, and 4,6-DMDBT in a hydrotreated SRGO containing about 8 wt ppm S, 7 wt ppm N; 21,7% mono-, 1,89% di- and 0,81% poli-aromatics. To examine the effect of the H₂S partial pressure the appropriate quantity of dimethyldisulfide (DMDS) was added to the oil feed to generate H₂S trough in-situ decomposition. The steady-state was reached after 8 hours, no catalyst deactivation was observed during the run.

Catalytic properties of the same catalyst in the HDS of SRGO were studied at 340 °C, 3.5 MPa, oil flow rate 2 h⁻¹, hydrogen/oil = 300 and 200. The SRGO contains 1,104 wt.% S, 138 ppmw N; 21,5% wt.% mono-, 8,33% wt.% di- and 1,05% wt% poli-aromatics.

The total concentrations of sulfur and nitrogen were determined by means of Antek 9000TNS. The aromatic compounds were measured by means of HPLC in accordance with IP 391/395. The specific sulfur compounds in the samples were analyzed by gas chromatograph Agilent 6890N, equipped with a capillary column HP-1MS (60.0 m × 250 μm × 1.00 μm) and an atomic emission detector JAS.

Result and discussion

Experimentally obtained concentration of the DBT, 4-MDBT and 4,6-DMDBT in the hydrotreated model mixture depending on reaction temperature and H₂S partial pressure are given at the Table 1.

Ratio of DMDS sulfur (0.5-2.5% wt.) to the heavy sulfur-containing species (Table 1) in the oil feed was high, so DMDS was assumed to be the only source of H₂S, additional H₂S from converted species was neglected.

Table 1 Concentrations of DBT, 4-MDBT and 4,6-DMDBT sulfur at the lab reactor outlet. Operation conditions: P=3.5 MPa, LHSV= 4 h⁻¹, H₂/feed = 200.

	320 °C		335 °C		350 °C	
	C _s , ppmw	P (H ₂ S) bar	C _s , ppmw	P (H ₂ S) bar	C _s , ppmw	P (H ₂ S) bar
DBT sulfur (C ₀ =500 ppmw)	35.6	0.59	7.8	0.59	0.9	0.59
	51.5	1.30	11.8	1.30	1.4	1.30
	81.7	2.61	19.4	2.61	3.2	2.61
4-MDBT sulfur (C ₀ =247 ppmw)	66.8	0.59	27.9	0.59	5.5	0.59
	73.4	1.30	31.2	1.30	6.6	1.30
	89.7	2.61	36.4	2.61	10.7	2.61
4,6-DMDBT sulfur (C ₀ =77 ppmw)	41.8	0.59	29.7	0.59	16.5	0.59
	40.8	1.30	29.7	1.30	16.7	1.30
	41.2	2.61	28.0	2.61	19.2	2.61

Langmuir-Hinshelwood equation type (1) was taken for the rates of the individual sulphur species conversion (DBT, MDBT, DMDBT):

$$\frac{dC_{S_i}}{d\tau} = -\frac{k_{S_i} C_{S_i}}{1 + K_{H_2S} P_{H_2S}} \quad (1)$$

Where:

τ - contact time, h ($\tau = \frac{1}{LHSV}$)

C_{S_i} - concentration of component's sulphur, ppmw

P_{H_2S} - H₂S partial pressure, bar

k_{S_i} , K_{H_2S} - kinetic parameters.

Fast DMDS decomposition and high ratio of DMDS sulfur to other sulfur-containing species provides nearly constant H₂S partial pressure at the catalyst bed height. At that conditions integrated eq.1 could be rewritten as follows:

$$-\frac{\tau}{\ln \frac{C_{S_i}}{C_{S_i}^0}} = \frac{1}{k_{S_i}} + P_{H_2S} \frac{K_{H_2S}}{k_{S_i}} \quad (2)$$

Linear approximation of plot of $-\frac{\tau}{\ln \frac{C_{S_i}}{C_{S_i}^0}}$ vs. P_{H_2S} gives $\frac{1}{k_{S_i}}$ from the intercept

and $\frac{K_{H_2S}}{k_{S_i}}$ from the slope (Fig. 1-2, Table 2,3.)

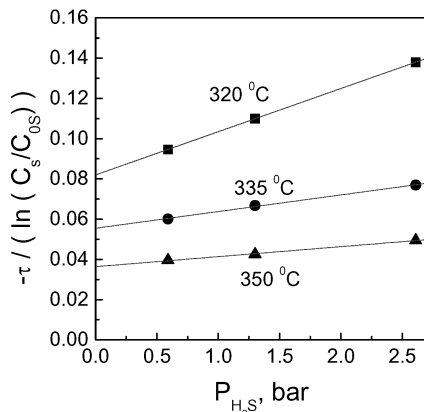


Fig. 1. Treatment of DBT conversion data (eq. 2)

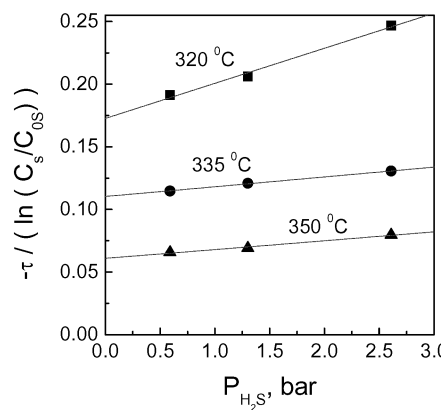


Fig. 2. Treatment of 4-MDBT conversion data (eq. 2)

Table 2. Calculated values of k_s and K_{H_2S} for DBT, 4-MDBT and 4,6 - DMDBT (eq. 1, Fig. 1-2)

	320 °C		335 °C		350 °C	
	k_s, h^{-1}	K_{H_2S}, bar^{-1}	k_s, h^{-1}	K_{H_2S}, bar^{-1}	k_s, h^{-1}	K_{H_2S}, bar^{-1}
DBT	12.2	0.26	18.0	0.15	27.5	0.14
4-MDBT	5.8	0.16	9.1	0.14	16.4	0.12
4,6-DMDBT	2.5	0	3.8	0	6.1	0

DBT conversion rate was found to be the most sensitive to the H_2S pressure, while 4,6-DMDBT conversion rate was practically independent on H_2S . It's well known for the MoS_2 HDS catalysts that sterically hindered S-containing species like 4,6-DMDBT transforms mainly through hydrogenation (HYD) route, while molecules like DBT transforms by direct desulfurization (DDS). Work [Logado'ttir, 2006] focused on the poisoning of the HYD pathway showed that the fully coordinated brim sites responsible for HYD pathway at the MoS_2 catalysts bind H_2S very weakly. Thus, the lack of significant inhibition of HYD pathway by H_2S can readily be explained.

The activation energy values calculated from our experiments is in good accordance with the obtained by other authors [Kim, 2005].

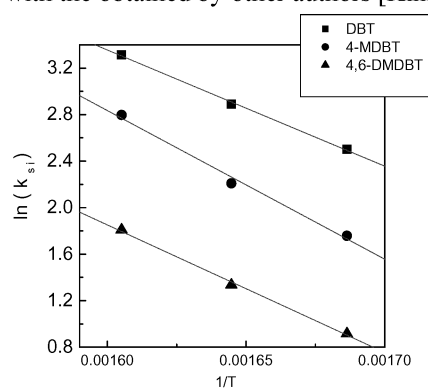


Fig. 3. Arrhenius plot of k_s (eq. 1) for DBT, 4-MDBT and 4,6-DMDBT

Table 3. Preexponential factors and activation energies for k_s (eq.1)

$k_s = k_{0,S} \cdot e^{-E_a/RT}$		
	$k_{0,S}, h^{-1}$	$E_a,$ kJ/mole
DBT	$2.56 \cdot 10^8$	83.1
4-MDBT	$1.3 \cdot 10^{10}$	106.2
4,6-DMDBT	$2.7 \cdot 10^8$	91.2

The change in the H₂S concentration during the investigation of HDS reaction in real SRGO was obtained by H₂/oil ratio variation while other conditions being kept constant. The effect of H₂S on deep HDS of industrial SRGO is shown at the table 4. It's seen that DBT conversion is practically complete at the reaction conditions, and 4,6-DMDBT conversion is independent on the H₂/oil ratio. Conversion of the 4-MDBT increases with the H₂/oil ratio increase owing to decreasing of the H₂S partial pressure.

It should be noted that overall sulphur content in the hydrotreated SRGO decreases by 65 % with the increasing of the H₂/oil ratio (table 4) assuming a presence of the significant amount of species that converted by the DDS pathway. Thus the effect of H₂S on the deep HDS catalyst performance is rather complicated. To predict the catalyst performance in the deep HDS conditions it is necessary to quantify carefully the sulphur

Table 4 The effect of H₂/oil ratio on the HDS of real SRGO (T=340°C, P = 3.5 MPa, LHSV = 2 h⁻¹).

	Sulphur in the feed, ppmw	Sulphur in HT of SRGO, H ₂ /oil =300	Sulphur in HT of SRGO, H ₂ /oil =200
DBT	147	< 1	< 1
4-MDBT	178	11	8
4,6-DMDBT	76	14	14
ΣS, ppmw	10400	171	111

individual compounds in the feedstock and reveal the transformation route for all of them (HYD or DDS).

Conclusions

Investigation of the effect of H₂S on the activity of the novel CoMo/Al₂O₃ catalyst in HDS of DBT, 4-MDBT and 4,6-DMDBT in the model mixture reveal that DBT and 4-MDBT conversion rates depends on the H₂S pressure, while 4,6-DMDBT conversion rate was practically independent on H₂S. These findings are supported by the results of SRGO hydrotreating. Thus, the effect of H₂S on the deep HDS of real feedstock is depending strongly on the individual sulphur compounds contents and their ability to react trough DDS or HYD route. From the practical point of view the result obtained clarify the importance of H₂/oil ratio in the deep HDS of SRGO.

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