

Catalytic hydrocracking of bitumen at mild experimental condition

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(Received 19 May 2009 • accepted 27 June 2009)

Abstract—Mo-containing catalysts were prepared by impregnation method using silica-based porous supports and their physical properties were characterized by BET, XRD and TEM. Catalytic hydrocracking of bitumen extracted from oil sand was carried out in a high pressure reactor using Athabasca oil sand over 5 wt% Mo containing catalyst supported on SiO₂, MCF(Meso Cellular Foam) and SBA-15, respectively, under the conditions of 200 °C, 20 h and 10 atm of H₂ gas. Catalytic hydrocracking activity was estimated by analyzing H/C mole ratio based on EA data, and TGA was employed to compare the thermal behavior of bitumen before and after reaction. Upon hydrocracking over Mo/MCF catalyst, H/C was increased from 1.50 (bitumen itself) to 1.66.

Key words: Oil Sand, Bitumen, Hydrocracking, Catalyst, TGA

INTRODUCTION

An enormous amount of potential bitumen resources are available worldwide. Refining of bitumen to lighter and more valuable liquid products is essential to substitute for conventional petroleum. Athabasca bitumen deposits in northeastern Alberta Canada are one of the world's largest reserves of petroleum [1]. Hydrocracking is an important refining process that converts high hydrocarbon molecules into lighter and more valuable liquid products by reacting them with H₂ over a catalyst at high pressure and temperature [2]. Hydrocracking of bitumen is one of the main processes for converting a heavy carbonaceous feedstock to lower-boiling products. The development of hydrocracking of bitumen is considered as a landmark in heterogeneous catalysis. The existing process of hydrocracking of bitumen involves the reaction of gaseous hydrogen on Mo and Ni containing catalyst at high temperatures (800 °C) and high pressures (100 MPa).

Hydrocracking of bitumen under such severe reaction conditions is energy-intensive as well as capital-intensive, although many advances in engineering have been made within the past few decades [3]. However, the catalytic hydrocracking of bitumen into low boiling narrow cuts under milder conditions has been a challenging and longstanding goal in catalysis. There is an urgent need in the hydrocracking of bitumen in the petroleum industry for a higher activity catalyst under low temperature and low pressure conditions. Mild hydrocracking occurs at higher severities of hydrotreating. Mild hydrocracking is considered as an important catalytic process for the production of high quality fuel from heavy feedstocks by improving cetane number [4,5]. Several attempts were taken earlier to modify NiMo/Al₂O₃ catalyst using boron and phosphorus or to develop new catalyst to improve catalysts' hydrodenitrogenation (HDN) and hydrosulfurization (HDS) activity [6,7]. Extensive studies about oxides-supported Ni and Mo catalysts for hydrocracking have been carried out [6-8]. Various supports, such as alumina [6-9] and

zeolite [10] for Mo and Ni catalysts, SBA-15 for Fe and Ni catalysts [11], and titania and silica for Co and Mo [12] base catalysts were used for the hydrocracking of bitumen.

The main objective of the present work was to investigate the influence of supports of catalysts on the catalytic activity of hydrocracking of bitumen. Mo-containing catalysts were prepared with various supports such as silica, MCF, SBA-15 with different pore structures and their hydrocracking activity was compared. It was observed that the basic physical properties such as pore volume, surface area, ratio of pore diameter and wall thickness are important factors in catalytic activity.

EXPERIMENTAL

The bitumen was separated from the Athabasca oil sand according to our previous work [13]. SBA-15 and MCF were prepared according to the literature [14,15], and SiO₂ was purchased from Junsei.

The catalysts, namely Mo/MCF, Mo/SiO₂ and Mo/SBA-15, were prepared by using incipient wetness method. Mo in all catalysts was maintained at 5 wt%. In this method an aqueous ammonia solution (28 wt% concentrated NH₃) was prepared at a pH of 9.5 using the required amount of ammonium heptamolybdate [(NH₄)₆Mo₇O₂₄·4H₂O]. The solution was heated at 70 °C until it produced a clear solution, and was impregnated with support, and dried for 12 h at 120 °C. The catalyst was then calcined in the air at 500 °C for 4 h.

The hydrocracking of bitumen was carried out in a high pressure batch reactor. Reactions were performed for 20 h at 200 °C and 10 atmospheric pressure of H₂ in all cases. The reaction time was calculated from the time when the desired reaction temperature was reached. After the reaction, the reactor was cooled quickly to room temperature. The hydrocracked bitumen was filtered and the catalyst was separated.

Carbon, hydrogen, nitrogen and sulfur content were analyzed with a CHNSO Fisons EA-1108 Elemental Analyzer. Thermo-gravimetric experiments were recorded on a TA instrument TGA Q500 operating in nitrogen with a flow rate of 100 ml min⁻¹ through the furnace in the following conditions: sample weight about 10 mg,

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varying heating rates of $10\text{ }^{\circ}\text{C min}^{-1}$, temperature range: 100-1,000 $^{\circ}\text{C}$.

RESULTS AND DISCUSSION

Hydrocracking of bitumen is one of the main processes for converting a heavy carbonaceous feedstock to lower-boiling products. Usually, heterogeneous catalysts such as sulfide of cobalt, molybdenum, or nickel supported by alumina or silica-alumina are used in the process. The constituents of higher molecular weight of bitumen deposit on the surface of the catalyst, block the pores of the catalyst, and then result in rapid decline of the hydrocracking activity. To meet this difficulty, various systems and mainly metals have been introduced and different supports used in order to get an active catalyst system.

It is well known and reported that catalyst plays an important role by providing hydrogen to larger molecules during hydrocracking reaction [16], which helps to suppress coke formation and enhances hydrogenation and hetero atom removal from products.

Table 1 shows the basic physical properties of silica-based supports such as MCF, SiO_2 , and SBA-15 and their Mo-containing catalysts used in this work. Pore volume and BET surface area were measured by N_2 adsorption/desorption experiment. And average wall thickness and average pore diameter were determined by TEM measurement. They have different properties, and the ratio of pore diameter and wall thickness is noted. Even though, for example, SBA-15 has the highest surface area, the ratio of pore diameter and wall thickness is the lowest. Average pore diameter of SBA-15 is relatively smaller than that of SiO_2 and MCF, and the pore volume of SiO_2 is very small. The physical properties of supports and their catalysts are almost the same each other, which indicates that Mo is highly dispersed over the supports.

To understand the relationship between the physical properties

of supports and their catalytic performance, hydrocracking of bitumen was performed.

Table 2 shows the elemental analysis results of bitumen before and after hydrocracking over various catalysts. H/C mole ratios of bitumen itself and the hydrocracked one in the absence of catalyst was about 1.50. In the presence of catalyst, some conversion was observed at mild hydrocracking conditions. Increment of H/C mole ratio indicates that the bitumen had been hydrocracked and relative hydrogen content increased. Unexpectedly, the H/C ratio of the product from the hydrocracking over Mo-SBA-15 was unchanged. However, interestingly, a reduction of nitrogen content after hydrocracking was observed. It seems that the existence of bigger mesopore can provide the active site easily accessible for reactant.

TGA was monitored to compare the thermal behavior of the bitumen and its fractions under N_2 atmosphere. The study of TGA of bitumen and its fractions is extremely complicated because of the presence of many complex constituents.

Fig. 1 indicates that (A) TGA results of bitumen itself (solid line) and bitumen hydrocracked over Mo/MCF (sample No. 1 in Table 2) and (B) Relative amount of thermally decomposed fraction of bitumen itself (X) and hydrocracked bitumen (Y). Figure (B) is plotted from the data of figure (A).

Conventional hydrocarbon can be fractionated by boiling point cut in the distillation technique as follows:

Naphtha: bp < 177 $^{\circ}\text{C}$ (region 1: R1)

Kerosene: 177 $^{\circ}\text{C}$ < bp < 343 $^{\circ}\text{C}$ (region 2: R2)

Gas oil: 343 $^{\circ}\text{C}$ < bp < 525 $^{\circ}\text{C}$ (region 3: R3)

Vacuum residue (VR): 525 $^{\circ}\text{C}$ < bp < 800 $^{\circ}\text{C}$ (region 4: R4)

Cokes: bp > 800 $^{\circ}\text{C}$ (region 5: R5)

Similar to the classification by boiling point, the TGA curve was

Table 1. The basic physical properties of supports and their Mo-containing catalysts used in this study

Catalyst Support	Pore volume (cc/g)	BET surface area (m^2/g)	Average wall thickness (nm)	Average pore diameter (nm)	Ratio of pore diameter/ wall thickness
Mo/MCF	1.96	250	9.6	45	4.7
MCF	1.99	256	10	45	4.5
Mo/ SiO_2	0.004	0.8	48	600	12.5
SiO_2	0.004	0.8	50	600	12
Mo/SBA-15	1.20	760	4.7	4.8	1.0
SBA-15	1.23	780	5.0	4.7	0.9

Table 2. Elemental analysis results of bitumen before and after hydrocracking over various catalysts

	5 wt% Mo-containing catalyst over	Elements (wt%)				H/C (mole ratio)
		N	C	H	S	
1	MCF	1.34	79.5	11.0	3.46	1.66
2	SiO_2	1.32	79.6	10.4	3.56	1.56
3	SBA-15	0.58	80.5	10.1	4.46	1.51
4	No catalyst*	1.60	80.2	10.2	4.67	1.50
5	Bitumen only**	1.63	82.8	10.4	4.78	1.50

*No catalyst indicates that the bitumen was hydrocracked in the absence of catalyst

**Bitumen only indicates the bitumen itself before hydrocracking

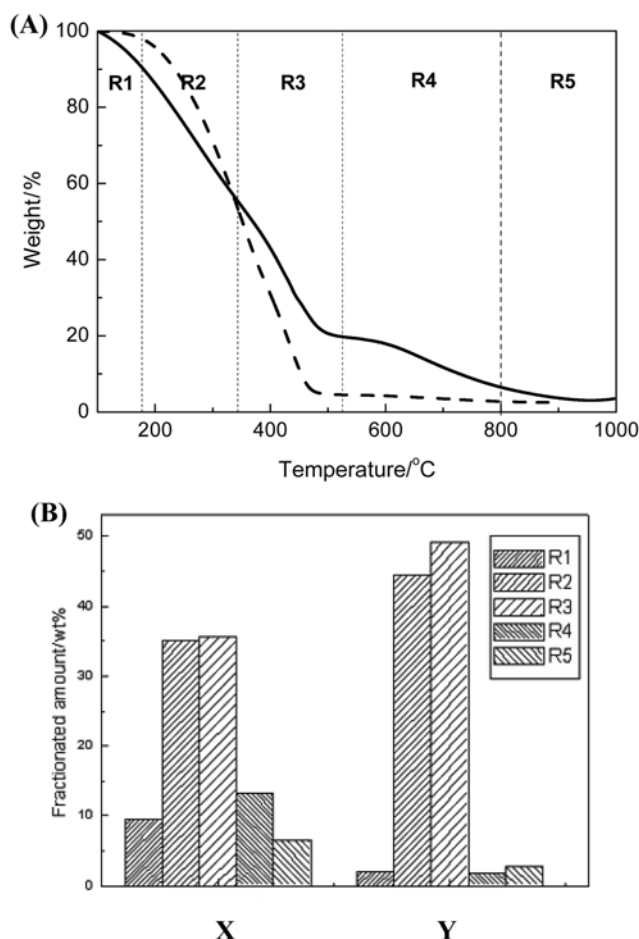


Fig. 1. (A) TGA results of bitumen itself (solid line) and hydrocracked bitumen (dotted line) obtained from the sample No. 1 as shown in Table 2. (B) Relative amount of thermally decomposed fraction of bitumen itself (X) and hydrocracked bitumen (Y). Figure (B) is plotted by reading figure (A) and it is clear that the remaining fraction in the range of 500–900 °C of Y is reduced by about 4 times than that of X.

separated into five regions, such as R1, R2, R3, R4 and R5 as shown in Fig. 1 [A]. Fig. 1 shows the TGA of bitumen showing different thermal decomposition behavior. It is assumed that the weight loss observed in the bitumen and its fractions represent the thermal decomposition [17,18]. The differences indicated in the thermogravimetric characteristic values of the samples, especially in terms of weight loss, are due to the different constituents. As shown in Fig. 1 [B], in the case of sample X (bitumen itself), the weight losses are about 9%, 35%, 36%, 15% and 7% for the region of R1, R2, R3, R4 and R5, respectively. In the case of sample Y (hydrocracked bitumen), the weight losses are about 2%, 45%, 50%, 2% and 3% for the region of R1, R2, R3, R4 and R5, respectively. The weight loss after 800 °C is almost negligible and carbon rich residue (coke) is formed. Similar observation has been reported by M. Benbouzid et al. [19]. Comparing the fractions in R1–R5 for both samples, fractions of R2 and R3 of sample Y are increased by about 25%, and at the same time fractions of R4 and R5 of sample Y are decreased by about 17% compared with sample X. After catalytic hydrocracking of bitumen sample X, the amount of heavier fraction in R4 and R5 was con-

verted into mainly lighter fraction of R2 and R3.

When bitumen was hydrocracked, in this work, a large number of unknown products were detected by GC/MS, which is the main reason why the product distribution was estimated based on TGA. When simple feed is hydrocracked, the product yield can be calculated by GC/MS [20]; however, heavy residue is cracked and product yield can be suggested based on boiling point cut [21]. Recently, we reported that bitumen can be fractionated by TGA, which shows similar results of boiling point cut [13]. Due to the above reasons, we have calculated product distribution based on TGA by comparing the results before and after hydrocracking.

CONCLUSIONS

Molybdenum containing silica-based porous catalysts were prepared and their hydrocracking activity was compared under mild reaction conditions such as 200 °C and H₂ 10 atm, and their results were explained based on the results of EA and TGA for the bitumen sample before and after reaction. TGA technique is a kind of indirect method to estimate the degree of reaction, and relative amount of each fraction before and after hydrocracking. From this study, support is one of the main factors determining the catalytic activity. Mo catalysts were catalytically active to hydrocrack bitumen at mild experimental condition. By comparing SiO₂ and SBA-15, pore diameter rather than surface area is important for governing the catalytic activity. It can be suggested that bigger mesopores show better activity as they may provide the acid sites easily accessible for reactants. In the case of Mo containing SBA-15 catalyst, hydrodenitrogenation reaction occurs rather than hydrocracking under mild reaction conditions, which is not clearly understood so far.

ACKNOWLEDGMENTS

This work was supported by MOCIE through the Institutional Research Program (KK-0901-A2).

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