Catalysis Today 150 (2010) 213–217

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Hydrodesulfurization with classic Co–MoS_2 and Ni–MoS_2/γ-Al_2O_3 and new Pt–Pd on mesoporous zeolite catalysts

Yinyong Sun [1], Huamin Wang [2], Roel Prins *

Institute of Chemical and Bioengineering, ETH Zurich, Wolfgang Pauli Strasse 10, 8093 Zurich, Switzerland

ARTICLE INFO

Article history:
Available online 29 August 2009

Keywords:
Hydrodesulfurization
Mechanism
Dibenzothiophene
4,6-Dimethyldibenzothiophene
Ni–MoS_2/γ-Al_2O_3
Co–MoS_2/γ-Al_2O_3
Pt
Pd
Mesoporous ZSM-5

ABSTRACT

The hydrodesulfurization (HDS) of dibenzothiophene (DBT), tetrahydrodibenzothiophene (THDBT) and hexahydrodibenzothiophene (HHDBT) was studied over Co–MoS_2/γ-Al_2O_3 and Ni–MoS_2/γ-Al_2O_3 catalysts, and the HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT) over metallic Pt–Pd catalysts supported on mesoporous NaH-ZSM-5. The desulfurization of DBT at 300 °C was faster than that of THDBT and HHDBT, both over Co–MoS_2/γ-Al_2O_3 and Ni–MoS_2/γ-Al_2O_3. Desulfurization of THDBT occurred directly to CHEB and CHB, but desulfurization of HHDBT occurred mainly by dehydrogenation to THDBT and subsequent desulfurization of THDBT. In most cases C–S bond breaking occurred by hydrogenolysis.

Pt–Pd/mesoporous NaH-ZSM-5 was much more active than Pt–Pd/γ-Al_2O_3, Pt–Pd/NaH-ZSM-5 and single metal Pt and Pd catalysts in the HDS of 4,6-DMDBT. The much higher rate of the Friedel–Crafts reaction of benzylalcohol with benzene demonstrated that mesoporous NaH-ZSM-5 had accessible mesopores. Noble metals on mesoporous zeolites are very active HDS catalysts and might be considered as catalysts in the second stage of a deep HDS process.

1. Introduction

To be able to reduce the sulfur content in gasoline and diesel fuel to very low levels, the hydrodesulfurization (HDS) mechanism of classic metal sulfide catalysts must be determined and better catalysts must be developed. Dibenzothiophene (DBT) alkylated at the 4 and 6 positions, as in 4,6-dimethyldibenzothiophene (4,6-DMDBT), is very difficult to desulfurize [1,2]. The methyl groups adjacent to the sulfur atom prevent σ-binding of the sulfur atom with the catalytic site [1–4] and desulfurization of 4,6-DMDBT mainly takes place via the hydrogenation (HYD) route. In this route, 4,6-DMDBT is first hydrogenated to tetrahydro (TH-), hexahydro (HH-) and dodecahydro (DH-) intermediates, which then are desulfurized to cyclohexylbenzenes and bicyclohexyls (Scheme 1) [1–8]. The alkyl groups do not hinder the π adsorption of 4,6-DMDBT on the catalyst surface and even slightly increase the rate of the HYD reaction [5,8].

The breaking of the C–S bonds of the intermediates has been studied over MoS_2/γ-Al_2O_3 and it was found that the ring opening of THDBT and HHDBT occurs by C–S hydrogenolysis [9,10]. The actual catalysts used in the industry contain Co or Ni in addition to MoS_2, because the Ni and Co atoms improve the catalytic activity of MoS_2 several fold [2]. We have extended the study of the desulfurization mechanism over metal sulfide catalysts to Co–MoS_2 and Ni–MoS_2 catalysts to gain further insight into the question how the sulfur atom is eventually removed from the THDBT and HHDBT and intermediates.

Because of the steric hindrance by the methyl groups, desulfurization of 4,6-DMDBT mainly takes place via the HYD route [1,2] and the hydrogenating ability of the catalyst is of critical importance for deep HDS. Supported noble metal catalysts are much better hydrogenation catalysts than metal sulfides [11–14], but are easily poisoned by sulfur. The sulfur sensitivity can be decreased by alloying [15] and by using an acidic support [16–19]. One explanation is that acids enable dealkylation and isomerization reactions of the alkyl substituents, which transforms refractory components into more reactive species and thus accelerate HDS [16,18]. Moreover, acidic supports may induce partial electron transfer from the metal particles to acidic sites of the support, making the resulting electron-deficient metal particles [20,21] more resistant to sulfur poisoning by decreasing the interaction with H_2S [20,22]. Another explanation is that hydrogen atoms can spillover from the metal particles to the aromatic sulfur-containing molecules that are adsorbed on acidic sites in the vicinity of the metal particles [11]. When the metal particles become poisoned by sulfur, they can still dissociate hydrogen molecules and hydrogenation by spillover hydrogen would still be possible [12].

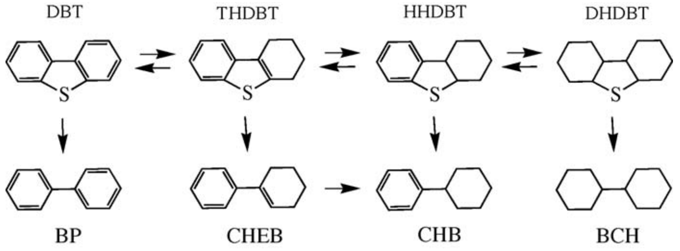
---

* Corresponding author. Tel.: +41 44 6325490; fax: +41 44 6331252.
E-mail address: prins@chem.ethz.ch (R. Prins).

[1] Present address: School of Chemical Engineering and Technology, Harbin Institute of Technology, Harbin 15001, China.

[2] Present address: Dept. Chem. Engineering, University of California, Berkeley, USA.

0920-5861/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2009.07.093



Scheme 1. Intermediates and final hydrocarbon products in the HDS of dibenzothiophene. Desulfurization reactions are indicated by vertical arrows and hydrogenation and dehydrogenation reactions by horizontal arrows.

Zeolites would be the acidic supports of choice, because they possess strong acidity and high stability. Unfortunately, large molecules such as 4,6-DMDBT cannot enter the micropores. They can only react on the outer surface of the zeolites where few acid centers are present. Noble metals supported on mesoporous amorphous silica–alumina (ASA) have a higher HDS activity than noble metals on γ-Al_2O_3 [19], but the recent discovery of mesoporous zeolites [23–25] opens the possibility to use these materials as support in HDS. We therefore studied alloyed Pt–Pd particles supported on mesoporous NaH-ZSM-5 in the HDS of 4,6-DMDBT.

2. Experimental

CoMo/γ-Al_2O_3 and NiMo/γ-Al_2O_3 catalysts were prepared by pore volume impregnation of γ-Al_2O_3 (Condea, 0.5 cm^3/g, 230 m^2/g) and in-situ sulfiding with H_2S/H_2 at 400 °C and 1.0 MPa for 4 h [9]. Pt, Pd and Pt–Pd on mesoporous NaH-ZSM-5 (M-NaH-ZSM-5) catalysts were prepared by pore volume impregnation with $M(NH_3)_4(NO_3)_2$ salts, drying, calcination and reduction with H_2 [26]. Mesoporous NaH-ZSM-5 was prepared as described before [24,27].

HDS reactions were carried out in a continuous-flow fixed-bed reactor at 300 °C with a feed of 1 kPa DBT (Acros), THDBT [28], HHDBT [10] or 4,6-DMDBT (Acros), and 130 kPa toluene or 130 kPa decane (as solvent), 8 kPa dodecane (as GC reference) and 2.8 or 4.8 MPa H_2. To investigate the inhibition of the HDS routes, 35 kPa H_2S was added to the feed. The reaction products were analyzed off-line. Each series of experiments over a fresh catalyst started with a stabilization period of at least 15 h (overnight) at the highest weight time. During two weeks of operation almost no deactivation of the catalyst was observed.

3. Results

3.1. Metal sulfides

DBT, THDBT and HHDBT react by desulfurization (DDS) reactions to hydrocarbons and by hydrogenation (HYD) and dehydrogenation (DEHYD) reactions to other sulfur-containing molecules (Scheme 1). The relatively fast HYD and DEHYD reactions made it difficult to determine from the yield–time curves if cyclohexylbenzene (CHB) and cyclohexen-1-yl-benzene (CHEB) were primary or secondary DDS products in the HDS of THDBT and HHDBT. Therefore, selectivities were calculated from the yields. Selectivities allow a better distinction between primary or secondary DDS products, because secondary and higher order products extrapolate to zero selectivity at zero space time, whereas primary products have a non-zero initial selectivity.

DBT reacted rapidly over Co–MoS_2/γ-Al_2O_3 and very rapidly over Ni–MoS_2/γ-Al_2O_3 [29] and biphenyl (BP), the product of the DDS pathway, was the main product (Fig. 1). Its (high) non-zero selectivity at space time zero shows that BP is a primary product. In addition, the intermediates THDBT and HHDBT and CHB, the final product of the HYD pathway, were observed. H_2S decreased the DBT conversion strongly, mainly due to a lowering of the DDS rate by about 23 times for Ni–MoS_2 and 6.5 times for Co–MoS_2, while the HYD rate was 4 times lower for Ni–MoS_2 and only 2 times lower for Co–MoS_2 (Table 1). As a consequence, the DDS rate constant of DBT was about 3 times higher than the HYD rate constant over Ni–MoS_2/γ-Al_2O_3 and 6 times higher over Co–MoS_2/γ-Al_2O_3. In the absence of H_2S the ratio between the DDS and HYD rate constants of DBT was even higher (about 20). Thus, the DDS pathway dominates the HDS of DBT over Ni–MoS_2/γ-Al_2O_3 and even more over Co–MoS_2/γ-Al_2O_3.

THDBT reacted fast but slower than DBT, mainly due to the slower desulfurization of THDBT than of DBT. THDBT did not react to DBT, but formed CHB, CHEB and HHDBT rapidly. All three behaved as primary products (Fig. 1) and the CHEB selectivity at $\tau = 0$ was substantial (30% for Ni–MoS_2 and 15% for Co–MoS_2), indicating that the hydrogenation of CHEB to CHB was not very fast at 3.0 MPa in the presence of THDBT. H_2S strongly decreased the DDS rate and slightly increased the HYD rate (Table 1). CHEB and HHDBT behaved as primary products at low space time and CHB as a secondary product (Fig. 2). This indicates that THDBT mainly undergoes hydrogenation to HHDBT and desulfurization to CHEB and that thereafter CHEB is hydrogenated to CHB.

HHDBT reacted fast, mainly to THDBT. The DEHYD rate constant was several times higher than the HYD rate constants of THDBT and DBT, and the DDS rate constant of HHDBT was lower than those of THDBT and DBT. A substantial amount of CHEB was observed (Fig. 1). H_2S inhibited the desulfurization of HHDBT, and hardly affected its dehydrogenation over Ni–MoS_2 and decreased it by 40% over Co–MoS_2/γ-Al_2O_3. While THDBT and CHEB behaved as primary products and CHB as a secondary product in the HDS of HHDBT over Ni–MoS_2/γ-Al_2O_3 in the presence of H_2S (Fig. 2), over Co–MoS_2/γ-Al_2O_3 both CHB and CHEB acted as secondary product and THDBT as the only primary product. This indicates that for Co–MoS_2/γ-Al_2O_3 desulfurization occurs exclusively by dehydrogenation of HHDBT to THDBT, followed by desulfurization of THDBT to produce CHEB and CHB. Over Ni–MoS_2/γ-Al_2O_3 this is

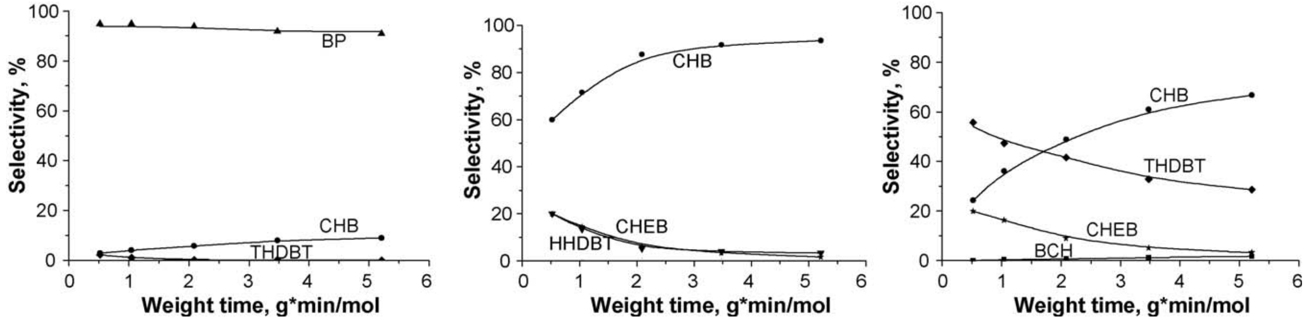


Fig. 1. Product selectivities of the HDS of DBT, THDBT and HHDBT over Ni–MoS_2/γ-Al_2O_3.

Table 1
Rate constants (in 10^{-2} kPa mol/(g min)) for the desulfurization (dds) and hydrogenation of DBT and THDBT and dds and dehydrogenation of HHDBT over Co–MoS_2/γ-Al_2O_3 and Ni–MoS_2/γ-Al_2O_3 at 300 °C and 3 MPa, without and with 35 kPa H_2S.

Catalyst		DBT	DBT	THDBT	THDBT	HHDBT	HHDBT
			H_2S		H_2S		H_2S
Co–MoS_2	dds	43	6.5	12	3	11	0
Ni–MoS_2	dds	114	5	20	2	15	2.5
Co–MoS_2	(de)hyd	2	1	6.5	9	75	45
Ni–MoS_2	(de)hyd	6	1.5	9	11	23	23

the main route for the HDS of HHDBT as well, but also some direct desulfurization of HHDBT to CHB occurred.

3.2. Noble metal catalysts

Metals are initially more active HDS catalysts than metal sulfide catalysts, but adsorb the resulting H_2S and become deactivated. To decrease the sulfur sensitivity we used the noble metals Pt and Pd, alloyed them and put them on an acidic, mesoporous NaH-ZSM-5 (M-NaH-ZSM-5) support. The powder XRD pattern of M-NaH-ZSM-5 was equal to that of ZSM-5. While NaH-ZSM-5 showed a type I isotherm, typical for microporous materials, M-NaH-ZSM-5 exhibited a type IV N_2 adsorption–desorption isotherm, typical for mesoporous materials, and a uniform pore distribution centered at around 4.9 nm was calculated from the BET isotherm of M-NaH-ZSM-5. The BET surface area and mesoporous volume of M-NaH-ZSM-5 were 579 m^2/g and 0.44 cm^3/g, respectively, much higher than those of NaH-ZSM-5 (375 m^2/g and 0.09 cm^3/g).

The rate of the reaction of benzene with benzylalcohol was more than 20 times higher over M-H-ZSM-5 than over H-ZSM-5 [27]. The alleviation of the diffusion limitation confirms the presence of mesopores in M-NaH-ZSM-5. The acidity of M-NaH-ZSM-5 was determined by means of the isomerization of 2-methyl-2-pentene [30]. The higher the molar ratio of 3-methyl-2-pentene (obtained by methyl shift) to 4-methyl-2-pentene (obtained by H shift) in the product isomers is, the stronger the acidity is. M-NaH-ZSM-5 not only had a higher conversion of 2-methyl-2-pentene than NaH-ZSM-5, due to its higher BET area, but also a high 3-methyl-2-pentene to 4-methyl-2-pentene ratio, much higher than γ-Al_2O_3, showing that M-NaH-ZSM-5 possesses relatively strong acidic sites.

The main products for Pt/M-NaH-ZSM-5 were 3,3′-DMCHB and 3,3′-DMBCH. Also (3-methylphenyl)(3′-methylcyclopentyl)-methane isomers were observed, probably due to acid-catalyzed 6- to 5-ring isomerization of the dimethyl-cyclohexenylbenzene intermediate [26]. 3,3′-DMBP had a low and constant selectivity throughout the reaction, indicating that 3,3′-DMBP did not hydrogenate further. The selectivities of 4,6-DM-THDBT and 4,6-DM-HHDBT were low at high space time, showing that these intermediates can be easily desulfurized. For Pt/NaH-ZSM-5, the same sulfur-containing intermediates and hydrocarbons were observed as over Pt/M-NaH-ZSM-5, but at lower concentrations. Just as for the Pt catalysts, Pd/M-NaH-ZSM-5 exhibited much higher catalytic activity than Pd/NaH-ZSM-5, proving that mesoporosity of the support plays a positive role in sulfur removal. Even compared with Pd/γ-Al_2O_3, Pd/M-NaH-ZSM-5 showed much higher HDS activity although it had a much lower metal dispersion (25 versus 73%), further revealing that acidity was beneficial for enhancing the HDS activity.

The bimetallic Pt–Pd/M-NaH-ZSM-5 catalyst was much more active than the monometallic Pt and Pd catalysts, proving that a chemical synergism between the noble metals was present and alloying had taken place. HDS conversion for Pt–Pd/M-NaH-ZSM-5 reached 73% at low weight time, but only 3% for Pt–Pd/NaH-ZSM-5 and 46% for Pt–Pd/γ-Al_2O_3. The sulfur removal was 2 times higher than that of Pt–Pd/γ-Al_2O_3 and 24 times higher than that for Pt–Pd/NaH-ZSM-5.

4. Discussion

4.1. Mechanism of hydrodesulfurization

The breaking of a C–S bond may take place by elimination or by hydrogenolysis [2]. Elimination involves the breaking of the α-C–S bond and a β-C–H bond and leads to the formation of an alkene. In the hydrogenolysis reaction, a C–S bond is broken and C–H and S–H bonds are formed simultaneously and an alkane is formed. Aliphatic thiols can react by elimination as well as by hydrogenolysis, as demonstrated by experimental [31,32] and theoretical studies [33,34] of the HDS of methanethiol to methane and of ethanethiol to ethene and ethane over metal sulfide catalysts.

Arylthiols seem to undergo a direct C–S bond breaking, e.g., the HDS of thiophenol leads exclusively to benzene [10,35] and the HDS of DBT leads mainly to BP. If aryl C–S bond breaking would take place by elimination, then a phenyl ring must first be hydrogenated to create a β-H atom. For DBT, a dihydro intermediate was therefore proposed [4,6,7,36], but this intermediate seems highly unlikely. It would lead to much higher activation energy than experimentally observed. Also, the hydrogenation of the double bond requires π adsorption, which cannot explain why methyl groups in the 4 and 6 positions constitute a steric problem in the DDS route of the HDS of 4,6-DMDBT. Therefore the DDS reaction is most likely a real hydrogenolysis reaction, in which thiophenol or DBT and hydrogen atoms on the catalyst surface react directly to benzene or BP, respectively. A DFT calculation of the HDS of DBT showed that the hydrogenolysis of the C–S bonds has a relatively low activation energy [37]. The two aryl C–S bonds of DBT will break in two steps, first forming

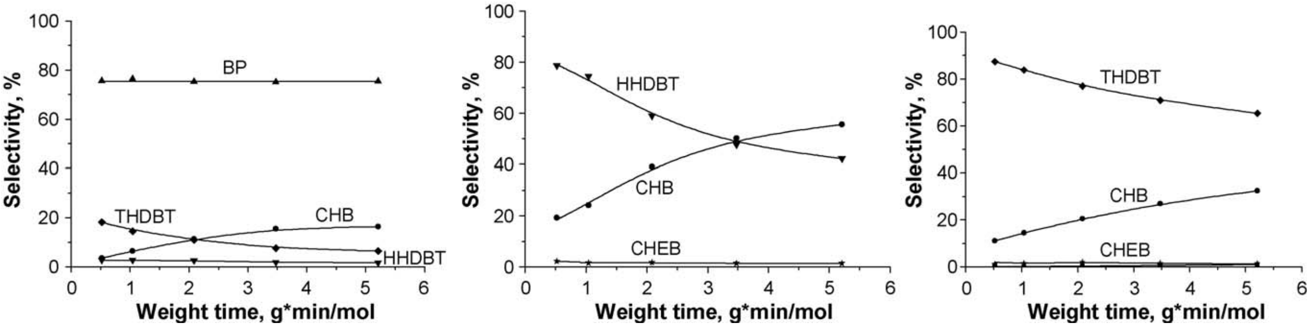
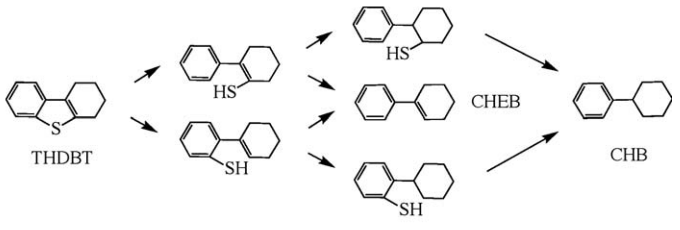
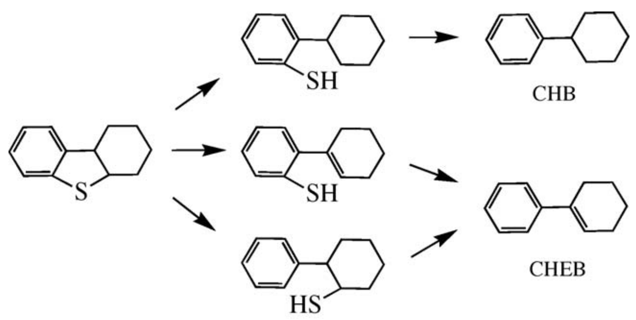


Fig. 2. Product selectivities of the HDS of DBT, THDBT and HHDBT over Ni–MoS_2/γ-Al_2O_3 in the presence of 35 kPa H_2S.



Scheme 2. Possible reactions of THDBT to CHEB and CHB.



Scheme 3. Possible reactions of HHDBT to CHEB and CHB.

2-phenyl-thiophenol and then BP. The very fast HDS reaction of thiophenol [10] explains why this intermediate has never been observed.

The hydrogenated intermediate THDBT reacted by desulfurization to CHEB and CHB. CHEB behaved as primary product in the absence as well as presence of H_2S, with increasing selectivity at decreasing space time, while CHB decreased with decreasing space time as if it was a secondary product, but extrapolated to a non-zero selectivity at $\tau = 0$ as if it was a primary product (Figs. 1 and 2). Probably THDBT reacts to CHB by a primary as well as by a secondary reaction. The secondary reaction would go through CHEB as the intermediate, which would explain why the CHEB selectivity decreases and the CHB selectivity increases with increasing weight time. Another explanation would be that CHB is only formed by a secondary reaction from CHEB. In that case CHEB must react very fast to CHB in the pores of the catalyst, so that even at short space time a non-zero CHB concentration is observed at the exit of the reactor. This explanation does not seem likely, because the sum of CHEB and HHDBT does not seem to approach 100% with decreasing space time (Figs. 1 and 2).

The reaction of THDBT to CHEB may occur by hydrogenolysis of the aryl C–S bond to form 2-phenyl-cyclohexene-1-thiol or of the vinyl C–S bond to form 2-(cyclohexen-1-yl)-thiophenol (Scheme 2). If the C–S bond breaking is followed by another C–S bond hydrogenolysis then CHEB is formed. It is also possible that first hydrogenation takes place to 2-phenyl-cyclohexanethiol or 2-cyclohexyl-thiophenol, which then hydrogenolyses to CHB.

When HHDBT was used as reactant, CHEB behaved as a primary product. In the presence of H_2S the CHEB selectivity was very low and also that of CHB approached zero. This indicates that HHDBT reacts mainly to THDBT in the presence of H_2S. CHB behaved as a secondary product, with a selectivity that decreased to low or even zero values with decreasing space time, indicating that a direct formation of CHB from HHDBT is not very important or does not occur at all. CHB might be formed by fast reaction of HHDBT to THDBT to CHB. The HDS of THDBT showed that THDBT reacted via CHEB to CHB, CHEB can behave as the exclusive primary product and CHB can behave as a secondary product.

The formation of CHEB suggests that an elimination reaction occurs in the desulfurization of HHDBT. If the cycloalkyl C–S bond is broken first, HHDBT can convert to 2-cyclohexyl-thiophenol by hydrogenolysis and to 2-cyclohexen-1-yl-thiophenol by elimination (Scheme 3). If the aryl C–S bond is broken first, it can only be broken by hydrogenolysis and then 2-phenyl-cyclohexanethiol is formed. A DFT calculation of the desulfurization of dihydrobenzothiophene over a Mo_3S_9 cluster showed that the hydrogenolysis of the aryl C–S bond in dihydrobenzothiophene has a lower activation energy than the breaking of the alkyl C–S bond [38]. Because of the similarity of HHDBT to dihydrobenzothiophene, with one part of the molecule being aromatic and the other part aliphatic, the desulfurization of HHDBT may well take place by hydrogenolysis of the aryl C–S bond, followed by elimination of H_2S from the resulting 2-phenyl-cyclohexanethiol to form CHEB (Scheme 3).

4.2. *Noble metals on mesoporous zeolites*

The same sulfur-containing intermediates (4,6-DM-THDBT and 4,6-DM-HHDBT) and final products (3,3′-DMCHB, 3,3′-DMBCH and 3,3′-DMBP) were produced in the HDS of 4,6-DMDBT over Pt and Pd catalysts (Fig. 3) as over metal sulfides [9], but the reaction rates were different. Hydrogenation and dehydrogenation were relatively faster and C–S bond breaking relatively slower over Pt and Pd catalysts than over metal sulfide catalysts. As a consequence, all sulfur-containing intermediates were observed, independent of the reactant (4,6-DMDBT, 4,6-DM-THDBT or 4,6-DM-HHDBT) and also 4,6-DMDBT was observed when 4,6-DM-THDBT or 4,6-DM-HHDBT was used as reactant [13].

The same sulfur-containing intermediates and hydrocarbons were observed over Pt/NaH-ZSM-5 as over Pt/M-NaH-ZSM-5, but at lower concentrations, indicating that more active sites were accessible in Pt/M-NaH-ZSM-5 due to the existence of mesopores, although the Pt dispersion was about equal in Pt/NaH-ZSM-5 and Pt/M-NaH-ZSM-5 (35 and 37%). Pt/γ-Al_2O_3 had a lower HDS activity than Pt/M-NaH-ZSM-5, although it possessed mesoporosity and a higher Pt dispersion (74%) than Pt/M-NaH-ZSM-5. This demonstrates that support acidity is more important for the HDS

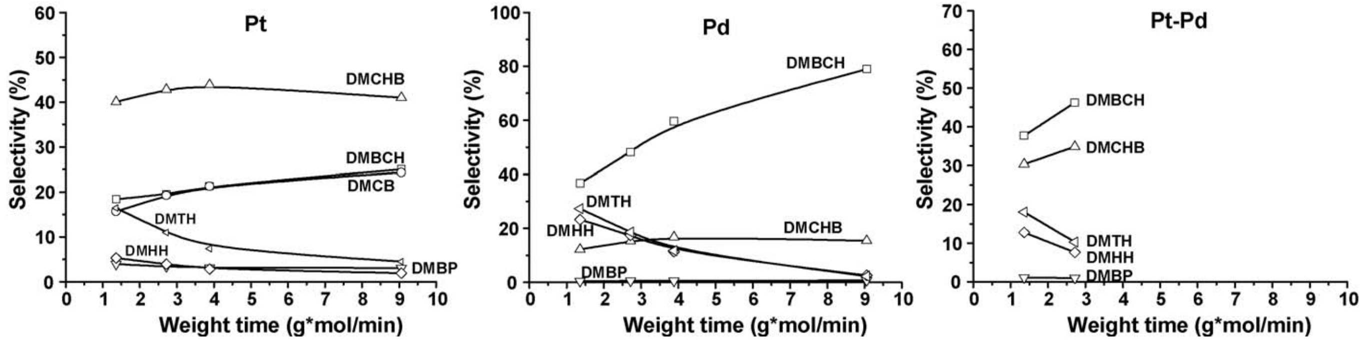


Fig. 3. Product selectivities of the HDS of DMDBT over Pt, Pd and Pt–Pd catalysts supported on mesoporous zeolite NaH-ZSM-5.

activity than metal dispersion. The same effects were observed for the Pd catalysts. Therefore, the combination of mesoporosity and acidity is the best way to promote sulfur removal. The superior HDS activity is attributed to the catalytically active sites on the noble metal catalyst particles in the mesopores of the mesoporous ZSM-5. The metal particles are not only accessible, but also promoted by the strong acidity of the zeolitic support.

5. Conclusions

The desulfurization of DBT at 300 °C was faster than that of THDBT and HHDBT over Co–MoS_2/γ-Al_2O_3 and Ni–MoS_2/γ-Al_2O_3. Desulfurization of THDBT occurred directly to CHEB and CHB, but desulfurization of HHDBT occurred mainly by dehydrogenation to THDBT and subsequent desulfurization of THDBT. In most cases C–S bond breaking occurred by hydrogenolysis.

Mesoporous zeolites are very good supports for noble metals and make them much more active HDS catalysts than noble metals on normal zeolites, alumina or ASA. Noble metals on mesoporous zeolites might be considered as catalysts in the second stage of a deep HDS process.

References

[1] D.D. Whitehurst, T. Isoda, I. Mochida, Adv. Catal. 42 (1998) 345.
[2] R. Prins, in: G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp (Eds.), 2nd ed., Handbook of Heterogeneous Catalysis, vol. 6, Wiley-VCH, Weinheim, 2008, p. 2695.
[3] T. Kabe, A. Ishihara, H. Tajima, Ind. Eng. Chem. Res. 31 (1992) 1577.
[4] V. Meille, E. Schulz, M. Lemaire, M. Vrinat, J. Catal. 170 (1997) 29.
[5] T. Kabe, A. Ishihara, Q. Zhang, Appl. Catal. A 97 (1993) L1.
[6] F. Bataille, J.L. Lemberton, P. Michaud, G. Pérot, M. Vrinat, M. Lemaire, E. Schulz, M. Breysse, S. Kasztelan, J. Catal. 191 (2000) 409.
[7] M. Macaud, A. Milenkovic, E. Schulz, M. Lemaire, M. Vrinat, J. Catal. 193 (2000) 255.
[8] M. Egorova, R. Prins, J. Catal. 225 (2004) 417.
[9] X. Li, A. Wang, M. Egorova, R. Prins, J. Catal. 250 (2007) 283.
[10] H. Wang, R. Prins, J. Catal. 258 (2008) 153.
[11] S.D. Lin, M.A. Vannice, J. Catal. 143 (1993) 539.
[12] L.J. Simon, J.G. van Ommen, A. Jentys, J.A. Lercher, J. Phys. Chem. B 104 (2000) 11644.
[13] A. Niquille-Röthlisberger, R. Prins, J. Catal. 242 (2006) 207.
[14] Y. Yoshimura, M. Toba, T. Matsui, M. Harada, Y. Ichihashi, K.K. Bando, H. Yasuda, H. Ishihara, Y. Morita, T. Kameoka, Appl. Catal. 322 (2007) 152.
[15] T. Matsui, M. Harada, M. Toba, Y. Yoshimura, Appl. Catal. A 293 (2005) 137.
[16] W. Robinson, J.A.R. van Veen, V.H.J. de Beer, R.A. van Santen, Fuel Process. Technol. 61 (1999) 103.
[17] H.R. Reinhoudt, R. Troost, A.D. van Langeveld, J.A.R. van Veen, S.T. Sie, J.A. Moulijn, Stud. Surf. Sci. Catal. 127 (1999) 251.
[18] F. Bataille, J.L. Lemberton, G. Perot, P. Leyrit, T. Cseri, N. Marchal, S. Kasztelan, Appl. Catal. A 220 (2001) 191.
[19] A. Niquille-Röthlisberger, R. Prins, Catal. Today 123 (2007) 198.
[20] P. Gallezot, Catal. Rev. Sci. Eng. 20 (1979) 121.
[21] W.M.H. Sachtler, A.Y. Stakheev, Catal. Today 12 (1992) 283.
[22] B.H. Cooper, B.B.L. Donnis, Appl. Catal. A 137 (1996) 203.
[23] F.-S. Xiao, L. Wang, C. Yin, K. Lin, Y. Di, R. Xu, D.S. Su, R. Schlögl, T. Yokoi, T. Tatsumi, Angew. Chem. Int. Ed. 45 (2006) 3090.
[24] M. Choi, H. Cho, R. Srivastava, C. Venkatesan, D. Choi, R. Ryoo, Nat. Mater. 5 (2006) 718.
[25] H. Wang, T.J. Pinnavaia, Angew. Chem. Int. Ed. 45 (2006) 7603.
[26] Y. Sun, R. Prins, Angew. Chem. Int. Ed. 47 (2008) 8478.
[27] Y. Sun, R. Prins, Appl. Catal. A 336 (2008) 11.
[28] J.C. DiCesare, L.B. Thompson, R.J. Andersen, J. Nail, J. Org. Prep. Proceed. Int. 32 (2000) 169.
[29] H. Wang, R. Prins, J. Catal. 264 (2009) 31.
[30] G.M. Kramer, G.B. McVicker, Acc. Chem. Res. 19 (1986) 78.
[31] R.L. Wilson, C. Kemball, J. Catal. 3 (1964) 426.
[32] P. Kieran, C. Kemball, J. Catal. 4 (1965) 380.
[33] T. Todorova, R. Prins, Th. Weber, J. Catal. 236 (2005) 190.
[34] T. Todorova, R. Prins, Th. Weber, J. Catal. 246 (2007) 109.
[35] H. Schulz, M. Schon, N.M. Rahman, Stud. Surf. Sci. Catal. 27 (1986) 201.
[36] G.H. Singhal, R.L. Espino, J.E. Sobel, J. Catal. 67 (1981) 446.
[37] Th. Weber, J.A.R. van Veen, Catal. Today 130 (2008) 170.
[38] X.Q. Yao, Y.W. Li, H. Jiao, J. Mol. Struct. THEOCHEM 726 (2005) 67.