

HYDRODESULFURIZATION OF DIBENZOTHIOPHENE OVER SUPPORTED AND UNSUPPORTED MOLYBDENUM CARBIDE CATALYSTS

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Abstract—A series of γ -Al₂O₃ supported molybdenum carbides [carbided Mo/ γ -Al₂O₃ (MCS), Co-Mo/ γ -Al₂O₃ (CMCS), and Ni-Mo/ γ -Al₂O₃ (NMCS)] and unsupported molybdenum carbide (MCUS) were prepared by the temperature-programmed carburization of their corresponding molybdenum nitrides with 20 % CH₄/H₂. XRD and SEM studies show that unsupported molybdenum carbide catalyst possesses a typical crystalline Mo₂C (FCC structure), while supported molybdenum carbide catalysts possess highly dispersed surface molybdenum carbide species on an alumina oxide support. The results of dibenzothiophene (DBT) hydrodesulfurization over molybdenum carbide catalysts show that the reactivity is strongly dependent on the type of catalyst. Supported molybdenum carbide catalysts possess a higher reactivity than the unsupported molybdenum carbide catalyst. In addition, Co or Ni promoted, supported molybdenum carbide catalyst possesses a higher reactivity than the unpromoted, supported molybdenum carbide catalyst. The reactivity, which is also dependent on the reaction conditions, increases with increasing reaction temperature and pressure and contact time. The CO uptakes of the molybdenum carbide catalysts correlate well with overall activity (total rate) for DBT hydrodesulfurization. The major reaction product is biphenyl, with cyclohexylbenzene next in abundance regardless of the type of catalysts and reaction conditions. It was also found that the molybdenum carbide catalysts exhibit stable initial reactivity due to the stable and weak acidic characteristics of these catalysts.

Key words: Carbided Mo/ γ -Al₂O₃, Mo₂C, Promoter, N₂ Adsorption, XRD, SEM, CO Chemisorption, Dibenzothiophene, Hydrodesulfurization

INTRODUCTION

It is well known that molybdenum sulfide catalysts catalyze the petroleum hydrotreating process (hydrodesulfurization, hydrodenitrogenation) commercially by acting as active catalysts [Kim et al., 1988; Lee et al., 1989, 1991, 1995; Shin et al., 1989; Park et al., 1990, 1997; Moon et al., 1994; Oh et al., 1997; Cho et al., 1997]. Recently an introduction of nitrogen or carbon instead of sulfur into transition metals (Mo, W) significantly altered their physical, chemical, electronic, and magnetic properties [Gregg et al., 1982; Volpe et al., 1985; Lee et al., 1988; Markel et al., 1990; Leclercq et al., 1996]. It has been recognized that the transition metal nitrides and carbides possess high thermal stability, mechanical strength, and comparable reactivity to the VIII group metals (Ru, Rh, Pt) for some reactions [Ledoux et al., 1992; Leclercq et al., 1989; Ranhotra et al., 1987]. The importance of transition metal nitrides and carbides in catalytic applications has led to numerous fundamental studies relating their specific surface properties to catalytic behavior [Nagai et al., 1993, 1995; Markel et al., 1990; Schlatter et al., 1988; Abe et al., 1993; Delporte et al., 1995; Lee et al., 1985, 1988, 1993].

The transition metal nitrides and carbides are in particular

attractive to hydrodesulfurization and hydrodenitrogenation due to their resistance to poisoning materials, such as S and N compounds, and to sintering at high temperature [Lee et al., 1993; Markel et al., 1990; Ranhotra et al., 1987]. In addition, Nagai et al. [1993, 1995] have also reported that the nitrided Mo/ γ -Al₂O₃ catalyst exhibits a higher reactivity for dibenzothiophene hydrodesulfurization than its sulfided form. However, their usage in the catalysis industry has been limited due to the low surface area. The transition metal nitrides and carbides with high surface area could be successfully prepared by using the topotatic reaction method [Oyama et al., 1988; Robert et al., 1994; Volpe et al., 1985]. However, these catalysts still possess relatively low average pore diameter so that a reaction involving a large size of reactant molecules, hydrodesulfurization or hydrodenitrogenation reaction, is limited due to the high restraint in internal mass transfer. Recently, several research groups have proposed supported transition metal nitrides and carbides in order to overcome the drawbacks of unsupported transition metal nitrides and carbides [Park et al., 1994, 1997; Nagai et al., 1993, 1995]. Park et al. [1994, 1997] have reported that the supported molybdenum nitrides possess much higher reactivity for dibenzothiophene hydrodesulfurization than the unsupported molybdenum nitrides. In addition, they have also reported that molybdenum nitrides and carbides require less H₂ during the hydrodesulfurization reaction than their sulfided forms [Park et al., 1994]. In this investiga-

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tion, we report the surface properties of supported and unsupported molybdenum carbide catalysts and their reactivity and selectivity for dibenzothiophene hydrosulfurization.

EXPERIMENTAL

1. Catalyst Preparation

The support material used in this investigation was γ - Al_2O_3 from Rhone-Poulenc Recherches, with a surface area of $220 \text{ m}^2\text{g}^{-1}$. The γ - Al_2O_3 supported Mo, Ni-Mo, and Co-Mo carbides and unsupported molybdenum carbide, Mo_2C , were prepared by the temperature programmed carburization of their corresponding molybdenum nitride precursors with 20% CH_4/H_2 . The molybdenum nitride precursors were prepared by the temperature-programmed reaction of 12 wt% $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$, 3 wt% NiO (or CoO)-12 wt% $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$, and MoO_3 with NH_3 , respectively. The detailed preparation procedure of molybdenum nitride precursors was described elsewhere [Park et al., 1997]. 0.5 g of molybdenum nitride precursor was charged into 6-mm-o.d. quartz tubular reactor. 100 mlmin^{-1} of 20% CH_4/H_2 (Sungkang Specialty Gas, 99.9% purity) was introduced to this system. The system increased its temperature to 673 K at 12 Kmin^{-1} and to a final temperature of 950 K at 0.5 Kmin^{-1} and was then maintained at this final temperature for 4 h. The samples were cooled down to room temperature and passivated for 1 h in a flowing mixture of 1% O_2/He in order to avoid drastic reoxidation when they were exposed to air.

2. N_2 Adsorption

BET surface areas of molybdenum carbide catalysts were determined by N_2 adsorption at 77 K using ASAP 2010 (Micromeritics). Prior to the N_2 adsorption, the catalyst was evacuated to be 10^{-3} torr at 623 K for 12 h in order to remove the moisture and impurities adsorbed on the catalyst surface.

3. X-ray Powder Diffraction (XRD) and Scanning Electron Microscopy (SEM)

XRD patterns of molybdenum carbide catalysts were obtained with a diffractometer (Rigaku, Dmax IIA, $\text{CuK}\alpha$, $\lambda = 1.5405$). The microstructure of molybdenum carbide catalysts was observed by SEM with a Hitachi Model H-6010.

4. CO Chemisorption

CO chemisorption was performed with a standard volumetric adsorption method using ASAP 2010 (Micromeritics). The molybdenum carbide catalysts were transferred to a vacuum system of ASAP 2010 without exposure to air and evacuated at 623 K to 10^{-5} torr. For 0.5, 100, 200, 300, and 400 torr of CO were admitted at 196 K (dry ice bath), respectively. The amounts of CO chemisorbed on the molybdenum carbide catalysts were determined by double isotherms.

5. Catalytic Reactions

Hydrosulfurization of dibenzothiophene (DBT) over molybdenum carbide catalysts was carried out in an isothermal fixed-bed continuous-flow reactor (Geomecanique Cataest, LPD model C) at different pressures ($10\text{--}50 \times 10^5 \text{ Pa}$) and temperatures (623–723 K) and contact times ($0.01\text{--}0.04 \text{ g}_{\text{cat}}\text{hml}^{-1}\text{feed}$). The reactor was held in a vertical position (19 mm-o.d. stainless tube), and the mixture of catalyst (50–80 mesh) and carborundum (SiC , 80 mesh) in the ratio of 1/5 weight base was treated in flowing H_2 at 950 K for 2 h. The mixture gas, $\text{H}_2/\text{DBT}=100$

(mol/mol), flowed from top to bottom of reactor. The reaction products were analyzed by an on-line gas chromatograph (HP 5890II) containing an ultra-performance capillary column ($50 \text{ m} \times 0.32 \text{ mm} \times 0.52 \text{ m}$, cross-linked methyl silicon gum, 19091A-115) with an FID detector. The catalytic activity and selectivity were measured at steady state, which was reached about 15 h after the initialization of the catalytic reaction.

RESULTS AND DISCUSSION

1. Surface Properties of Molybdenum Carbide Catalysts

BET surface areas of supported and unsupported molybdenum carbide catalysts and their corresponding molybdenum nitride precursors are shown in Table 1. The molybdenum carbide catalysts possess 19–25% lower surface area than the molybdenum nitride precursors. This result suggests that a further modification of the aluminum oxide support occurred during the temperature-programmed carburization of molybdenum nitride precursors by CH_4 at 950 K.

XRD patterns of supported and unsupported molybdenum carbide catalysts are shown in Fig. 1. The unsupported molybdenum nitride (MNUS) precursor possesses (111), (200), (220), and (311) planes of the crystalline Mo_2N at $2\theta=37.0, 43.0, 62.4$, and 74.8 , respectively [Markel et al., 1990; Choi et al., 1994]. The unsupported molybdenum carbide catalyst (MCUS) possesses an XRD pattern assigned to the (111), (200), (221), (023), (042), and (223) planes of the crystalline Mo_2C (FCC structure) at $2\theta=36.8, 42.7, 52.5, 62.5, 72.1$, and 75.0 , respectively [Ranhotra et al., 1987]. The absence of crystalline Mo_2N phases in the XRD pattern of unsupported molybdenum carbide catalyst suggests that the precursor, crystalline Mo_2N , is completely converted to the crystalline Mo_2C during carburization by CH_4 at 950 K. On the other hand, the XRD patterns of supported molybdenum carbide catalysts (MCS, NMCS, CMCS) exhibit only the diffraction line due to the aluminum oxide support. SEM studies of supported and unsupported molybdenum carbide catalysts provide further information on the surface morphology of catalysts. The surface morphology of unsupported molybdenum carbide catalyst (MCUS), Mo_2C , in Fig. 2(b) is essentially unchanged during the temperature-programmed carburization and possesses a large platelet shape that is similar to the molybdenum nitride (MNUS) precursor, Mo_2N , in Fig. 2(a). Whereas, the surface molybdenum carbide species on the supported molybdenum carbide catalysts were highly dispersed and only small grains for alumina support were ob-

Table 1. Surface properties of molybdenum carbide catalysts

Symbols	Catalysts	BET surface area $/\text{m}^2\text{g}_{\text{cat}}^{-1}$
MCUS	Unsupported molybdenum carbide catalyst (Mo_2C^a)	37 (49) ^b
MCS	Carbided $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$	161 (200)
CMCS	Carbided $\text{Co-Mo}/\gamma\text{-Al}_2\text{O}_3$	148 (182)
NMCS	Carbided $\text{Ni-Mo}/\gamma\text{-Al}_2\text{O}_3$	142 (183)

^a Determined by XRD.

^b Numbers in the parentheses represent BET surface areas of molybdenum nitride precursors.

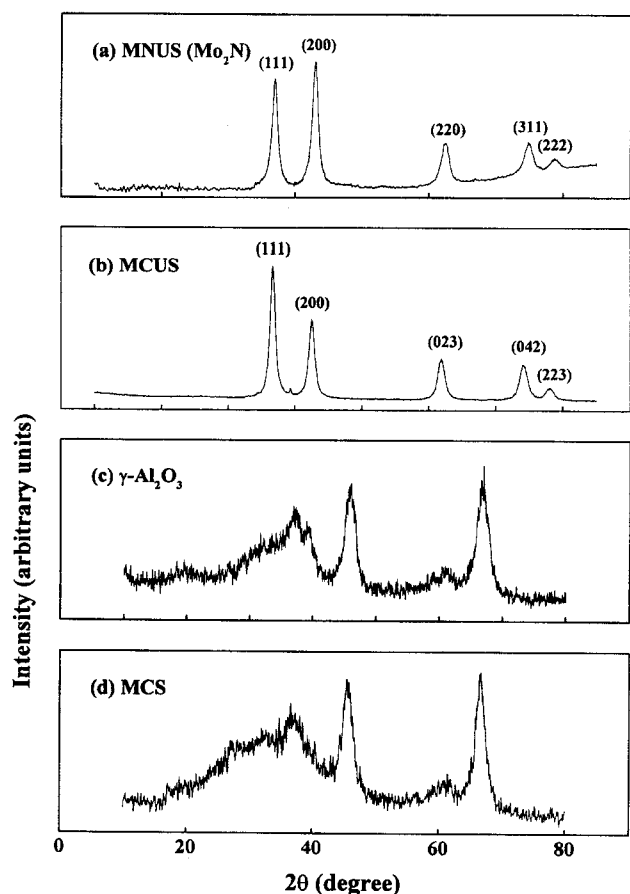


Fig. 1. XRD patterns of supported and unsupported molybdenum carbide catalysts. The symbols are the same as in Table 1.

served. XRD and SEM studies suggest that the N-C exchange reaction over Mo_2N precursor proceeds without any change in surface morphology and produces crystalline Mo_2C phases during the temperature-programmed carburization with CH_4 up to 950 K. On the other hand, the absence of crystalline Mo_2C phases in the XRD and SEM for supported molybdenum carbide catalysts suggests that for these catalysts the surface molybdenum carbide species are highly dispersed on the alumina support and present in either an amorphous state or small crystallites of less than 4 nm in diameter, which are undetectable by XRD or SEM.

2. Hydrodesulfurization of Dibenzothiophene (DBT)

The blank runs for DBT hydrodesulfurization were performed on a stainless tube packed with carborundum (SiC) and quartz wool at different reaction conditions, and only the reaction products produced by thermal cracking of DBT were observed. The conversion caused by the packing materials is less than 2% under reaction conditions used in this investigation; this value is minimal in comparison to the reactivity of the molybdenum carbide catalysts.

The relation between time on stream and reactivity for DBT hydrodesulfurization over molybdenum carbide catalysts is shown in Fig. 3. The molybdenum carbide catalysts exhibit very stable initial reactivity for DBT hydrodesulfurization independent of the reaction time. A similar observation was also made for molybdenum nitride catalysts [Park et al., 1994, 1997]. It was generally accepted that the acid sites present on the sulfided molybdena catalyst facilitate the deposition of coke and result in the loss of surface area [Absi-Halabi et al., 1991]. In addition, Absi-Halabi et al. [1991] also reported that the rapid initial deactivation for hydrodesulfurization over sulfided molyb-

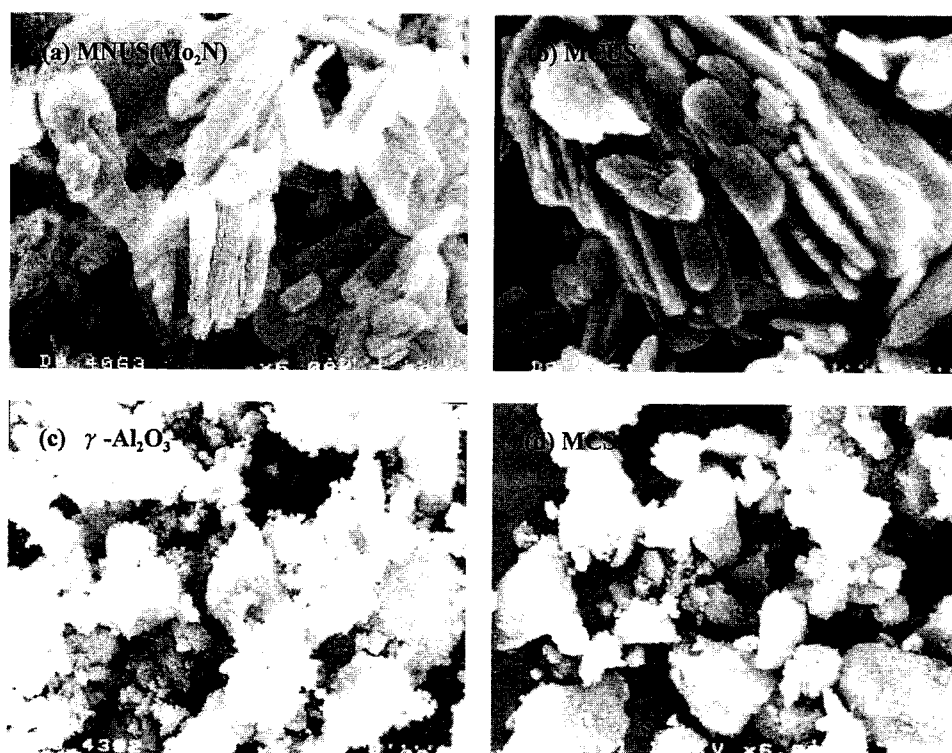


Fig. 2. SEM patterns of supported and unsupported molybdenum carbide catalysts. The symbols are the same as in Table 1.

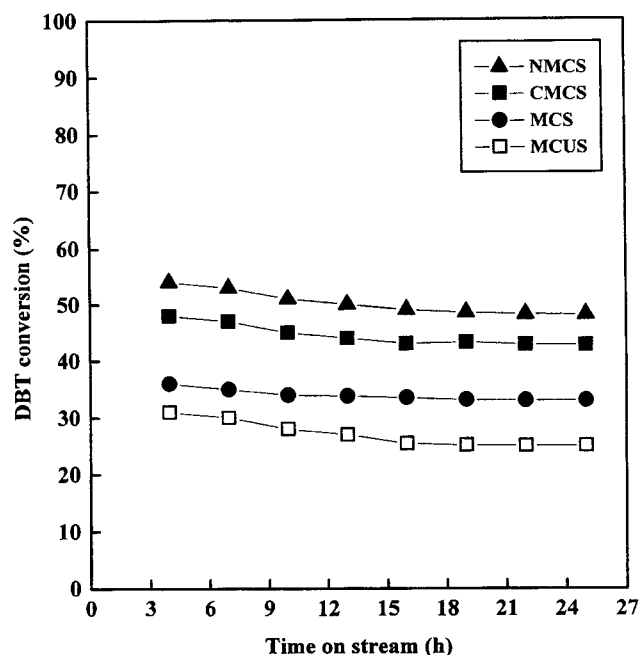


Fig. 3. The relation between conversion and reaction time for DBT hydrodesulfurization over molybdenum carbide catalysts ($T=673$ K, $P=30 \times 10^5$ Pa, $1/\text{LHSV}=0.02 \text{ g}_{\text{cat}}\text{hml}^{-1}\text{feed}$). The symbols are the same as in Table 1.

dena catalyst is associated with the deposition of significant quantities of coke within the first few hours after initiation of the catalytic reaction. Therefore, stabilization of initial reactivity for DBT hydrodesulfurization would be attributed to the weak acidic and stable characteristics of molybdenum carbide catalysts.

The influence of reaction conditions on the reactivity for DBT hydrodesulfurization over supported and unsupported molybdenum carbide catalysts was investigated and the results are shown in Fig. 4-6. The reactivity for DBT hydrodesulfurization increases with increasing reaction temperature and pressure and contact time. It was also found that the reactivity for DBT hydrodesulfurization over molybdenum carbide catalysts is strongly dependent on the type of catalyst regardless of reaction conditions and it decreases in the order: $\text{NMCS} > \text{CMCS} > \text{MCS} > \text{MCUS}$. The result suggests that the supported molybdenum carbide catalysts (MCS, CMCS, and NMCS) possess a higher reactivity than the unsupported molybdenum carbide catalyst (MCUS), and the Co and Ni promoted molybdenum carbide catalysts (CMCS and NMCS) possess a higher reactivity than the unpromoted carbide catalyst (MCS). The major reaction product is biphenyl (BP) and the cyclohexylbenzene (CHB) is next in abundance. The selectivity for BP increases slightly with increasing reaction temperature, but it decreases when the reaction pressure increases. On the other hand, the contact time does not influence the selectivity of BP. Only a trace amount of bicyclohexyl (BCH), *o*-phenylthiophenol (*o*-PTP), 1, 2,3,4-tetrahydrodibenzothiophene (THBDT), and perhydrodibenzothiophene (PDBT) is detected by using GC-mass spectroscopy.

An attempt was made to use CO chemisorption to determine the number of catalytically active sites on the molybdenum

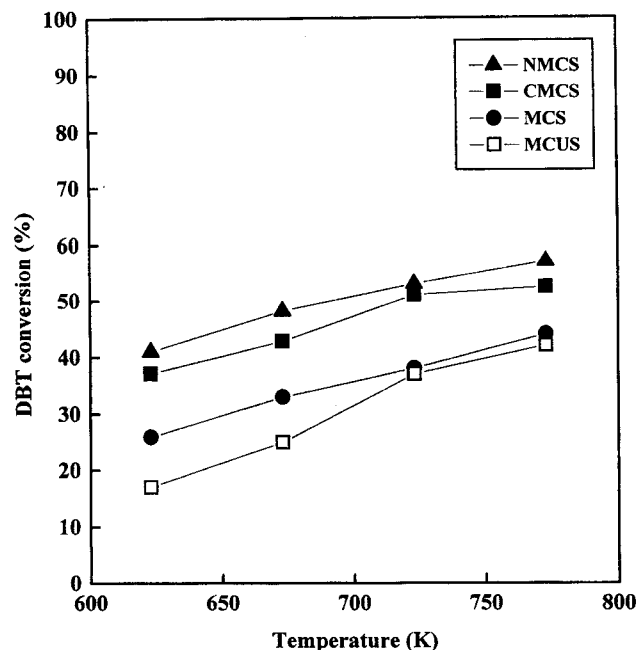


Fig. 4. Catalytic activity for DBT hydrodesulfurization over molybdenum carbide catalysts at different reaction temperatures ($P=30 \times 10^5$ Pa, $1/\text{LHSV}=0.02 \text{ g}_{\text{cat}}\text{hml}^{-1}\text{feed}$). The symbols are the same as in Table 1.

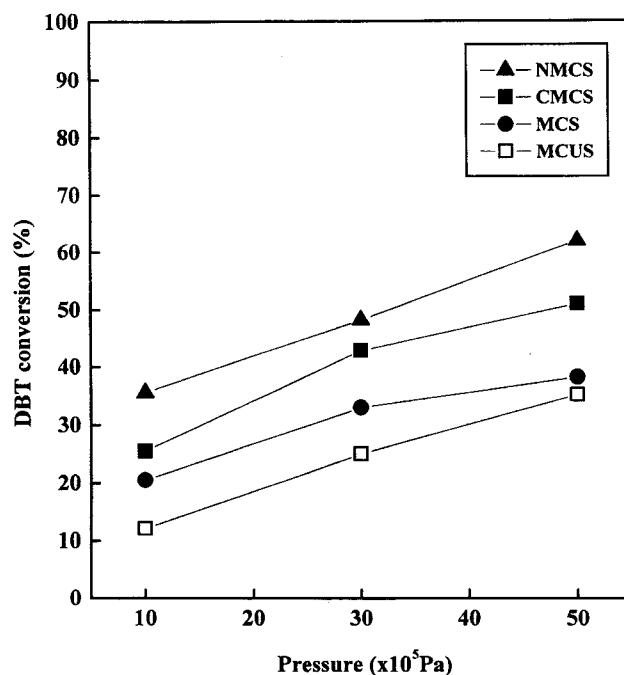


Fig. 5. Catalytic activity for DBT hydrodesulfurization over molybdenum carbide catalysts at different reaction pressures ($T=673$ K, $1/\text{LHSV}=0.02 \text{ g}_{\text{cat}}\text{hml}^{-1}\text{feed}$). The symbols are the same as in Table 1.

carbide catalysts since CO was selectively adsorbed on the coordinately unsaturated Mo sites (catalytically active sites) [Peri, 1984; Zaki et al., 1986]. As shown in Table 2, the amounts of CO adsorbed on the molybdenum carbide catalysts are 0.091, 0.132, 0.142, and 0.145 $\text{mmol g}_{\text{cat}}^{-1}$ for MCUS, MCS, CMCS,

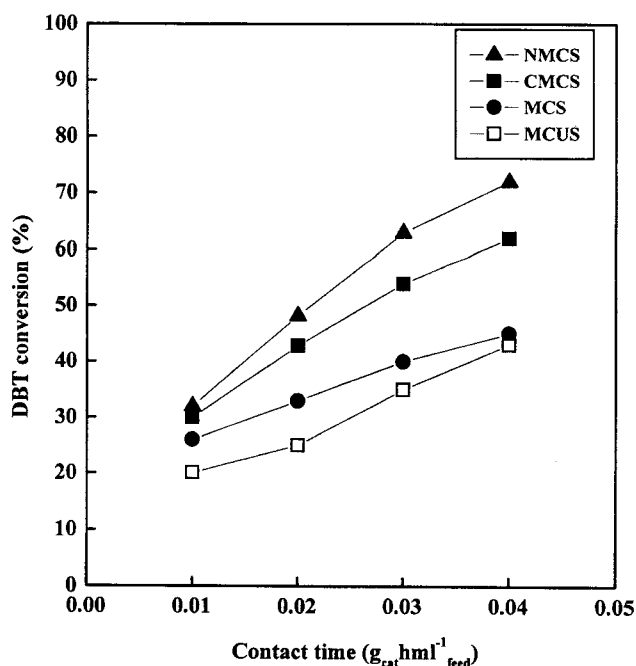


Fig. 6. Catalytic activity for DBT hydrodesulfurization over molybdenum carbide catalysts at different contact times ($T=673$ K, $P=30 \times 10^5$ Pa). The symbols are the same as in Table 1.

Table 2. The relation between CO uptakes and reactivity of DBT hydrodesulfurization over molybdenum carbide catalysts

($T=673$ K, $P=30 \times 10^5$ Pa, $1/\text{LHSV}=0.02 \text{ g}_{\text{cat}} \cdot \text{h ml}^{-1} \text{ feed}$)

Catalysts	CO uptake /mmol g ⁻¹ cat	Number of active sites/g ⁻¹ cat	Total rate /mmol g ⁻¹ cat h ⁻¹	STY ^a /s ⁻¹ site
MCUS	0.091	5.46×10^{19}	43.5	0.1332
MCS	0.132	7.92×10^{19}	55.7	0.1177
CMCS	0.142	8.52×10^{19}	73.9	0.1451
NMCS	0.145	8.70×10^{19}	82.8	0.1592

The symbols are the same in Table 1.

^a: STY represents the site time yield at given reaction conditions.

and NMCS, respectively, and those values correspond to the 5.46×10^{19} , 7.92×10^{19} , 8.52×10^{19} , 8.70×10^{19} of active sites per gram of catalyst, respectively. The result suggests that the supported molybdenum carbide catalysts (MCS, CMCS, NMCS) possess a higher number of active sites than those of unsupported molybdenum carbide catalyst (MCUS). The overall activity (total rate), expressed in millimoles of DBT conversion per gram of catalyst per hour, for MCUS, MCS, CMCS, and NMCS is 43.5, 55.7, 73.9, and 82.8 mmol g⁻¹ cat h⁻¹, respectively. The CO uptakes of the molybdenum carbide catalysts correlate well with total rate for DBT hydrodesulfurization. It is interesting to note that MCUS possesses a higher site time yield than MCS. This result suggests that the activity per site of MCUS for DBT hydrodesulfurization is much higher than that of MCS. Therefore, the lower reactivity of unsupported molybdenum carbide catalyst for DBT hydrodesulfurization is attributed to a lower number of active sites than the supported molybde-

num carbided catalysts. In addition, it is also attributed to the high restraint of internal mass transfer since the ratio of pore diameter of MCUS (22Å) and molecular size of DBT (12Å) is 1.83; this value falls in the region of Knudsen diffusion. The Co and Ni promoted molybdenum carbide catalysts (CMCS and NMCS) possess a higher total rate and site time yield than the unpromoted molybdenum carbide catalyst (MCS). The origin of promotion effect on the DBT hydrodesulfurization over carbided Co (or Ni)-Mo/ γ -Al₂O₃ catalysts is not fully understood in the literature. However, the results of CO chemisorption and DBT hydrodesulfurization over carbided Co (or Ni)-Mo/ γ -Al₂O₃ catalysts suggest that new catalytically active surface species and/or catalytically active sites will be produced during the carburization. Systematic studies are required to clarify the influence of promoter on the reactivity for DBT hydrodesulfurization over carbided Co (or Ni)-Mo/ γ -Al₂O₃ catalysts.

CONCLUSIONS

A series of supported and unsupported molybdenum carbide catalysts were prepared by the temperature-programmed carburization of their corresponding molybdenum nitrides with 20% CH₄/H₂. XRD and SEM studies show that the unsupported molybdenum carbide catalyst (MCUS) possesses a typical crystalline Mo₂C with FCC structure. On the other hand, the supported molybdenum carbide catalysts (MCS, CMCS, and NMCS) possess a highly dispersed molybdenum carbide species. The results of DBT hydrodesulfurization over supported and unsupported molybdenum carbide catalysts show that the reactivity is dependent on the type of catalysts and it decreases in the order: NMCS > CMCS > MCS > MCUS. It was also found that the reactivity is also dependent on the reaction conditions and it increases with increasing reaction temperature, pressure and contact time. The main reaction product is BP, and CHB is next in abundance regardless of the type of catalyst and reaction conditions. In addition, the molybdenum carbide catalysts possess relatively stable initial reactivity due to their weak acidic and stable characteristics.

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