EFFECTS OF CATALYST MORPHOLOGY ON HYDROTREATING REACTIONS

TYE CHING THIAN

School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus,
14300 Nibong Tebal, Seberang Prai Selatan, Pulau Pinang, Malaysia
Email: chcttye@eng.usm.my

Abstract

Due to the new environmental regulations for fuel quality, refineries need to process cleaner fuel. This requires an improvement in performance of hydrotreating catalysts. Improvements in catalyst activity require knowledge of the relationships between catalyst morphology and activity. Molybdenum sulfide, the generally agreed catalysts that give the best performance in hydrocracking and hydrotreating was investigated for its morphology effects on hydrotreating reactions. Three types of MoS_2 catalysts with different morphology were studied. They are crystalline MoS_2, exfoliated MoS_2 and MoS_2 derived from a precursor, molybdenum naphthenate. Exfoliated MoS_2 with minimal long range order, with much higher rim edges has shown relative higher hydrogenation activity. Generally, results of MoS_2 catalyst activities in hydrogenation, hydrodesulfurization, hydrodenitrogenation and hydrideoxygenation are in agreement with the rim-edge model.

Keywords: Hydrotreating, catalyst morphology, rim-edge model

1. Introduction

The increasing world energy demand and decreasing conventional crude oil reserves have spurred the mankind to search for economically feasible alternative energy sources. In view of this, increasing amount of unconventional crude oil such as heavy oil and bitumen extracted from tar sand with lower quality will need to be refined in order to meet the energy demand of the world. Typical unconventional heavy oil not only has higher liquid volume of residue with boiling point higher than $525^{o}C$, but also has much higher heteroatom (S, N and O) and metals (Ni and V) compared to the conventional crude oil. In the mean time, new stringent

regulations for fuel quality, driven by environmental concerns, require an improvement in the performance of hydrotreating catalysts [1].

Hydrotreating a petroleum distillate involves a combination of reactions occurring simultaneously, such as hydrodesulfurization (HDS), hydride-nitrogenation (HDN), hydrodeoxygenation (HDO) and hydrogenation of aromatics. Among these, HDS has been the main concern of hydrotreating in both industry and academic. This is due to the increasing use of heavy crude oils with high sulfur content and global reductions in the sulfur content allowance of automotive fuels [2]. HDN is another issue that received much attention since the presence of nitrogen-containing compounds affects the deep HDS process. HDN is required mostly to minimize catalyst poisoning in subsequent hydrotreating processes. The presence of nitrogen-compounds inhibits HDS and other reactions due to their preferential adsorption on catalytic sites. HDN is also required to meet NO_x emission standards from combustion, in order to minimize air pollution [3]. HDN is more difficult since nitrogen-containing aromatic rings require hydrogenation prior to nitrogen removal, and hydrogenation of the nitrogen-containing aromatic rings is difficult because of steric and thermodynamic limitations [4]. Relatively, HDO receives less attention compared to HDS and HDN in heavy oil hydroprocessing because of the low O content of these oils.

Improvements of hydrotreating catalyst activity require knowledge of the relationships between catalyst morphology and activity. It is generally agreed that molybdenum based catalysts give the best performance in hydrocracking and hydrotreating. Generally, two types of active sites have been identified: one that promotes hydrogenation reactions and a second one that promotes hydrogenolysis of the carbon-heteroatom bond of heterocyclic organic compounds present in the oil. The activity of MoS_2 is generally accepted to be due to the edge planes of MoS_2, whereas the basal plane is considered inert. Daage and Chianelli [5] proposed a rim-edge model in which hydrogenation reaction occurred exclusively on the top and bottom edge planes (rim sites) of MoS_2 crystallites while the hydrogenolysis reaction was catalyzed on all of the edge planes. Most of the studies related to MoS_2 structure-activity relationships were carried out using model compound and focused on HDS and hydrogenation reactions, rather than HDN and HDO reactions.

MoS_2 is a layered structure in which sheets of MoS_2 are held together by weak van der Waals forces between each layer. Joensen et al [6] introduced the exfoliation method that transforms MoS_2 crystallites into highly dispersed, single-layered MoS_2 suspended in aqueous solution. Exfoliated MoS_2 offers an opportunity to examine the MoS_2 structural effects without interference from the catalyst support and catalyst promoters. In the present study, a comparative study has been conducted to evaluate the performance of MoS_2 catalysts, prepared with varied morphology, in hydrotreating reactions using model compounds.

2. Experimental

2.1. Catalyst preparation

Three types of MoS_2 catalysts were investigated. The first type of catalysts was prepared by *in situ* decomposition of soluble Mo precursor molybdenum

naphthenate (MoNaph) (6.0 wt% Mo). The second one is the commercially available crystalline MoS_2 powder and the third, exfoliated MoS_2 was prepared from the crystalline MoS_2.

Exfoliated catalyst was prepared according to Joensen et al [6]. 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 Li-intercalated MoS_2 was subsequently exposed to water. 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 neutral. Finally, the washing process was repeated by replacing water with isopropanol and isopropanol with decalin. Note that the exfoliated MoS_2 mentioned in this paper refers to exfoliated MoS_2 dispersed in decalin.

The catalysts used herein were characterized by BET specific surface area, X-ray diffraction (XRD), and transmission electron microscopy (TEM).

2.2. Catalyst activity test

The catalyst activity test was carried out in a stirred batch reactor loaded with 100 mL of n-hexadecane and 600 ppm 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, 0.2 wt% quinoline for HDN, 10 wt% naphthalene for the hydrogenation reaction and 5 wt% for HDO. 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 to the reaction temperature at 350^oC. 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, washed and dried before characterization. Liquid samples were analyzed with a gas chromatograph using a flame ionization detector (FID) fitted with a capillary column (AT-5, 30 m x 0.32 mm x 0.25 μm) [7].

3. Results and Discussion

3.1. Catalyst properties

In order to study catalyst structure-activity relationships, the properties of the catalysts must be determined. The properties of unused, exfoliated MoS_2 and crystalline MoS_2 were determined through a series of characterizations. In the case of MoS_2 synthesized by *in situ* decomposition of MoNaph, the properties of the solid material recovered from the reactor after reaction, were determined. The detail characterization results are reported elsewhere [8]. The TEM of MoS_2 before and after exfoliation are shown in Fig. 1. The properties of different MoS_2 catalysts summarized from the result of characterization were reported in Table 1. It was found that three types of catalysts used possessed different morphologies.

The different catalysts were identified for their particle slab length, stack height and number of layers. Particle slab length refers to the lateral dimension of MoS_2 particle and the stack height refers to MoS_2 particle size perpendicular to (002) plane, both determined from XRD. From Table 1, it was found that, the

exfoliated MoS_2 had an average of 9 layers of MoS_2 in large sheet morphology (0.40 μm) compared to the crystalline MoS_2 with 57 layers and average slab length of 0.56 μm. In contrast, MoS_2 derived from MoNaph precursor had a small slab length of approximately 10 nm with 1 to 3 layers of MoS_2 in the crystallites.
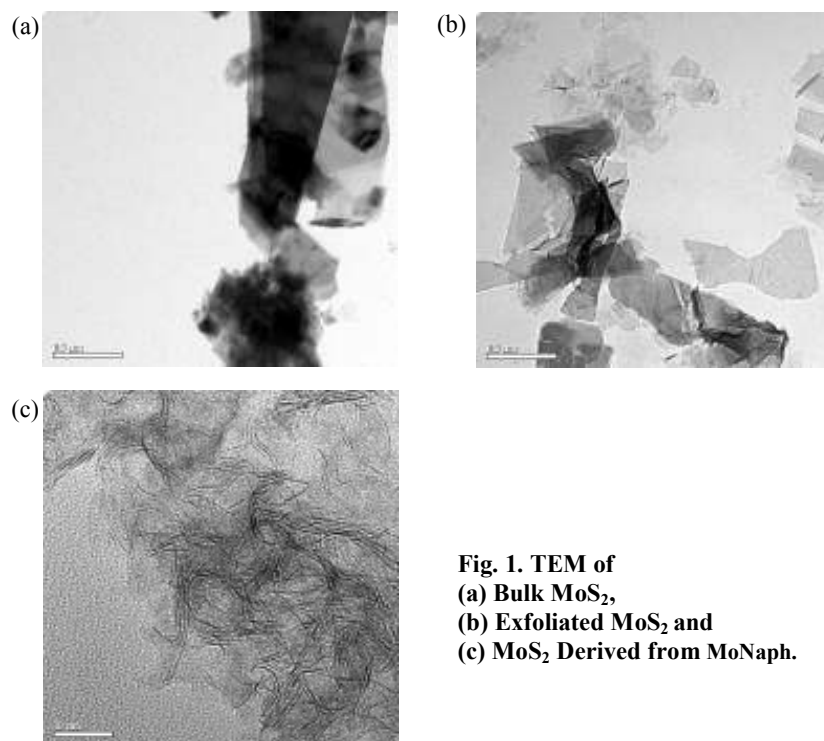
Fig. 1. TEM of
(a) Bulk MoS_2,
(b) Exfoliated MoS_2 and
(c) MoS_2 Derived from MoNaph.

Table 1. Characterization of Different MoS_2 Catalysts.

Average	Crystalline MoS_2	Exfoliated MoS_2	MoNaph derived MoS_2[a]
Slab length, nm (*d*)	560	400	10
Stack height, nm	35.8	5.5	1.8 (0.8)[b]
Number of layers (*n*)	57	9	2.8 (1.3)*

[a] MoS_2 synthesized by *in situ* decomposition of molybdenum naphthenate
[b] MoS_2 synthesized by *in situ* decomposition of ammonium heptamolybdate
* From TEM analysis.

3.2. Catalyst activity

Catalyst activity of MoS_2 catalysts with different morphologies were first compared in HDS of DBT. DBT was chosen as the model reactant for HDS reaction since the reaction mechanism is well established [9, 10]. In addition, DBT allows the study of sulfur removals through different parallel pathways. One pathway is by direct sulfur-removal or hydrogenolysis leading to biphenyl, the

other is by hydrogenation of an aromatic ring prior to sulfur removal. In view of this, the effect of morphology or structure of catalyst on the catalyst activity in hydrogenation and hydrogenolysis get to be investigated through HDS of DBT.

Table 2 compares the DBT conversion, and HDS activity on the three different MoS_2 catalysts at 350^oC and an initial pressure of 2.8 MPa. After a 5-h batch reaction, the order of DBT conversion achieved was crystalline MoS_2 (12.6%) < MoNaph derived MoS_2 (15.9%) < exfoliated MoS_2 (35.3%). However, the order in terms of HDS activity (HDS, %) was MoNaph derived MoS_2 (3.3%) < crystalline MoS_2 (8.9%) < exfoliated MoS_2 (25.8%). HDS activity is defined as the total yield of desulfurized products. MoS_2 catalyst derived from MoNaph provided DBT conversion comparable to crystalline MoS_2. However, the MoNaph HDS activity was less than crystalline MoS_2. DBT conversion using exfoliated MoS_2 was almost double that obtained when using MoNaph derived MoS_2 [8, 11].

Table 2. DBT Conversion and Hydrodesulfurization (HDS)
Activity for Different Catalysts
(600 ppm Mo, 350^oC, Initial Pressure 2.8 MPa, 5-h Reaction).

Catalyst/precursor	Conversion, %	HDS, %
Crystalline MoS_2	12.6	8.9
Exfoliated MoS_2	35.3	25.8
MoNaph	15.9	3.3

The overall performance of the MoNaph derived MoS_2 and exfoliated MoS_2 in hydrogenation, HDS, HDN and HDO reactions using model reactants is compared in Table 3. The results show that the MoS_2 derived from MoNaph had a slightly higher activity for hydrogenation reactions compared to the exfoliated MoS_2. The naphthalene conversion was higher on the MoNaph derived catalyst (35.8%) than the exfoliated MoS_2 (27.0%) and the same trend was observed in the HDN of quinoline. In the HDN case, carbon-nitrogen bond cleavage only occurred after hydrogenation of at least one aromatic ring. Since the hydrogenation reaction was favored on the MoNaph derived MoS_2, conversion in HDN was higher on MoNaph derived MoS_2 compared to the exfoliated MoS_2.

The conversion of quinoline using MoNaph derived MoS_2 and exfoliated MoS_2 as catalyst was found to be 100% and 76.5% respectively. Using MoNaph derived MoS_2 gave higher conversion as well as HDN activity in HDN of quinoline.

Table 3. Comparison of Conversion in Different Model Reactions
(350^oC, Initial Pressure 2.8 MPa and 5-h Reaction).

Reaction	Reactant	MoNaph		Exfoliated MoS_2	
		Conversion, %	Heteroatom removal, %	Conversion, %	Heteroatom removal, %
HYD	Naphthalene	35.8	-	27.0	-
HDS	Dibenzothiophene	15.9	3.3	35.3	25.8
HDN	Quinoline	100	68.9	76.5	28.2
HDO	Phenol	11.1	11.1	15.0	15.0

The exfoliated MoS_2, however, had a higher activity in HDS of DBT and HDO of phenol compared to that of the MoS_2 derived from MoNaph. DBT conversion occurs through two parallel reaction paths: direct desulfurization or hydrogenation of the aromartic ring followed by C-S hydrogenolysis. Since the exfoliated MoS_2 had a high activity for the direct desulfurization of DBT to yield biphenyl, compared to the MoNaph derived MoS_2 that yielded tetrahydro-dibenzothiophene (THDBT), the former catalyst had overall higher HDS activity. For HDO of phenol, oxygen removal from phenol proceeded through direct hydrogenolysis of C-O without ring saturation. Higher phenol conversion was obtained using exfoliated MoS_2 than MoNaph derived MoS_2. These results showed that exfoliated MoS_2 has better hydrogenolysis activity than MoNaph derived MoS_2.

3.3. MoS_2 structure-activity relations

Molybdenum sulfide based catalysts are extensively used in hydrocracking and hydroprocessing of feeds containing heteroatoms such as nitrogen, sulfur and oxygen. Due to their widespread use, they have been widely studied. However, the exact chemical nature and the structure of active phase are still debated.

The active sites in MoS_2 are generally accepted to lie on the edge planes of the crystal whereas the basal plane is quite inert. Daage and Chianelli [5] proposed a "rim-edge model" for unsupported MoS_2 based on HDS of DBT (Fig. 2(a)). According to the rim-edge model, hydrogenation reactions are catalyzed predominantly by the top and bottom layers of the MoS_2 slab (the rim sites) for large molecules like DBT, while both hydrogenation and hydrogenolysis are catalyzed on all the edge planes. The basal plane of MoS_2 is considered to be inert catalytically. Rim sites and edge sites are shown in Fig. 2. It was presumed that when single or bi-layers occur, selectivity is dominated by the degree of coordinative instauration present. Smaller sulfur-containing molecules may not exhibit the rim-edge effect due to the absence of steric interference.
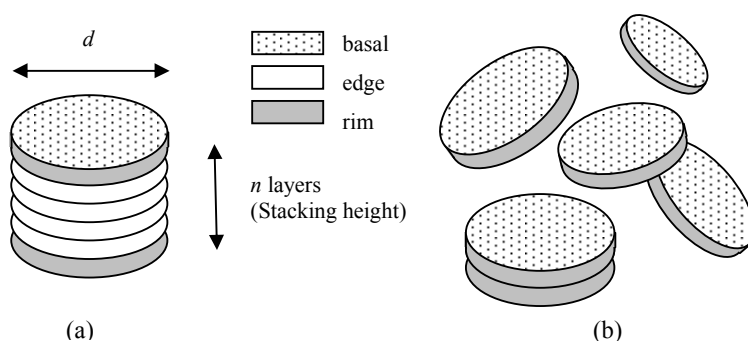

Fig. 2. (a) MoS_2 Particle Rim-Edge Model and (b) Exfoliated MoS_2.

The performance of the exfoliated MoS_2 is associated with its morphology. In the case of single model compound reactants, the differences in catalyst perform-

ance follow previous suggestions that the hydrogenation occurs preferentially on rim-edge sites. Since the MoNaph derived MoS_2 morphology yields a greater fraction of rim-edge sites than the exfoliated MoS_2, the former catalyst has higher HDN and hydrogenation activity. Hydrogenolysis of C-S bond occurs preferentially on edge sites and since the exfoliated MoS_2 has a greater fraction of edge sites (Fig. 2(b)), this catalyst has higher HDS activity than that of the MoNaph derived MoS_2.

4. Conclusions

In this study, effect of MoS_2 catalysts' morphology in hydrotreating was found to follow the rim-edge model. In this model, a straightforward relation between the MoS_2 layers and selectivity was reported. However, the MoS_2 catalysts with different structure used in the current study were prepared through very different methods and the average size of different MoS_2 particles size was varied over a wide range. Further, reactions were carried out in the presence of H_2S.

References

1. Grange P. and Vanhaeren X. (1997). Hydrotreating catalysts, an old story with new challenges. *Catal. Today*, 36 (4), 375-391.
2. Plantenga F. L. and Leliveld R. G. (2003). Sulfur in fuels: more stringent sulfur specifications for fuels are driving innovation. *Appl. Catal. A-Gen.*, 248 (1-2), 1-7.
3. Furimsky E. (2005). Hydrodenitrogenation of petroleum. *Catal. Rev.-Sci. and Eng.*, 47 (3), 297-489.
4. Trytten L. C., Gray M. R., and Sanford E. C. (1990). Hydroprocessing of Narrow-Boiling Gas Oil Fractions - Dependence of Reaction-Kinetics on Molecular-Weight. *Ind. and Eng. Chem. Res.*, 29(5), 725-730.
5. Daage M. and Chianelli R. R. (1994). Structure-Function relations in Molybdenum Sulphide Catalysts: The "Rim-Edge" Model. *J. Catal.*, 149, 414-427.
6. Joensen P., Frindt R. F., and Morrison S. R. (1986). Single-layer MoS_2. *Mater. Res. Bull.*, 21, 457-461.
7. Tye, C. T. (2006), PhD thesis, University of British Columbia, Canada
8. Tye, C. T. and Smith, K. J. (2006a). Catalytic Activity of Exfoliated MoS_2 in Hydroprocessing Reactions. *Topics Catal.*, 37(2-4), 129-135.
9. Gates B. C. and Topsoe H. (1997). Reactivities in deep catalytic hydrodesulfurization: Challenges, opportunities, and the importance of 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene. *Polyhedron*, 16 (18), 3213-3217.
10. Mochida I. and Choi K. H. (2004). An overview of hydrodesulfurization and hydrodenitrogenation. *J. Japan Petro. Inst.* 47 (3), 145-163.
11. Tye, C. T. and Smith, K. J. (2006b). Hydrodesulfurization of dibenzothiophene over exfoliated MoS_2 catalyst. *Catal. Today*, 116, 461–468.