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Preparation and Application of an Oil-Soluble CoMo Bimetallic Catalyst for the Hydrocracking of Oil Sands Bitumen

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ABSTRACT: An oil-soluble CoMo bimetallic catalyst was prepared for an application to hydrocracking reaction of heavy oil. Layered ammonium cobalt molybdate was synthesized by precipitation, and the bimetallic dispersed catalyst was prepared by coating the layered material with oleic acid as an organic ligand. The prepared catalyst was characterized by X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy. The oleic acid added during the preparation step was found to be chemisorbed as a carboxylate onto the particles. The activities of the CoMo bimetallic dispersed catalyst were compared to those of other monometallic dispersed catalysts and simple physical mixtures of these catalysts in an effort to evaluate the applicability and synergistic catalytic effect of the CoMo bimetallic dispersed catalyst in the hydrocracking of heavy oil. The catalyst promoted the asphaltene and sulfur conversion activities, maximizing the yield of the liquid product. These results suggest that a bimetallic effect can be created when two metals are chemically bound to form a single catalyst.

1. INTRODUCTION

The use of oil-soluble dispersed catalysts in the hydrocracking of heavy oil has recently been studied intensively by many researchers to avoid the pore-plugging problem of conventional supported catalysts.[1−4] Oil-soluble metal precursors are regarded as promising catalysts, owing to their highly dispersive characteristics in heavy oil and their high ratio of surface area/volume. An additional benefit of oil-soluble metal precursors is that they are transformed *in situ* during reactions into metal sulfides, which are active species in the upgrading of heavy oil.[5]

As oil-soluble dispersed catalysts for hydrocracking, Mo-based precursors are commonly studied. There have been several attempts to transplant inexpensive promoters, such as Ni, Co, or Fe, into a Mo-based dispersed catalyst, because the addition of a promoter may decrease the cost of the catalyst and enhance its hydrocracking activity.[6−8] However, in previous studies, dispersed catalysts composed of more than two metal substances were simple physical mixtures of different monometallic precursors. Bimetallic dispersed catalysts, in which the metal precursors are chemically bound, are rare.

In a previous study by the authors,[9] a new method for the preparation of oil-soluble bimetallic materials via the layered transition-metal molybdate (LTM) precursor was reported. The LTM precursor, synthesized by precipitation from an aqueous solution, was bound with oleic acid to form an organic ligand that renders the precursor soluble in a heavy oil phase.

In this study, an oil-soluble CoMo bimetallic catalyst was prepared as described above. The organic ligand in the CoMo bimetallic catalyst was identified from spectroscopic analyses for a better understanding of its chemical structure. The activity of the CoMo bimetallic catalyst was then compared to those of other monometallic dispersed catalysts and mixtures of catalysts in an effort to evaluate its applicability in the heavy oil hydrocracking process. In addition, the synergistic effect of the bimetallic catalyst, expected to emerge when two metals are chemically combined, was investigated and compared to that of a simple mixture of monometallic dispersed catalysts.

2. EXPERIMENTAL SECTION

2.1. Preparation of the Oil-Soluble CoMo Bimetallic Catalyst. Layered ammonium cobalt molybdate $[(NH_4)HCo_2(MoO_4)_2 \cdot (OH)_2]$ was prepared by a procedure detailed in a previous study.[10,11] In brief, ammonium heptamolybdate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O)$ and cobalt nitrate $(Co(NO_3)_2 \cdot 6H_2O]$ were dispersed in distilled water to prepare a solution containing Mo and Co at the desired molar contents of 0.1 mol of Mo and 0.1 mol of Co. The addition of ammonium hydroxide (28.8%, NH_3) precipitated a pale purple solid, which was collected by filtration, washed with distilled water, and dried at 100 °C.

The obtained powder was mixed with excess oleic acid in a three-neck round flask and stirred under nitrogen to bind the organic ligand. The mixture was held at 250 °C for 1 h. When the reaction was completed, the mixture appeared as a brown solution. Acetone was then added to precipitate the CoMo bimetallic catalyst. The precipitate was washed 3 times with acetone to remove free oleic acid and then dried in a vacuum oven at 70 °C.

2.2. Characterization. The crystalline structures of the layered ammonium cobalt molybdate and the CoMo bimetallic catalyst, calcined under N_2, were investigated by X-ray diffraction (XRD, Rigaku D/Max-III C, Japan) using Cu $K\alpha$ radiation. The crystalline phases were identified by a comparison of the measured XRD patterns with Joint Committee on Powder Diffraction Standards (JCPDS) or literature data.

The infrared (IR) spectra were recorded on a Bomem MB-154 spectrometer (ABB Bomem, Quebec City, Quebec, Canada). A ZnSe crystal attachment together with a mercury cadmium telluride detector was used to record the attenuated total reflectance (ATR) spectrum of the pure liquid oleic acid. The transmission spectra for the CoMo bimetallic catalyst were taken after the material was pelletized with KBr powder.

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Table 1. Properties of Athabasca Oil Sands Bitumen

density at 15.4 °C (g/cm^3)	1.0121
API gravity	8.31
calorific value (kcal/kg)	9690
C5-asphaltene (wt %)	16.33
SIMDIS distillation fractions (temperature, °C)	
<200	0.2
200−350	18.3
350−500	32.3
>500	49.2
elemental analysis (wt %)	
carbon	81.86
hydrogen	10.32
nitrogen	0.53
sulfur	5.40

Transmission electron microscopy (TEM) images were obtained using a Tecnai F30S-Twin (FEI, Hillsboro, OR) microscope at an operating voltage of 300 kV. All samples were well-dispersed in ethanol with ultrasonication and then deposited on a copper grid with a hollow carbon film for the TEM measurements.

2.3. Activity Test. Athabasca bitumen was used as a feedstock for the hydrocracking reaction. The properties of this feedstock are shown in Table 1. The hydrocracking reaction was conducted in batch mode using a 200 mL autoclave. The catalysts were applied directly to the feedstock in the autoclave. Various commercial compounds containing a transition metal were applied as dispersed catalysts along with the CoMo catalyst prepared in this study to evaluate the activity of the bimetallic catalyst: cobalt naphthenate (Co naph), Mo octoate (Mo octo), and a simple mixture of these two materials at a molar ratio of Co/Mo of 1.

In a typical experiment, 70 g of Athabasca bitumen was mixed with the catalyst and charged into a reactor. The dosage of the catalysts was 1000 ppmw on the basis of the metal species. After purging with nitrogen, the reactor was then pressurized to 7 MPa with hydrogen, heated to the reaction temperature (420 °C) at a ramping duration of 60 min, and kept at this isothermal condition for 40 min. The reaction pressure was recorded continuously during the experiments.

At the end of the run, the autoclave was rapidly quenched and vented. The vented gas was recovered with a gas-sampling bag to measure the hydrogen consumption during the reaction. The liquid and solid products of the reactions were recovered while washing the reactor wall and lid with dichloromethane (DCM). This mixture was stirred for 1 h and then filtered through a Millipore Teflon filter (0.2 μm) to separate the DCM-soluble material from the residues (coke and metal catalyst). The amount of coke was therefore calculated by subtracting the weight of the catalyst from the residue.

The DCM-soluble product was deasphalted with an addition of 40 volumes of *n*-pentane to calculate the amount of asphaltene. The saturates, aromatics, resins, and asphaltenes (SARA) fractions and sulfur content of the DCM-soluble product were also analyzed by thin layer chromatography (TLC) flame ionization detection (FID) (IATROSCAN MK-6, Japan) and a sulfur analyzer (ANTEK 7000S, Houston, TX), respectively. The boiling point range of the products was determined with a HP 6890 gas chromatograph (Agilent, Santa Clara, CA) using the simulated distillation method (SIMDIS) described as American Society for Testing and Materials (ASTM) method D7169.

3. RESULTS AND DISCUSSION

3.1. Characterization of the CoMo Bimetallic Catalyst.

Figure 1 shows XRD patterns of the layered ammonium cobalt molybdate prepared by the co-precipitation of ammonium heptamolybdate and cobalt nitrate. Although the detailed structural data of the prepared compound was not found in the JCPDS database, these XRD patterns were identified by the isostructural phase (JCPDS card number 40-674), which belongs to a family of ammonium−divalent cation−molybdenum oxides, as reported by Astier et al.[11]

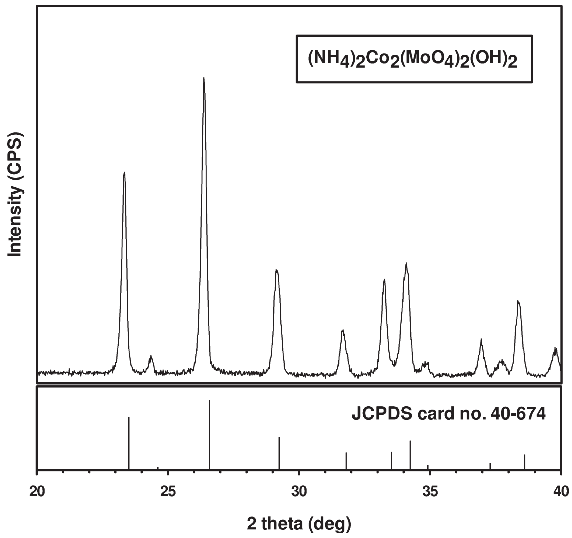

Figure 1. XRD patterns of the layered ammonium cobalt molybdate [$(NH_4)HCo_2(MoO_4)_2\cdot(OH)_2$].

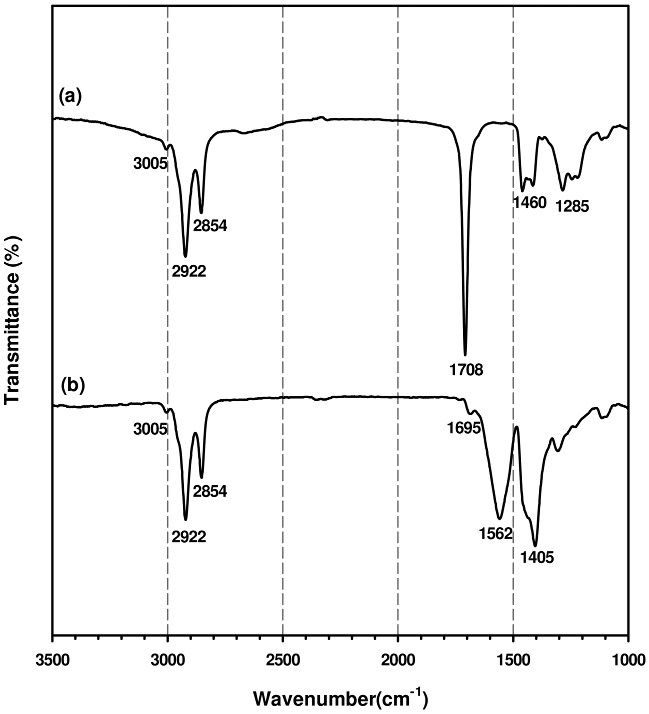

Figure 2. FTIR spectrum of (a) pure oleic acid and (b) CoMo bimetallic catalyst.

For a better understanding of the adsorption mechanism of oleic acid on the surface of layered ammonium cobalt molybdate, FTIR analyses were carried out for pure oleic acid and the CoMo bimetallic catalyst. Figure 2a represents the typical FTIR

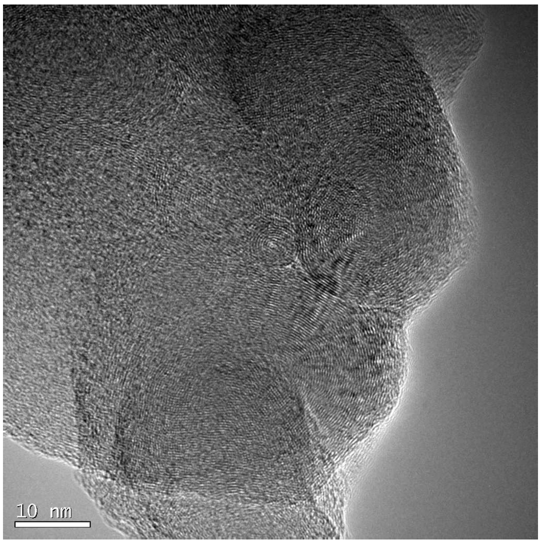

Figure 3. TEM image of the CoMo bimetallic catalyst (4000k).

spectrum of pure oleic acid. The intense peak at 1708 cm^{-1} can be assigned to either the carbonyl group of oleic acid or the asymmetric vibrations of unidentate carboxylate. However, the latter is less common. The band at 1285 cm^{-1} exhibits the presence of a C$-$O stretch, while an O$-$H in-plane band appears at 1460 cm^{-1}.[12]

Figure 2b illustrates the FTIR spectrum for the CoMo bimetallic catalyst. The relative intensity of the band at 1708 cm^{-1}, identified as the C$=$O stretch band of the carboxyl group, decreased significantly and slightly shifted in the IR spectrum of the CoMo bimetallic catalyst. The band related to the C$=$O stretching mode of the COOH group shifts to a lower wavenumber upon its ionization to a carboxylate ion (COO^-). Two new bands at 1562 and 1405 cm^{-1} are characteristics of the asymmetric $\upsilon_\mathrm{a}[\mathrm{COO}^-]$ and symmetric $\upsilon_\mathrm{s}(\mathrm{COO}^-)$ stretch.[13] In general, the asymmetric stretching mode of an isolated COO^- ion ($\upsilon_\mathrm{a}[\mathrm{COO}^-]$) occurs around 1550 cm^{-1}.[14] This implies that oleic acid is chemisorbed as a carboxylate onto the layered ammonium cobalt molybdates, while two oxygen atoms in the carboxylate are coordinated symmetrically to the surface of the layered ammonium cobalt molybdates.

As shown in the TEM image of the CoMo bimetallic catalyst (Figure 3), its layered feature was preserved after binding with oleic acid. To assess the oil-soluble characteristics of the catalyst, 5 g of the CoMo bimetallic catalyst was dissolved in toluene and then filtered through a membrane filter (0.2 μm). The amount of insoluble material was only 0.055 g. Moreover, the catalyst was dispersed in methylene chloride and stored at room temperature. Figure 4 shows a photograph of methylene chloride solution, in which the CoMo bimetallic catalyst (1000 ppm) is dispersed. There was no precipitation after 2 weeks, indicating its stability in an organic phase.

3.2. Catalytic Activity of the CoMo Bimetallic Catalyst.

The catalytic activities of the CoMo bimetallic catalyst were compared to those of other monometallic dispersed catalysts and a simple mixture of the catalysts. The synergistic effects of the bimetallic catalysts, expected to emerge when the two metals were chemically bound together, were also investigated.

Figure 4. Photograph of the CoMo bimetallic catalyst dispersed in the methylene chloride solution.

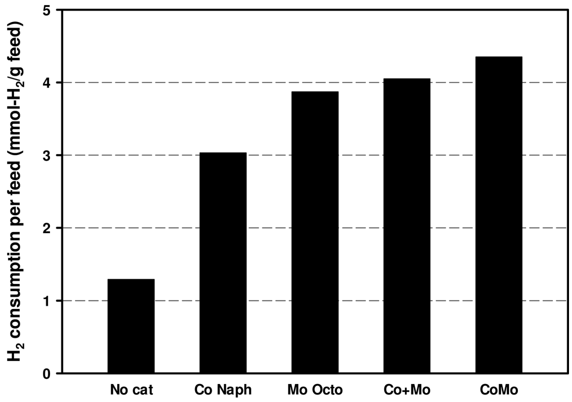

Figure 5. Hydrogen consumptions of various dispersed catalysts.

Figure 5 shows the hydrogen consumption per gram of oil feedstock of various dispersed catalysts after the hydrocracking reaction. The catalyst that consumes the most hydrogen is preferable in this case, because it is reasonable to assume that this catalyst suppresses the formation of hydrocarbon gases and promotes hydrogen uptake. The hydrogen-consuming feature is a characteristic differentiating the reaction with the dispersed catalyst from a thermal reaction without catalyst.

As expected, the CoMo bimetallic catalyst showed the highest level of hydrogen consumption compared to the other dispersed catalysts. In addition, when the CoMo bimetallic catalyst was used, the pressure in the autoclave decreased rapidly even before the temperature approached the set point (420 °C), demonstrating that the hydrocracking temperature was lowered by its enhanced catalytic activity (data not shown).

Table 2 summarizes the performances of the dispersed catalysts in terms of the product yields. CoMo bimetallic catalysts showed the highest level of effectiveness for coke suppression as well as the best control of gas production.

Table 2. Product Yields of Hydrocracking Reactions with Various Dispersed Catalysts

catalysts	no catalyst	Co naph	Mo octo	Co + Mo	CoMo
gas yield (wt %)	21.16	14.77	13.78	13.22	12.38
liquid yield (wt %)	76.27	83.77	85.41	86.00	87.08
<200 °C	19.40	14.33	16.34	16.59	16.65
200−350 °C	22.42	23.64	22.28	23.44	24.57
350−500 °C	21.37	28.05	26.04	27.53	27.76
>500 °C	13.08	19.39	19.11	18.44	18.10
coke yield (wt %)	2.56	1.46	0.81	0.78	0.55

Asphaltene molecules are large, multiply stacked, porphyrin structures containing high concentrations of heteroatoms. These structural characteristics often cause severe problems in the hydrocracking process of heavy oil. Therefore, asphaltene conversion to less problematic chemicals has increasingly been an attractive subject of interest.

Thermal cracking without a catalyst showed a very poor asphaltene conversion, whereas the conversion was enhanced with the dispersed catalysts in the order of Co naph < Mo octo < Co + Mo < CoMo bimetallic catalyst. Although the simple mixture of the monometallic catalysts, Co + Mo, showed greater asphaltene conversion compared to the monometallic catalysts, the combination of Co metal and Mo metal in the CoMo bimetallic catalyst prepared in this study resulted in considerably higher catalytic activity in terms of the asphaltene conversion. This increased catalytic activity is attributed to the synergistic effect, as shown in transition-metal-promoted supported catalysts, in which the transition metals are within the same chemical proximity range. It was reported that the addition of a second transition metal, Co or Ni, to a binary sulfide, such as MoS_2 or WS_2, could produce a great enhancement of the catalytic activity.[15]

To achieve the full benefit from the chemical binding of two metals, it is desirable that the CoMo bimetallic catalyst maintains a chemically bound form, $CoMoO_4$, during the hydrocracking reaction, rather than decomposing into its individual metal compounds. The CoMo bimetallic catalyst was calcined at 500 °C for 3 h in a N_2 atmosphere to investigate its phase change in the reaction. XRD patterns of the calcined CoMo bimetallic catalysts are shown in Figure 6. The patterns of the CoMo bimetallic catalyst calcined at 500 °C can be indexed to β-$CoMoO_4$ (JCPDS card number 21-0868), as indicated by the appearance of the characteristic peak at 26.6°.[16] The oil-soluble and bimetallic feature of the catalyst with its high surface area can contribute to the enhancement of the catalytic activity.

3.3. Analysis of the Liquid Product. The performance of the hydrocracking process depends upon not only the asphaltene conversion and the liquid yield but also the composition of the product oil. As summarized in Table 2, the CoMo bimetallic catalyst gave the lowest resid (boiling point > 500 °C) yield and the highest distillate yield (boiling point = 200−350 °C) among the catalysts tested. Thermal reaction without a catalyst can achieve a high naphtha (boiling point < 200 °C) and a low resid yield, but the liquid yield in this case was relatively low because of the significant production of gas and cokes.

Table 3 shows SARA fractions of the liquid product obtained via hydrocracking with various dispersed catalysts. SARA analysis divides heavy oil components according to their polarizability and polarity using a family of related analytical techniques.

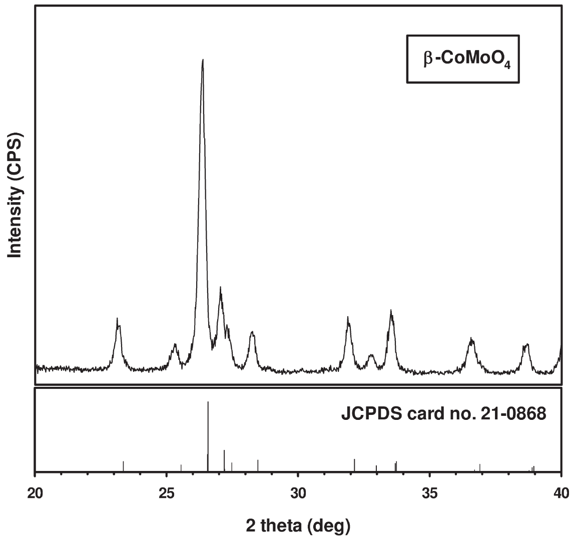

Figure 6. XRD patterns of the CoMo bimetallic catalyst calcined under a N_2 flow.

Table 3. SARA Fractions of Liquid Products

catalysts	bitumen	no catalyst	Co naph	Mo octo	Co + Mo	CoMo
saturates (%)	8.16	10.30	12.18	16.44	18.50	20.25
aromatics (%)	49.78	58.24	54.67	58.87	55.16	53.08
resins (%)	25.73	18.17	21.09	13.10	15.81	17.28
C5-asphaltenes (%)	16.33	13.29	12.06	11.59	10.53	9.40

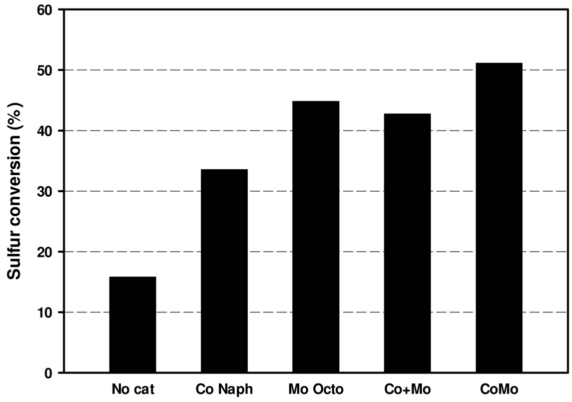

Figure 7. Sulfur conversions of various dispersed catalysts.

Among the various dispersed catalysts, the CoMo bimetallic catalyst produced more saturates and fewer asphaltenes than the monometallic catalysts and their simple mixture.

The sulfur conversion in the hydrocracking reaction is shown in Figure 7. The thermal reaction without a catalyst appears to possess little ability to remove sulfur, while the use of catalysts can enhance sulfur conversion in hydrocracking reactions. Among various dispersed catalysts, a higher sulfur conversion was achieved in the order of Co naph < Co + Mo < Mo octo < CoMo bimetallic catalyst. One peculiar feature is that a bimetallic effect of Co + Mo was not observed clearly during the sulfur conversion process, in contrast to that during the asphaltene conversion. It has been widely accepted regarding the supported catalyst that the hydrodesulfurization (HDS) activity promotion arises from the increase in the intrinsic activity by the active metal sulfide through a chemical structure, such as Co−Mo−S.[17,18] However, in the case of Co + Mo, the possibility that a chemical phase, such as Co−Mo−S, forms to a certain degree is thought to be low because most of the metal species would be separately present in the heavy oil. This indicates that the bimetallic effect can be created when two metals are chemically combined into a single product, such as the CoMo bimetallic catalyst.

4. CONCLUSION

The results of this work confirm the applicability of the oil-soluble CoMo bimetallic catalyst in hydrocracking reactions of heavy oil.

The oil-soluble CoMo bimetallic catalyst, which is composed of Co and Mo, can be prepared easily from layered ammonium cobalt molybdate. The FTIR spectrum of the CoMo bimetallic catalyst indicates that oleic acid is chemisorbed as a carboxylate onto the particle, while two oxygen atoms in the carboxylate are coordinated symmetrically to the surface of the particles.

The prepared CoMo bimetallic catalyst showed excellent performance compared to the monometallic dispersed catalysts and a simple mixture of these catalysts. The CoMo bimetallic dispersed catalyst showed enhanced activity toward asphaltene and sulfur conversion, maximizing the yield of the liquid product containing higher saturated fractions. Although the simple mixing of Co and Mo dispersed catalysts offered synergistic advantages to some extent, their performance levels were lower than those of the CoMo bimetallic catalyst. This is attributed to the low possibility that a chemical phase, such as Co−Mo−S, can form, because two dispersed catalysts should be separately present in heavy oil.

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