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Activity and thermal stability of sonochemically synthesized MoS_2 and Ni-promoted MoS_2 catalysts

Ara Cho [a], Jae Hyun Koh [a], Sang Il Lee [a,b], Sang Heup Moon [a,*]

[a] School of Chemical and Biological Engineering and Institute of Chemical Processes, Seoul National University, San 56-1, Shillim-dong, Kwanak-ku, Seoul 151-744, Republic of Korea
[b] SK Energy Corporation, Yuseong-ku, Daejeon 305-712, Republic of Korea

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ABSTRACT

Sonochemically synthesized MoS_2/Al_2O_3, which had a hydrodesulfurization (HDS) activity that was significantly greater than that of a catalyst prepared by impregnation, exhibited low thermal stability due to sintering of MoS_2 crystallites at high temperatures. The thermal stability was improved when the catalyst was promoted with Ni. In this study, we compared the activity and thermal stability of different Ni-promoted MoS_2 catalysts, which were prepared by addition of Ni to MoS_2 using either impregnation (IMP) or chemical vapor deposition (CVD). After use in the HDS of dibenzothiophene (DBT) at 673 K for 2 h, the initial activity of the un-promoted catalyst was partially lost, while that of the Ni-promoted catalysts was preserved. Ni added by CVD interacted more intimately with MoS_2 than Ni added by impregnation because CVD allowed selective deposition of Ni on the MoS_2 edge sites. Another advantage of the CVD method over the impregnation method is that $Ni(CO)_4$, which was used as the Ni precursor in the former method, could be decomposed at much lower temperatures than in the case of $Ni(NO_3)_2$, which was used in the impregnation method. As a result, Ni-promoted catalysts prepared using Ni-CVD showed superior HDS activity compared with those prepared using Ni-impregnation.

1. Introduction

Currently, deep hydrodesulfurization (HDS) is an important issue facing refineries due to stringent environmental regulations and the necessity of using low-quality feedstocks [1,2]. The development of a high-performance hydrotreating catalyst is necessary to meet the above demands. Co(Ni)-promoted Mo(W) sulfides supported on phosphorus-containing alumina, which are prepared by impregnation, are commonly used as industrial HDS catalysts [3].

Numerous studies have described the development of new catalysts with greater activity than the current industrial catalysts, using various strategies: (1) new active components, such as metal phosphides and metal carbides [4–7]; (2) new supporting materials, such as MCM-41, zeolite and mixed oxide [8–10]; (3) additives, such as chelating agents (EDTA, NTA) for the formation of a Type II phase [11]; and, (4) new preparation methods, such as sonochemical synthesis [12–14], chemical vapor deposition (CVD) [15–19] and liquid phase adsorption [20]. In particular, sonochemically synthesized MoS_2 catalysts exhibit exceptionally high HDS activities due to the high dispersion and loading of the active phase in the catalysts [12,14].

However, in addition to exhibiting high activity, it is also important that the catalysts are resistant to deactivation under the conditions of practical use. As sonochemically synthesized MoS_2 particles interact weakly with the supporting material [13], these particles are likely to be more vulnerable to sintering than those prepared by impregnation.

In this study, we investigated the thermal stability of sonochemically synthesized MoS_2/Al_2O_3, in particular, its sintering at elevated temperatures. The activity and sintering behavior of two Ni-promoted MoS_2/Al_2O_3, prepared by chemical vapor deposition (CVD) and impregnation (IMP), were compared.

2. Experimental

2.1. Catalyst preparation

MoS_2/Al_2O_3 was synthesized using a sonochemical method, as described previously [14,16,17,19]. First, $Mo(CO)_6$ and elemental sulfur (S_8) were dissolved in a mixed solvent of n-hexadecane (65 ml) and mesitylene (5 ml) at 333 K with stirring. After addition of γ-Al_2O_3 (CONDEA, 206 m^2/g, 0.49 cm^3/g) to the solution, the slurry was exposed to high-intensity ultrasonic irradiation

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[*] Corresponding author. Tel.: +82 2 880 7409; fax: +82 2 875 6697.
E-mail address: shmoon@surf.snu.ac.kr (S.H. Moon).

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(20 kHz) in an argon atmosphere at 333 K for 1.5 h. The un-reacted component and solvent were removed by filtration and washing with n-hexane, followed by drying in vacuum at 473 K for 2 h. The resulting sample was designated as Mo(s).

The other MoS_2/Al_2O_3 catalyst, designated as Mo(i), was prepared by impregnating γ-Al_2O_3 with an aqueous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. This was followed by drying in air at 383 K for 12 h and calcination in air at 723 K for 4 h. The oxide catalyst was pre-sulfided prior to the reaction in a 12.9% H_2S/H_2 gas mixture at 673 K for 2 h.

Ni was deposited on Mo(s) by flowing $Ni(CO)_4$, which was obtained by reacting Ni/C with CO at 308 K, into a reactor containing Mo(s) at room temperature for 5 min [18,19]. The catalyst was then treated with flowing N_2 at 373 K for 0.5 h to completely decompose the surface Ni-carbonyl to Ni. Another set of Ni-promoted catalysts was prepared by impregnating Mo(s) with an aqueous solution of $Ni(NO_3)_2\cdot 6H_2O$, followed by drying in air at 573 or 673 K for 2 h. Prior to the HDS reaction, the catalysts were pre-sulfided in a solution containing 18% dimethyldisulfide (DMDS) and pentadecane under H_2 pressurized to 4.0 MPa at 573 K for 4 h. The resulting catalysts were designated as Ni(c)Mo(s) or Ni(i)Mo(s), depending on whether Ni was introduced using CVD or impregnation. The metal content of the catalysts was analyzed by inductively coupled plasma and atomic emission spectrometry (ICP-AES).

2.2. Pre-treatment of prepared catalysts

Excess sulfur and other species that remained in the prepared Mo(s), as observed in our previous study [14], were removed by treatment of the catalyst with diluted H_2 (5% H_2/Ar). The optimal temperature for removal of the residues without significant loss of activity during H_2-treatment of the catalysts was determined based on the results of the HDS reaction. Although the results are not shown here, activity was maximal after treatment at 473 K and then decreased with an increase in temperature: Mo(s)_H_2 473 K $\geq$ Mo(s)_no treatment $>$ Mo(s)_H_2 573 K $>$ Mo(s)_H_2 673 K. It is noteworthy that the activity of the untreated catalyst was similar to that of the catalyst treated at 473 K, indicating that the untreated catalyst was automatically activated by the conditions of the reaction. Therefore, we fixed the pre-treatment conditions for Mo(s) prior to the reaction test at 473 K in 5% H_2/Ar flow for 2 h. The pre-treated catalysts were subsequently treated in N_2 at temperatures, ranging between 473 and 673 K, for different periods, ranging from 2 to 8 h, to determine their thermal stability, i.e., sintering behavior.

2.3. Activity test

Activities of the catalysts for the HDS of dibenzothiophene (DBT) were measured in an autoclave at 593 K under H_2 pressurized to 4.0 MPa. The autoclave initially contained 30 mg of DBT, which was dissolved in 30 cm^3 of pentadecane. The catalyst loadings used in the reaction tests were 100 and 88 mg for Mo and NiMo, respectively. During the reaction, the reaction mixture was sampled through a tube for a period of up to 240 min. The products were analyzed using a Hewlett Packard 5890 gas chromatograph (GC) equipped with a silicone capillary column and a flame ionized detector (FID).

2.4. Characterization

The powder X-ray diffraction (XRD) patterns of the heat-treated catalysts were measured using a M18XHF-SRA (MAC Science Co.) instrument with Cu radiation at 40 kV and 200 mA. MoS_2 and γ-Al_2O_3 phases were identified by comparison with the data of the International Centre for Diffraction Data (ICDD). Temperature programmed oxidation (TPO) was conducted with a Hiden Mass spectrometer. A sample of the catalyst contained in the reactor was pre-treated with Ar at 423 K for 1 h to remove possible contaminants from the catalyst surface. After cooling the catalyst to room temperature, a 5% O_2/Ar mixture was introduced into the reactor at 20 cm^3/min, while the catalyst was heated at a rate of 10 K/min. Mass spectrometry was used to detect NO, the decomposed species of nitrate, in the outlet gases from the reactor. X-ray photoelectron spectra (XPS) of the catalysts in either the calcined or sulfided state were obtained using an AXIS (KRATOS) spectrometer equipped with a magnesium anode. The spectra were recorded at chamber pressures lower than 10^{-8} mbar. The binding energies of the samples were estimated with XPSPEAK41 software using the C 1s line observed at 284.6 eV as a reference.

NO was used as a probe molecule to estimate the number of active sites on the catalysts. NO uptake was measured using a pulse injection method with a Catalyst Analyzer (BET-CAT, BEL JAPAN, Inc.). Prior to the first adsorption, the catalyst sample was pre-treated in 5% H_2/Ar at 473 K for 2 h and then heated in Ar at temperatures between 473 and 673 K for either 2 or 4 h. After cooling the catalyst to room temperature, 5% NO/Ar gas was injected in pulses through a 1-cm^3 loop to a reactor containing the heat-treated catalyst. This process was repeated several times. After saturating the sample surface with NO, physisorbed NO was removed from the surface by flowing Ar into the reactor at 393 K for 1 h. The second adsorption of NO was conducted in the same manner as the first. The amounts of chemisorbed NO were calculated from the difference in the amounts adsorbed during the first and second adsorption experiments and were normalized according to the catalyst weight.

3. Results and discussion

3.1. Mo(s)

Fig. 1 shows the conversions of DBT obtained using either Mo(i) or Mo(s) at different reaction temperatures, indicates that Mo(s) is more active than Mo(i), as reported previously [14,21]. The conversions obtained using Mo(s) at 553 K were comparable to those obtained using Mo(i) at 593 K, suggesting that the reaction temperature could be lowered by approximately 40 K when Mo(s) was used instead of Mo(i). However, the activity of Mo(s) decreased when the catalyst was treated in N_2 at temperatures higher than 623 K and for a longer period, 4 h, as shown in Fig. 2.

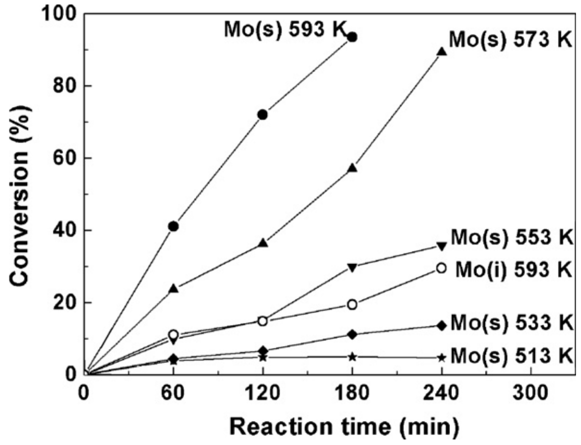

Fig. 1. DBT conversions obtained using Mo(s) at different reaction temperatures and Mo(i) at 593 K.

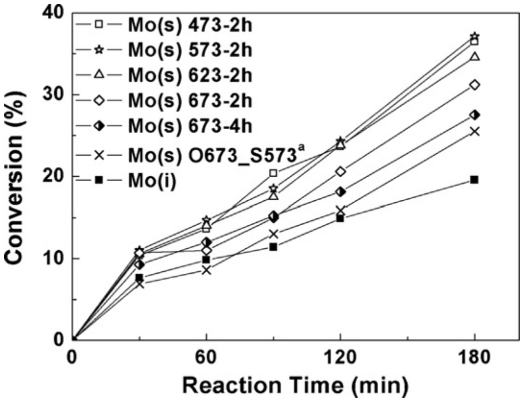

Fig. 2. Rate of DBT HDS obtained using Mo(s), which was heat-treated in N_2 at various temperatures, and Mo(i).

According to Table 1, which shows the distribution of products obtained using catalysts treated under different conditions, BP that was produced by direct desulfurization (DDS) of DBT was suppressed to a greater extent than cyclohexylbenzene (CHB) and dicyclohexyl (DCH) that were produced by hydrogenation (HYD) when the heat-treatment temperature was raised. These results suggest that the treatment decreased the edge sites of MoS_2, which are responsible for the DDS route, rather than the rim sites, which are responsible for the HYD and DDS routes [22]. In Fig. 3, the amounts of NO adsorbed on Mo(s) decreased with an increase in the heat-treatment temperature, suggesting that Mo(s) particles were sintered after the treatment for extended periods.

The effect of heat-treatment on the structure of Mo(s) was assessed using XRD, as shown in Fig. 4. A peak at $2\theta = 14.4^\circ$, which represents the multi-stacked (0 0 2) structure of MoS_2, was not observed even when Mo(s) was heated to 673 K. On the other hand, a peak at approximately $2\theta = 60^\circ$, which represents the (1 1 0) planar structure of MoS_2, increased in intensity due to treatment at high temperatures, particularly at 673 K. The above results agree with previous reports that sonochemically synthesized MoS_2 has a disordered, fractured and minimal layer-stacking nature compared with conventionally impregnated MoS_2, which has multi-stacked and ordered layers [13,14]. Therefore, it can be concluded that Mo(s), which was initially prepared in small particles of poor crystallinity, underwent lateral growth in the (1 1 0) direction, rather than stacking of MoS_2 layers, after treatment at 673 K.

In the case of Mo(s), this result was attributed to a weak interaction between MoS_2 and the support. Dhas et al. reported that sonochemically prepared unsupported Co–Mo–S and supported Co–Mo–S/Al_2O_3 showed similar binding energies in the X-ray photoelectron spectra (XPS), indicating a negligible interaction between the metal sulfide and support [13]. This property leads to an increase in HDS activity, but also to easier sintering of the active sites at high temperatures compared with catalysts prepared by impregnation.

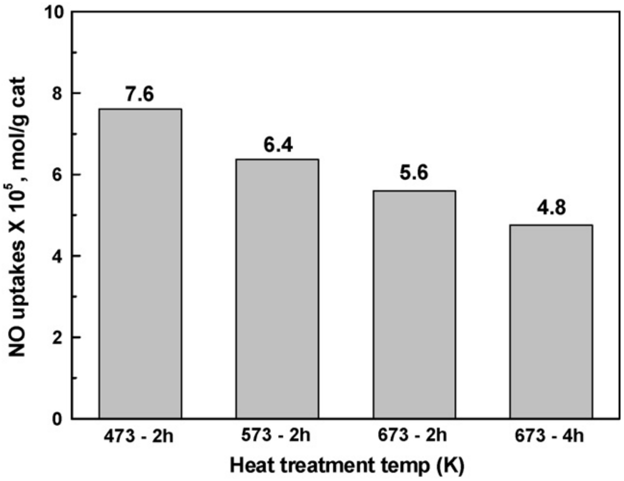

Fig. 3. NO uptakes by Mo(s), which was heat-treated in N_2 at different temperatures between 473 and 673 K.

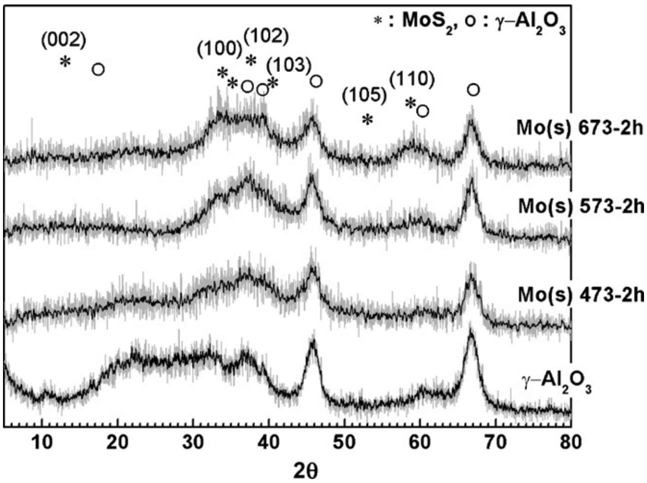

Fig. 4. XRD patterns of Mo(s), which was heat-treated in N_2 at various temperatures.

3.2. Ni-promoted Mo(s)

Fig. 5 compares DBT conversions obtained using Mo(s) and Ni-promoted Mo(s) catalysts, i.e., Ni(i)Mo(s) and Ni(c)Mo(s), which were prepared by addition of Ni via impregnation and CVD, respectively, followed by treatment at different temperatures. The activity was enhanced by Ni-promotion, as reported previously [19,23]. In Fig. 5, it is noteworthy that the activity of Ni(c)Mo(s) was significantly greater than that of Ni(i)Mo(s), which suggests that Ni added by CVD promoted Mo(s) more efficiently than Ni added by impregnation. Unlike Mo(s), Ni(c)Mo(s) did not show a decrease in the activity nor in the NO uptake (Table 2) after treatment at 673 K, supporting the argument that Ni effectively

Table 1
Distribution of products obtained by DBT HDS for 120 min using Mo(s) treated at different temperatures.

Catalyst	Heat-treatment temp. (K)	Conversion (%) (relative values)	Product distribution ($\times 10^5$ mol) (relative values)	
			BP	CHB + DCH
Mo(s)	473-2 h	23.7 (1.00)	2.4 (1.00)	1.5 (1.00)
	573-2 h	24.3 (1.02)	2.4 (1.00)	1.5 (1.00)
	623-2 h	23.8 (1.00)	2.3 (0.96)	1.6 (1.07)
	673-2 h	20.6 (0.87)	1.8 (0.75)	1.6 (1.07)
	673-4 h	18.1 (0.76)	1.6 (0.67)	1.3 (0.87)

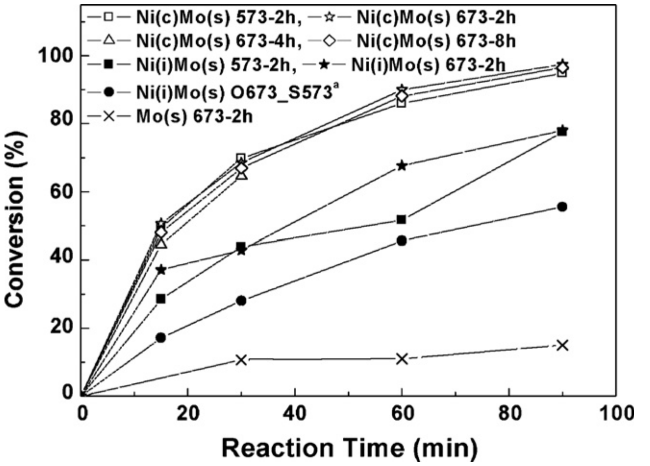

Fig. 5. Rate of DBT HDS obtained using Ni(c)Mo(s) and Ni(i)Mo(s), which was heat-treated in N_2 at various temperatures. [a]Calcination at 673 K for 2 h followed by re-sulfidation at 573 K.

Table 2
NO uptakes by Ni(c)Mo(s), which was heat-treated in N_2 at 573 and 673 K.

Heat-treatment temp. (K)	NO uptakes ($\times 10^5$) (mol/g cat)
573-2 h	12.1
673-2 h	11.9

suppressed the sintering of MoS_2 particles that were produced by a sonochemical method.

One reason for the lower activity of Ni(i)Mo(s) compared with Ni(c)Mo(s) is the incomplete decomposition of $Ni(NO_3)_2$, which was used as the Ni precursor in the impregnation process. Fig. 6 presents the results of the TPO experiments performed using three different Ni(i)Mo(s) samples: simply dried at 383 K; dried at 383 K and calcined at 573 K; and, dried at 383 K and calcined at 673 K. An NO peak at approximately 500 K originated from the Ni nitrate precursor remaining in the sample catalyst. The results indicate that the Ni precursor remained in the catalyst at 573 K, but was completely decomposed at 673 K.

The XPS results in Fig. 7 show four major peaks, including one at 226 eV originating from S2 s, and three at higher energies due to Mo 3d. The peaks of Mo 3d were deconvoluted into 6 peaks, representing Mo $3d_{5/2}$ and Mo $3d_{3/2}$, according to their oxidation states. Mo $3d_{5/2}$ peaks observed at 229, 231 and 233 eV originated

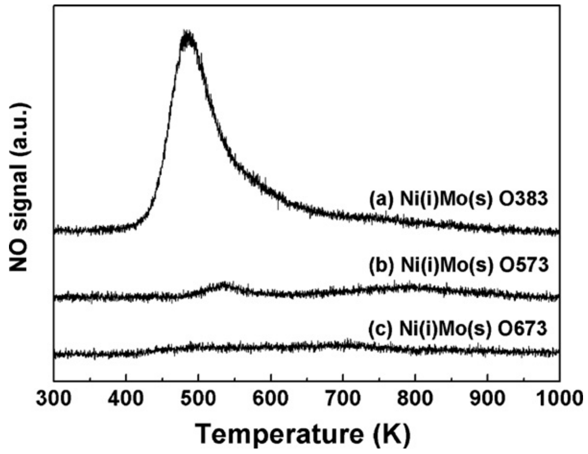

Fig. 6. TPO patterns of Ni(i)Mo(s) catalysts: after (a) drying at 383 K, (b) drying at 383 K followed by calcinations at 573 K, and (c) drying at 383 K followed by calcinations at 673 K.

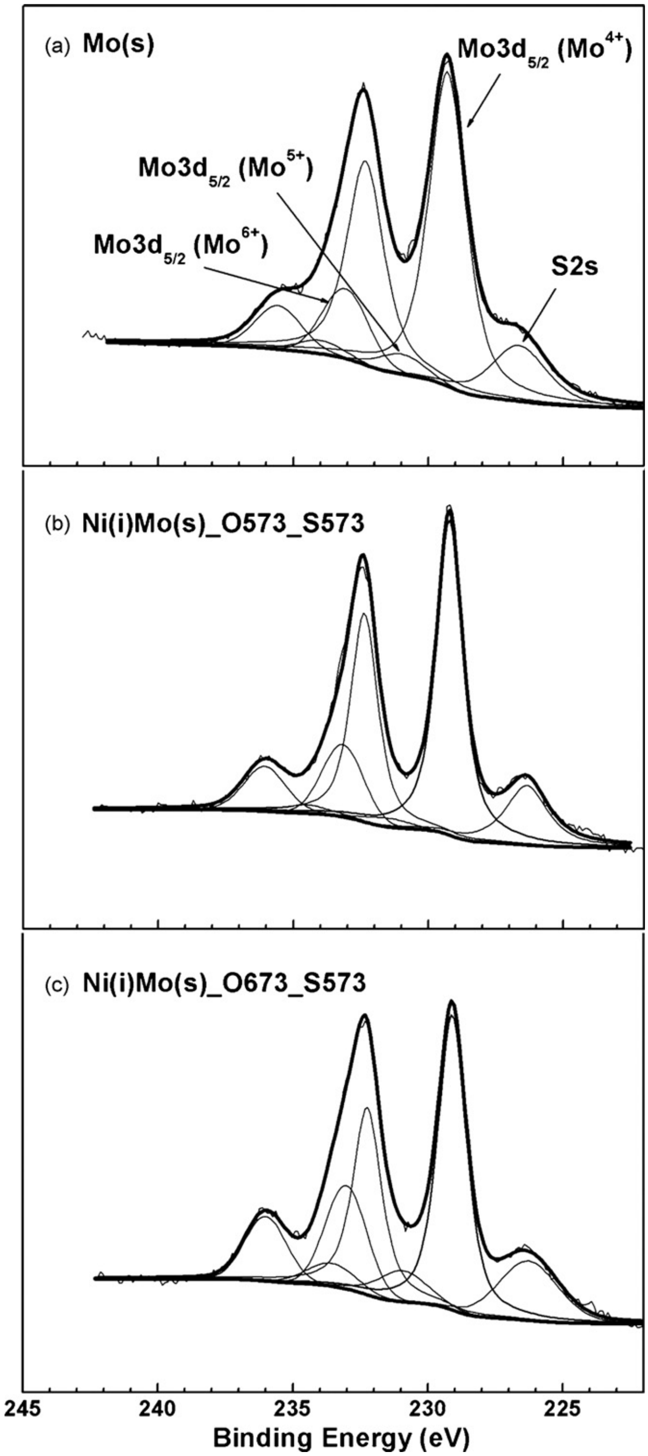

Fig. 7. XPS spectra of Mo 3d obtained for Mo(s) and Ni(i)Mo(s) catalysts: (a) Mo(s), (b) Ni(i)Mo(s) calcined at 573 K followed by sulfidation at 573 K, and (c) Ni(i)Mo(s) calcined at 673 K followed by sulfidation at 573 K.

Table 3
Distribution of the Mo species of different oxidation states in Mo(s) and Ni(i)Mo(s) catalysts.

Catalysts	Mo $3d_{5/2}$ (%)		
	Mo^{4+}	Mo^{5+}	Mo^{6+}
Mo(s)	79	5	16
Ni(i)Mo(s) O573 S573	77	3	20
Ni(i)Mo(s) O673 S573	65	10	25

Table 4
Distribution of products obtained by DBT HDS for 60 min using Ni(c)Mo(s) and Ni(i)Mo(s) treated at different temperatures.

Catalyst	Heat-treatment temp. (K)	Conversion (%) (relative values)	Product distribution ($\times10^5$ mol) (relative values)	
			BP	CHB + DCH
Ni(c)Mo(s)	573-2 h	86.0 (1.00)	10.9 (1.00)	3.1 (1.00)
	673-2 h	90.0 (1.05)	11.1 (1.02)	3.5 (1.13)
	673-4 h	85.1 (0.99)	10.5 (0.96)	3.4 (1.10)
	673-8 h	88.1 (1.02)	10.9 (1.00)	3.5 (1.13)
Ni(i)Mo(s)	673-2 h	67.7 (0.79)	8.2 (0.75)	2.8 (0.90)
	O673_S573	45.6 (0.53)	5.4 (0.50)	2.0 (0.65)

from Mo^{4+} of MoS_2, Mo^{5+} of partially oxidized MoS_xO_y, and Mo^{6+} of MoO_3, respectively. All of the Mo 3d binding energies agree with previously reported values [24,25]. Table 3 lists the relative concentrations of the above three Mo species estimated from the intensities of the individual peaks. Mo(s) contained 79% of Mo as MoS_2. A similar fraction of MoS_2, 77%, was contained in Ni(i)Mo(s)_O573_S573, which had been calcined and subsequently sulfided at 573 K. However, the fraction was lowered to 65% when Ni(i)Mo(s) had been calcined at 673 K prior to sulfidation at 573 K, as in the case of Ni(i)Mo(s)_O673_S573.

The above results suggest that Mo(s), which had been oxidized at 673 K for the decomposition of $Ni(NO_3)_2$, could not be re-sulfided to the initial state. When the catalyst had been calcined at 573 K, re-sulfidation was possible, but the Ni precursor was incompletely decomposed, as demonstrated by the TPO results shown in Fig. 6. Both decreased sulfidation of Mo species and the incomplete decomposition of $Ni(NO_3)_2$ in Ni(i)Mo(s) will eventually lower the HDS activity. On the other hand, Ni(c)Mo(s) should not suffer from the above problems because the Ni precursor used in the CVD process, $Ni(CO)_4$, was readily decomposed at 373 K, as reported in our previous study [18,19].

The other reason for the different activities of Ni(i)Mo(s) and Ni(c)Mo(s), observed in Fig. 5, is explained below. The HDS of DBT proceeds largely via DDS rather than HYD [26]. It was also reported that the DDS route was promoted on the Ni–Mo–S species that formed on the edge sites of MoS_2 by interaction with added Ni, while HYD was favored on the species that formed on the rim sites of MoS_2 [22]. Our previous study indicated that Ni added to Mo(s) via CVD was selectively deposited on MoS_2, preferentially on the edge sites, such that DDS was favored over HYD [18,19]. On the other hand, Ni added via impregnation was not preferentially deposited on MoS_2, but, rather, was randomly deposited on the catalyst surface. Consequently, the interaction between added Ni and MoS_2 was expected to be less intimate than in the case of Ni-CVD. In fact, the above difference in the effects of added Ni on the HDS activity between the two methods of Ni addition was observed in this study. In Table 4, Ni(i)Mo(s) shows relatively low conversions, corresponding to 53–79% of those of Ni(c)Mo(s). This was due to a greater decrease in the DDS rates than in the HYD rates. In the case of Ni(i)Mo(s), BP production via DDS was significantly suppressed, to 50–76% of BP production for Ni(c)-Mo(s). In contrast, the decrease in the production of CHB and DCH via HYD was less significant, to 65–89% of production with Ni(c)Mo(s).

4. Conclusions

Sonochemically synthesized MoS_2, which was highly active for HDS, partially lost the activity after treatment at temperatures higher than 623 K due to the lateral growth of surface MoS_2 layers. The thermal stability of the catalyst, as well as its activity, was improved when the catalyst was promoted with Ni, as indicated by the results of NO uptakes and reaction tests. Between two methods of Ni addition that were used in this study, CVD and impregnation, the former was more effective for promoting the catalyst with Ni because the method allowed the selective deposition of Ni on the edge sites of MoS_2. The other advantage of the CVD method was that $Ni(CO)_4$, which was used as the Ni precursor in the process, was decomposed at a relatively low temperature, 373 K, whereas $Ni(NO_3)_2$, which was the Ni precursor in the impregnation process, was decomposed by calcination at 673 K. Consequently, Ni(i)Mo(s) catalyst was only partially re-sulfided after the heat-treatment at 673 K and showed the activity lower than that of Ni(c)Mo(s).

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