Catalytic activity of exfoliated MoS$_2$ in hydrodesulfurization, hydrodenitrogenation and hydrogenation reactions

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The activity of exfoliated MoS$_2$ in the hydrodesulfurization (HDS) of dibenzothiophene, the hydrodenitrogenation (HDN) of carbazole and the hydrogenation of naphthalene has been determined. The catalytic activity was compared to MoS$_2$ prepared by the decomposition of molybdenum naphthenate (MoNaph). Exfoliated MoS$_2$ was found to give better overall HDS activity compared to MoNaph derived MoS$_2$ catalyst, whereas MoNaph derived MoS$_2$ was found to give higher hydrogenation and HDN activity. These results are discussed in terms of the morphology of the two catalysts. The relative activity of the two catalysts in the hydrotreating reactions is shown to be different to that obtained during Cold Lake bitumen hydrocracking.

KEY WORDS: exfoliated MoS$_2$; catalyst; hydrodesulfurization; hydrodenitrogenation; hydrogenation

1. Introduction

MoS$_2$ supported on γ-Al$_2$O$_3$ and promoted with Co or Ni is widely used as a catalyst in petroleum hydro-processing. Model catalyst studies using unsupported MoS$_2$ to eliminate support or promoter effects [1–4] in hydrodesulfurization [1,2,4–7] have been reported. Unsupported MoS$_2$ is also an important catalyst in heavy oil hydrocracking [8]. The effects of rapid catalyst deactivation by coke and metals deposition during hydrocracking can be minimized by performing the reaction in a slurry reactor using small particles of MoS$_2$ dispersed in the heavy oil [8–11]. High levels of catalyst dispersion, and hence activity, can usually be achieved by introducing water- or oil-soluble catalyst precursors to the feed that decompose and form the active metal sulfide *in situ* [12].

The activity of MoS$_2$ in both hydroprocessing and hydrotreating reactions is dependent upon the morphology of the catalyst and a number of studies have reported on structure-activity relationships for MoS$_2$ catalysts [13–15]. In previous work, we investigated exfoliated MoS$_2$ as a catalyst for Cold Lake bitumen hydrocracking in the slurry phase [16]. Bulk MoS$_2$ was exfoliated into single layer platelets held in suspension using a modified version of the method reported by Joensen *et al.* [17]. The study showed that exfoliated MoS$_2$ had a low coke yield that was comparable to MoS$_2$ prepared by *in situ* decomposition of molybdenum naphthenate (MoNaph) [16]. Furthermore, the exfoliated MoS$_2$ had significantly higher activity for nitrogen and metals removal, as well as microcarbon

residue (MCR) conversion compared to the MoS$_2$ derived from MoNaph [16].

Del Valle *et al.* [18] reported a 3.5-fold increase in thiophene HDS activity of exfoliated MoS$_2$ compared to crystalline MoS$_2$. It was suggested that the increase in catalyst activity was due to the increase in catalytically active edge sites generated by exfoliation. Recently, the exfoliation method was also used to prepare single layered MoS$_2$ supported on alumina. The exfoliated catalyst was compared with MoS$_2$/Al$_2$O$_3$, prepared by wet impregnation, for the HDS of thiophene and tetrahydrothiophene [19]. With the same Mo loading, similar activity and selectivity were observed. A similar conclusion was made by Kochubey *et al.* [20]. Bockrath and Parfitt [21,22] tested the hydrogenation (HYD) activity of exfoliated MoS$_2$ catalysts in coal liquefaction and residue upgrading [21,22]. For Hondo residue upgrading, no significant difference in hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) activity between the exfoliated and original MoS$_2$ was observed [21].

In the present study we have extended the comparison between exfoliated MoS$_2$ and dispersed MoS$_2$ prepared by decomposition of molybdenum naphthenate, and have determined the activity of both catalysts for hydrodesulfurization (HDS), hydrodenitrogenation (HDN) and hydrogenation (HYD) reactions separately, using single model reactants. The results are compared to data obtained previously [16] on the same catalysts during Cold Lake bitumen hydrocracking.

2. Experimental

The catalysts used herein were characterized by BET specific surface area, X-ray diffraction, energy dispersive

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X-ray emission and transmission electron microscopy. Characterization procedures have been reported in detail elsewhere [23,24].

Dispersed MoS_2 was prepared by *in situ* decomposition of molybdenum naphthenate (ICN Biomedicals Inc.). The molybdenum naphthenate (MoNaph) was mixed with the reactant and *n*-hexadecane solvent, and placed in the reactor described below. The reactor was heated to 350 °C in an $H_2(95\%)/H_2S(5\%)$ atmosphere and during this period MoS_2 was produced *in situ* by the decomposition of the MoNaph and reaction with H_2S.

Exfoliated catalyst was prepared under argon atmosphere in a glove box using a modified method of Joensen *et al.* [17]. MoS_2 powder was soaked in hexane containing *n*-butyllithium in excess (Li : Mo ratio > 1). The suspension was sealed in a sample bottle and left to stand for at least 72 h so that all the Li was intercalated into the MoS_2. The intercalated MoS_2 settled to the bottom and the top layer of solution was decanted. The Li-intercalated MoS_2 was subsequently exposed to water and sonicated for 30 min followed by 30 min of stirring. Excess *n*-butyllithium was removed by a series of washing steps in which the exfoliated MoS_2 was separated by centrifuge and re-dispersed in water. The washing process was repeated until the solution pH reached 7. Finally, the washing process was repeated three more times, replacing water with isopropanol and isopropanol with decalin. The exfoliated MoS_2 dispersion was adjusted to 2 wt% of MoS_2 dispersed in decalin.

Reactions were carried out in a 300 mL Autoclave Engineers stirred, batch reactor loaded with 100 mL of *n*-hexadecane and 600 ppmw Mo equivalent of the MoS_2 catalyst. An amount of the single model reactant was mixed with the *n*-hexadecane solvent for each reaction to yield 0.5 wt% dibenzothiophene (DBT) for HDS, 0.26 wt% carbazole for HDN and 10 wt% naphthalene for the hydrogenation reaction. The reactor was pressurized with $H_2(95\%)/H_2S(5\%)$ to 2.8 MPa at room temperature and stirred at 1200 rpm, and then heated at a rate of 10 °C/min to the desired reaction temperature (325–375 °C). The reaction proceeded at this temperature for 5 h. During the reaction, liquid samples (3–5 mL) were withdrawn at 30 min intervals for the first 2 h then at 1 h intervals for the remaining 3 h. After reaction, the solids present in the reactor were recovered by filtration, washed with pentane, vacuum dried for 3 h at 100 °C and dried further at 160 °C for 2 h before characterization.

Liquid samples were analyzed with a Shimadzu gas chromatograph (model GC-14A) using a flame ionization detector (FID) fitted with a capillary column (AT-5, 30 m×0.32 mm×0.25 μm) operating at an initial temperature of 60 °C, ramping to 170 °C at 5 °C/min, followed by 10 °C/min to 280 °C. The identities of the products were determined by comparison with pure reference samples and by GC/MS analysis of selected liquid samples. The carbon mole balance for all experiments was within ±5%. The calculations of conversion (100×((initial−residual)/initial concentration) of dibenzothiophene, carbazole, and naphthalene were based on product analysis, assuming a 100% mole balance. Furthermore, the activity for each reaction was calculated using the following definitions:

HDS, % = 100×(moles of desulfurized product)/(initial moles of DBT)

HDN, % = 100×(moles of denitrogenated product)/(initial moles of carbazole)

HYD, % = 100×(moles of hydrogenated product)/(initial moles of naphthalene)

3. Results and discussion

The properties of the two MoS_2 catalysts studied in the present work are summarized in table 1. The data show that the morphology of the exfoliated MoS_2 was very different to the MoS_2 obtained from decomposition of the molybdenum naphthenate. The exfoliated MoS_2 had an average nine layers of MoS_2 in a large sheet morphology (0.40 μm) compared to the MoS_2 derived from MoNaph that had a slab length of approximately 10 nm with 1 to 2 layers of MoS_2 in the crystallites. Consequently, the fraction of Mo atoms on the edge planes of the MoS_2 crystallites was calculated as 0.3% in the case of the exfoliated MoS_2 and 9.7% in the case of the MoS_2 derived from MoNaph.

3.1. HDS of dibenzothiophene

Table 2 compares the HDS activity of the exfoliated MoS_2 catalyst with the MoS_2 prepared by the decomposition of molybdenum naphthenate, and figure 1

Table 1
Characterization of exfoliated MoS_2 and MoNaph derived MoS_2

Catalyst	BET specific surface area, m²/g	Slab length[+], nm	Stack height[++], nm	Number of layers
Exfoliated MoS₂	7.8	400	5.5	9
MoNaph derived MoS₂	253	10	1.8 (0.8*)	2.8 (1.3*)

[+] Slab length: lateral dimension of MoS_2 particle, determined from XRD.
[++] Stack height: MoS_2 particle size perpendicular to (002) plane, determined from XRD.
*Determined from TEM [23, 24].

Table 2
Comparison of the catalytic activity of exfoliated MoS$_2$ and MoS$_2$ prepared from MoNaph, at 350 °C and 2.8 MPa after 5 h reaction

	Exfoliated MoS$_2$	MoS$_2$ prepared from MoNaph
Dibenzothiophene		
Conversion, %	35.3	15.9
HDS, %	25.8	3.3
k, mL/(g Mo s)	7.24 ± 1.32	2.94 ± 0.64
E_{app}, kJ/mol	186	149
Carbazole		
Conversion, %	32.6	37.7
HDN, %	20.4	30.4
k, mL/(g Mo s)$\times 10^2$	7.57 ± 0.42	8.92 ± 0.37
E_{app}, kJ/mol	83	51
Naphthalene		
Conversion, %	27.0	35.8
k, mL/(g Mo s)$\times 10^2$	5.74 ± 0.96	7.68 ± 1.20
E_{app}, kJ/mol	99	86

E_{app}: Apparent activation energy with error ±10%.
k: rate constant with 95% confidence limit.

compares the HDS activity as a function of dibenzothiophene (DBT) conversion obtained over the two catalysts. After 5 h reaction at 350 °C, the DBT conversions were 35.3% and 15.9% on the exfoliated MoS$_2$ and the MoNaph derived MoS$_2$, respectively. The HDS activity was higher on the exfoliated MoS$_2$ compared to the MoS$_2$ prepared from MoNaph over a range of DBT conversions (figure 1). Furthermore, the first order rate constant k, mL/(g Mo s) for DBT conversion and the estimated apparent activation energy of the rate constant, were higher on the exfoliated MoS$_2$ catalyst than on the MoS$_2$ derived from MoNaph.

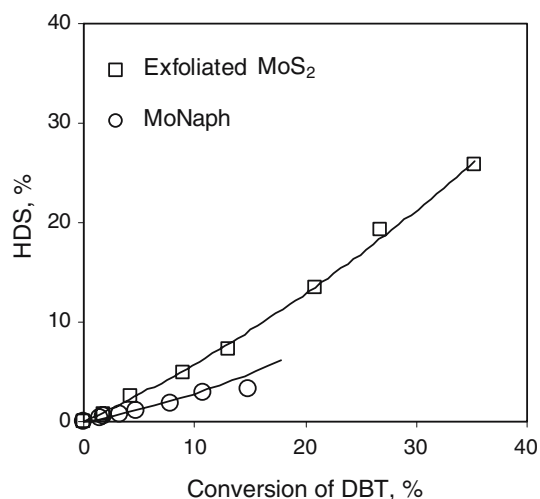The products of DBT reaction were tetrahydrodibenzothiophene (THDBT), biphenyl (BP), cyclohexyl-

Figure 1. HDS versus conversion of DBT for exfoliated MoS$_2$ and MoNaph derived MoS$_2$ at 350 °C and 2.8 MPa. (HDS, %: 100×(moles of desulfurized product)/(initial moles of DBT); — trend line.

benzene (CHB), and bicyclohexyl (BCH) as shown in figure 2. Biphenyl (BP) is a product of direct desulfurization (DDS) of DBT whereas THDBT, CHB and BCH are products of hydrogenation. The product distributions for the two catalysts are compared as a function of DBT conversion in figure 3.

The products with exfoliated MoS$_2$ were BP, THDBT, CHB and BCH, with BP being greater than THDBT over the range of conversions. The major product with MoS$_2$ derived from MoNaph, was THDBT, with BP and CHB being produced in much lower quantities. These data show that MoS$_2$ derived from MoNaph favors the HDS of DBT through the hydrogenation of one of the DBT rings to yield THDBT, followed by hydrogenolysis, whereas on the exfoliated MoS$_2$, HDS of DBT proceeded through both the direct desulfurization and the hydrogenation routes.

3.2. HDN of carbazole

The activities of exfoliated MoS$_2$ and the MoS$_2$ derived from MoNaph for the HDN of carbazole are compared in table 2 and figures 4 and 5. After 5 h reaction at 350 °C, the MoNaph derived MoS$_2$ gave a higher carbazole conversion (37.7%) and HDN (mole % defined as the total mole of denitrogenated products divided by total mole of carbazole fed to the reactor) (30.4%) compared to the exfoliated MoS$_2$ (32.6% and 20.4%, respectively). The estimated apparent activation energy for the carbazole conversion first order rate constant was also significantly lower on the MoNaph derived MoS$_2$ (51 kJ/mol) compared to that obtained on the exfoliated MoS$_2$ (83 kJ/mol).

The product yields as a function of carbazole conversion are reported in figure 5 for both catalysts and the data show that both catalysts had a similar trend in product yield versus carbazole conversion. The overall reaction pathway for HDN of carbazole proposed by Nagai *et al.* [25,26] is shown in the simplified reaction scheme of figure 6. The hydrogenated nitrogen product tetrahydrocarbazole (THCBZ) was detected in significant quantities. Successive hydrogenated carbazole compounds such as hexahydrocarbazole, octahydrocarbazole and perhydrocarbazole were not detected under the current operating conditions due to their high reactivity, in agreement with the work of Nagai *et al.* [25]. The denitrogenation products are cyclohexylbenzene (CHB), cyclohexyl-cyclohexene (CHCHe) and bicyclohexyl (BCH). In addition, there were some side reactions such as isomerization of BCH to hexyl-cyclohexane (HCH) and cyclopentylmethyl-cyclohexane (CPMCH). Hydrocracking of one of the saturated rings in BCH resulted in the formation of HCH. These isomerization products were also reported in HDN of carbazole over bulk molybdenum carbide in the presence of 50 ppm sulfur in the feed at 360 °C and 6 MPa [27].
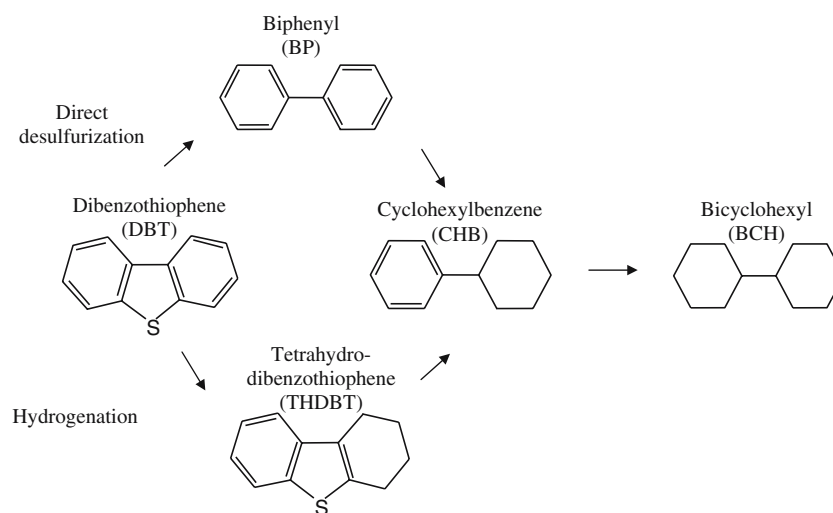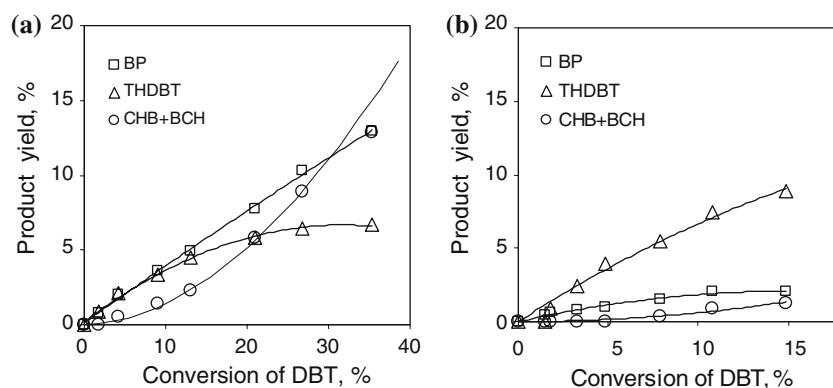
Figure 2. Reaction network of dibenzothiophene.

Figure 3. Product yield versus conversion of DBT at 350 °C and 2.8 MPa for (a) exfoliated MoS₂ and (b) MoNaph derived MoS₂ (product yield, %: $100\times$(the mole of product divided by initial moles of DBT)); — trend line.

After a 5 h batch reaction at 350 °C over MoNaph derived MoS₂, the major products obtained were HCH (11 mol%) and CPMCH (10 mol%), followed by THCBZ (9 mol%), BCH (6 mol%), CHB (1 mol%) and CHCHe (1 mol%). For HDN of carbazole over the exfoliated MoS₂, the products obtained after 5 h reaction were in order THCBZ (13 mol%), CPMCH (7 mol%), HCH (6 mol%), BCH (5 mol%), CHB (2 mol%) and CHCHe (1 mol%). Note that biphenyl (BP) was not detected in the reaction products and a similar observation has been made over Mo₂C catalyst [27], and nitrided and sulfided Mo/Al₂O₃ [28,29]. The mechanism in figure 6 shows that the hydrogenation of carbazole is required before C–N bond hydrogenolysis can occur regardless of the type of catalyst. Direct de-nitrogenation through hydrogenolysis was not observed with carbazole over the two MoS₂ catalysts.

3.3. Hydrogenation of naphthalene

Naphthalene is hydrogenated to tetralin and decalin, sequentially. Table 2 summarizes the results of naphthalene hydrogenation using exfoliated MoS₂ and MoS₂ derived from MoNaph. The MoS₂ derived from MoNaph gave a higher conversion (35.8%) after 5 h reaction at 350 °C compared to the exfoliated MoS₂ (27.0%). Similarly the first order rate constant for naphthalene conversion was greater on the MoS₂ derived from MoNaph (7.7×10^{-2} mL/g Mo s) compared to the exfoliated MoS₂ (5.7×10^{-2} mL/g Mo s). Both catalysts produced tetralin with little decalin (<1 mol%) (figure 7).

MoS₂ derived from MoNaph had been previously reported for the hydrogenation of naphthalene in the presence of sulfur, with high concentration of catalyst (3000 ppm Mo) and reaction conditions relevant to coal liquefaction (380 °C, 18.6 MPa) in a batch micro-reactor [30]. It was reported that MoNaph derived MoS₂ promoted partial saturation of the multiring aromatic to hydroaromatic species but did not promote further saturation. The catalytic reaction using MoNaph derived MoS₂ produced nearly complete naphthalene conversion, yielding tetralin as the primary product (92%) and a small amount of decalin (5%) compared to
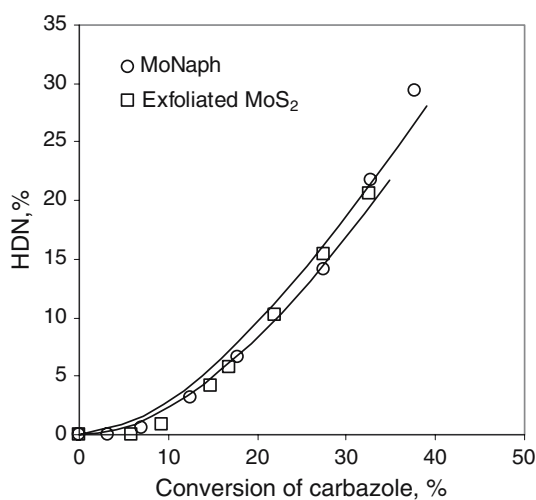
Figure 4. HDN as a function of carbazole conversion at 350 °C and 2.8 MPa. (HDN, % : 100×(moles of denitrogenated product)/(initial moles of carbazole)); — trend line.

Ni–MoS$_2$/Al$_2$O$_3$ that produced 9.5% tetralin and 86.6% of decalin [30]. The results with MoS$_2$ derived from MoNaph are in agreement with the results from the present study.

3.4. Catalyst comparison

The performance of the MoNaph derived MoS$_2$ and that of the exfoliated MoS$_2$ in HDS, HDN and hydrogenation reactions using single model reactants, shows that the MoS$_2$ derived from MoNaph had at 350 °C a slightly higher activity for hydrogenation reactions compared to the exfoliated MoS$_2$. The naphthalene conversion was higher on the MoNaph derived catalyst than the exfoliated MoS$_2$ and the same trend was observed in the HDN of carbazole. In the latter case, C–N hydrogenolysis only occurred after hydrogenation of an aromatic ring and since the hydrogenation reaction was favored on the MoNaph derived MoS$_2$, HDN

conversion was higher on this catalyst compared to the exfoliated MoS$_2$.

The exfoliated MoS$_2$, however, had a significantly higher HDS of DBT activity than the MoS$_2$ derived from MoNaph. DBT conversion occurs through two parallel reaction paths: direct desulfurization or hydrogenation of the aromatic ring followed by C–S hydrogenolysis. Since the exfoliated MoS$_2$ had a high activity for the direct desulfurization of DBT to yield BP, compared to the MoNaph derived MoS$_2$ that yielded THDBT, the former catalyst had overall higher HDS activity. Although carbazole has the same skeletal structure as DBT, nitrogen removal only occurs after at least one of the adjacent rings has been hydrogenated.

The comparison of the same catalysts for Cold Lake bitumen hydrocracking at 415 °C and 600 ppmw Mo has been reported previously [16]. In [16], exfoliated MoS$_2$, dispersed in water rather than decalin, had a higher removal of S, N, MCR (microcarbon in the residue) and asphaltenes, than the MoS$_2$ derived from MoNaph. The effect of dispersing solvent on the exfoliated MoS$_2$ in Cold Lake bitumen hydrocracking was also examined previously, at a Mo concentration of 900 ppmw [16]. A higher S, N and asphaltene removal was obtained when the exfoliated MoS$_2$ was dispersed in decalin rather than water. Consequently, we can conclude that exfoliated MoS$_2$ dispersed in decalin would give better performance in Cold Lake bitumen hydrocracking at 415 °C and 600 ppmw Mo, than MoNaph derived MoS$_2$. In hydrocracking, catalyst performance is associated with the ability of the catalyst to transfer hydrogen to prevent condensation among carbon radicals.

The performance of the exfoliated MoS$_2$ is associated with its morphology. In the case of single model compound reactants, the difference in catalyst performance follows previous suggestions that the hydrogenation occurs preferentially on rim-edge sites [1]. Knowing the crystallite dimensions (table 1) the fraction of rim or edge sites can be calculated using the geometric
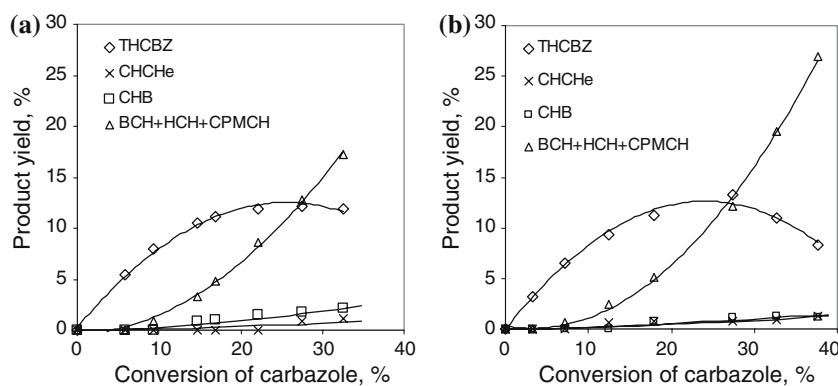

Figure 5. Products yield versus conversion of carbazole at 350 °C and 2.8 MPa for (a) exfoliated MoS$_2$, and (b) MoNaph derived MoS$_2$ (product yield %: 100×(the mole of product divided by initial moles of carbazole)); — trend line.
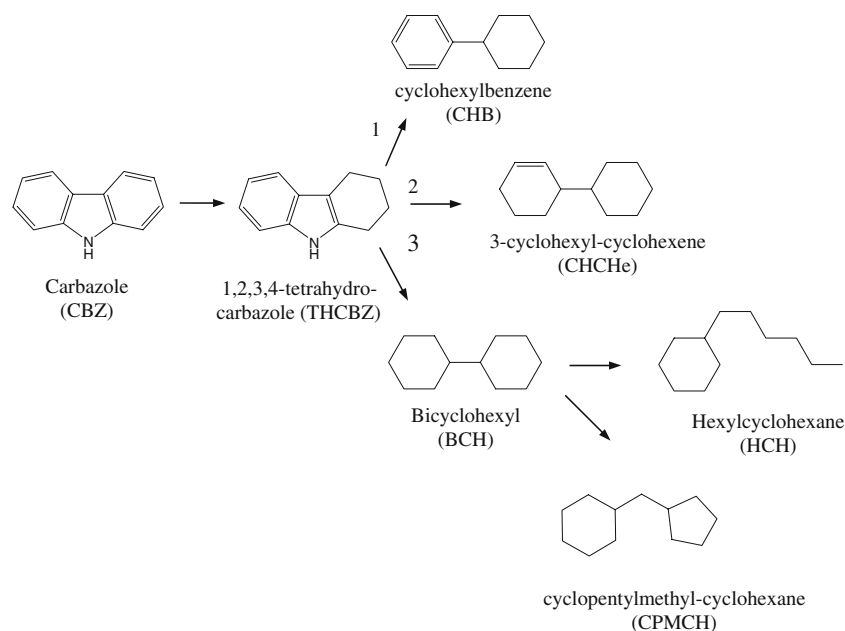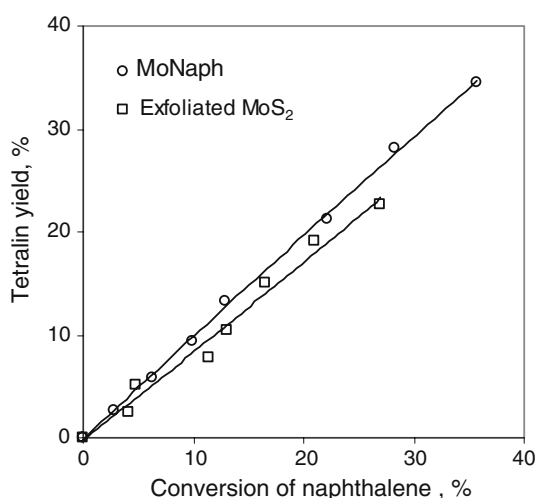
Figure 6. Simplified reaction network for carbazole.

Figure 7. Tetralin yield versus conversion of naphthalene at 350 °C and 2.8 MPa for exfoliated MoS₂, and MoNaph derived MoS₂ (tetralin yield, %: $100 \times$(the mole of tetralin divided by initial moles of naphthalene)); — trend line.

arguments of Kasztelan [31]. Since the MoNaph derived MoS₂ morphology yields a greater fraction of rim-edge sites (93%) than the exfoliated MoS₂ (22%), the former catalyst has higher HDN and hydrogenation activity [23,24]. Hydrogenolysis of C–S occurs preferentially on edge sites and since the exfoliated MoS₂ has a greater fraction of edge sites, this catalyst had higher HDS activity than the MoNaph derived MoS₂ [23,24]. However, the differences in the catalyst performance during hydrocracking are more complex. In this case, thermal reactions dominate and hydrogen transfer to cap free radicals becomes important. The results from [16] and the present study show that the exfoliated MoS₂ is better suited for this Cold Lake hydrocracking probably because of a combination of hydrogenolysis and hydrogen transfer capability. Although the exfoliated MoS₂ had lower HDN activity than the MoS₂ derived from MoNaph in the case of carbazole as reactant, at higher temperature with Cold Lake bitumen, N removal occurred to a higher degree on the exfoliated MoS₂ [16].

4. Conclusion

The catalyst activities of exfoliated MoS₂ and that of MoNaph derived MoS₂ were compared for the HDS of dibenzothiophene, the HDN of carbazole and the hydrogenation of naphthalene. The results provide a quantitative comparison between exfoliated MoS₂ and MoS₂ prepared from MoNaph. Exfoliated MoS₂ was found to give better overall HDS compared to MoNaph derived MoS₂ catalyst, whereas MoNaph derived MoS₂ was found to give higher hydrogenation and HDN activity. These results are a consequence of the morphology of the two catalysts and the fraction of edge sites present in the crystallites. In the case of Cold Lake bitumen hydrocracking, however, the relative activity of the two catalysts is shown to be different, and the higher S, N and MCR removal of the exfoliated MoS₂ compared to MoS₂ prepared from MoNaph, is likely a consequence of a combination of high hydrogenolysis and hydrogenation activity on this catalyst.

References

[1] M. Daage and R.R. Chianelli, J. Catal. 149 (1994) 414.

[2] Y. Iwata, K. Sato, T. Yoneda, Y. Miki, Y. Sugimoto, A. Nishijima and H. Shimada, Catal. Today 45 (1998) 353.

[3] Y. Iwata, Y. Araki, K. Honna, Y. Miki, K. Sato and H. Shimada, Catal. Today 65 (2001) 335.

[4] H. Farag, K. Sakanishi, M. Kouzu, A. Matsumura, Y. Sugimoto and I. Salto, J. Mol. Catal. A 206 (2003) 399.

[5] H. Farag, K. Sakanishi, M. Kouzu, A. Matsumura, Y. Sugimoto and I. Saito, Ind. Eng. Chem. Res. 42 (2003) 306.

[6] M. Del Valle, J. Cruz-Reyes, M. Avalos-Borja and S. Fuentes, Catal. Lett. 54 (1998) 59.

[7] E. Devers, P. Afanasiev, B. Jouguet and M. Vrinat, Catal. Lett. 82 (2002) 13.

[8] A. Del Bianco, N. Panariti and M. Marchionna, Chemtech 25 (1995) 35.

[9] A. Del Bianco, N. Panariti, S. Dicarlo, J. Elmouchnino, B. Fixari and P. Leperchec, Appl. Catal. A 94 (1993) 1.

[10] R. Lott, L.K. Lee, Proceedings of AIChE Spring National Meeting (AIChE, New Orleans, Louisiana, April 2003) 577.

[11] L. Kane and S. Romanow, Hydrocarb Process 82 (2003) 32.

[12] N. Panariti, A. Del Bianco, G. Del Piero and M. Marchionna, Appl. Catal. A 204 (2000) 203.

[13] E.J.M. Hensen, P.J. Kooyman, Y. van der Meer, A.M. van der Kraan, V.H.J. de Beer, J.A.R. van Veen and R.A. van Santen, J. Catal. 199 (2001) 224.

[14] H. Schweiger, P. Raybaud, G. Kresse and H. Toulhoat, J. Catal. 207 (2002) 76.

[15] H. Topsoe and B.S. Clausen, Catal. Rev. -Sci. Eng. 26 (1984) 395.

[16] C.T. Tye and K.J. Smith, Catal. Lett. 95 (2004) 203.

[17] P. Joensen, R.F. Frindt and S.R. Morrison, Mater. Res. Bull. 21 (1986) 457.

[18] M. Del Valle, M. Avalos-Borja, J. Cruz and S. Fuentes, Mater. Res. Soc. Symp. Proc. 351 (1994) 287.

[19] W.P. Boone and J.G. Ekerdt, J. Catal. 193 (2000) 96.

[20] D.I. Kochubei, V.A. Rogov, V.P. Babenko, S.V. Bogdanov and V.I. Zaikovskii, Kinetics Catal. 44 (2003) 135.

[21] B.C. Bockrath and D.S. Parfitt, Coal Sci. Tech. 24 (1995) 1343.

[22] B.C. Bockrath and D.S. Parfitt, Catal. Lett. 33 (1995) 201.

[23] C.T. Tye, PhD thesis, University of British Columbia, (2006) .

[24] C.T. Tye and K.J. Smith, Catal. Today (Accepted).

[25] M. Nagai, T. Masunaga and N. Hanaoka, Energy Fuels 2 (1988) 645.

[26] E. Furimsky, Catal. Rev. -Sci. Eng. 47 (2005) 297.

[27] A. Szymanska, M. Lewandowski, C. Sayag and G. Djega-Mariadassou, J. Catal. 218 (2003) 24.

[28] F.E. Massoth and S.C. Kim, Ind. Eng. Chem. Res. 42 (2003) 1011.

[29] M. Nagai, Y. Goto, A. Irisawa and S. Omi, J. Catal. 191 (2000) 128.

[30] H.G. Kim and C.W. Curtis, Energy Fuels 4 (1990) 206.

[31] S. Kasztelan, H. Toulhoat, J. Grimblot and J.P. Bonnelle, Appl. Catal. 13 (1984) 127.