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Properties of unsupported MoS_2 species produced in the preparation of MoS_2/Al_2O_3 using a sonochemical method

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Abstract−Unsupported MoS_2 particles, which were produced in the preparation of MoS_2/Al_2O_3 using a sonochemical method, were successfully separated from the prepared sample catalyst by adding oleylamine as an agent for dispersing the unsupported particles. The fraction of the unsupported MoS_2, which was estimated based on Mo balance, varied between 0.03 and 0.4, independent of the Mo loading levels investigated (6-54 wt% of Mo). The activity of the unsupported MoS_2 for the hydrodesulfurization of dibenzothiophene was nearly the same as that of the Al_2O_3-supported MoS_2, indicating that the activity of the prepared catalyst was not affected by the presence of the unsupported MoS_2 particles.

Key words: Hydrodesulfurization, Dibenzothiophene, Sonochemistry, MoS_2, Oleylamine

INTRODUCTION

The development of active catalysts for deep hydrodesulfurization (HDS) has become of great importance in recent years due to the reinforcement of environmental regulations that limit sulfur levels in oil fractions. One of the strategies to improve the activity of HDS catalysts is to increase the Mo content, while maintaining the high dispersion of catalytically active MoS_2 species. A conventional method for the preparation of MoS_2/Al_2O_3 catalysts is to impregnate Al_2O_3 with an aqueous solution of molybdenum precursor, e.g., ammonium heptamolybdate. However, this method has a drawback of producing catalysts of limited dispersion because MoS_2 particles easily agglomerate at high Mo loading [1,2]. Alternatively, a sonochemical method allows the synthesis of nanostructured MoS_2 particles, which results in an increased dispersion of MoS_2 species. Our previous studies reported that the activity of MoS_2/Al_2O_3 catalyst, prepared using a sonochemical method, was remarkably improved as compared with that of impregnated one, and that the activity enhancement was attributed to an increase in the dispersion of MoS_2 [3-5]. The activity of the sonochemically prepared catalyst was further enhanced by promotion with Co or Ni using an impregnation or a chemical vapor deposition (CVD) method [6-8].

The sonochemistry in a solution is the result of acoustic cavitation, which consists of three steps. By irradiating a high-intensity ultrasound, small bubbles are created and grow in the solution by repeated expansion and compression. Eventually, the bubbles explode and collapse. Local hot spots, which have extremely high temperature (~5,000 K), pressure (~2,000 atm), and rapid cooling rate ($\sim 10^{10}$ K/s), are created in the collapsing bubbles. These conditions provide an energy that is high enough to initiate the decomposition of organometallic compounds such that the nano-structured materials can be finally synthesized [9-11].

During the preparation of MoS_2/Al_2O_3 using the sonochemical method, MoS_2 nano-particles that are produced in the pore structures of Al_2O_3 can be easily deposited on the Al_2O_3 surface. However, the MoS_2 particles can also be produced at positions far from the Al_2O_3, in which case the particles are hardly deposited on Al_2O_3. Accordingly, fractional amounts of produced MoS_2 can be unsupported. The presence of the unsupported MoS_2 can lead to the misinterpretation of the performance and the characteristics of prepared MoS_2/Al_2O_3 sample catalysts.

One of the objectives of the present work was to measure the amounts of unsupported MoS_2 particles produced in the preparation of MoS_2/Al_2O_3 catalysts by using the sonochemical method. We attempted to find experimental conditions that allowed the separation of the unsupported MoS_2 from the prepared sample catalyst. Fractional amounts of the unsupported MoS_2 were measured for the sample catalysts prepared under different conditions. The main factor responsible for the fractional amounts was investigated for samples of different Mo content, which were analyzed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). We also compared the performance of both the supported and the unsupported MoS_2 in the HDS of dibenzothiophene (DBT) to study the effect of the unsupported MoS_2 on the apparent activity of the prepared sample catalyst.

EXPERIMENTAL

1. Catalyst Preparation

Typical procedures for the preparation of MoS_2/Al_2O_3 using a sonochemical method have been described previously [3-8]. A slurry of molybdenum hexacarbonyl ($Mo(CO)_6$) and elemental sulfur (S_8) in a mixed solvent containing 65 ml of hexadecane and 5 ml of mesitylene was vigorously stirred in a flowing Ar atmosphere at 333 K for 1 h to dissolve $Mo(CO)_6$ and S_8 in the solution. Al_2O_3 (CONDEA, 206 m^2/g surface area and 0.46 cm^3/g pore volume) was added to the solution, which was subsequently purged with Ar at 333 K for 30 min. The slurry solution was irradiated with a high-intensity ultrasound (Sonics & Materials, model VCX-600, 1 cm diameter

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Ti horn, 20 kHz, 100 W/cm^2) in Ar atmosphere at 333 K for 1.5 h. The prepared MoS_2/Al_2O_3 powder was washed with excess amounts of *n*-hexane, prior to being used for the separation of the unsupported MoS_2 as described in the subsequent section.

To adjust the Mo content of the catalyst, different amounts of $Mo(CO)_6$ and Al_2O_3 were added to the slurry solution. The amount of added $Mo(CO)_6$ was varied from 0.264 g (1 mmol Mo) to 1.32 g (5 mmol Mo), and that of Al_2O_3 from 0.1 g to 1.0 g. The amount of added sulfur was adjusted such that the atomic ratio of S/Mo was equal to 2. As a result, the Mo content in the prepared catalysts was in the range of 6-54 wt%.

Unsupported MoS_2 catalysts were also prepared by the same method for comparison. Conditions were the same as for the preparation of MoS_2/Al_2O_3 except that Al_2O_3 was not included in the reaction solution.

2. Separation of Unsupported MoS_2

Unsupported MoS_2 particles, which were included in the MoS_2/Al_2O_3 catalysts prepared by the sonochemical method, were separated from the prepared sample by adding oleylamine ($C_{18}H_{37}N$) to the solution containing the prepared catalysts. 0.65 g of oleylamine was added to the slurry containing 0.2 g of MoS_2/Al_2O_3 and 200 ml of *n*-hexane, followed by agitation in an ultrasonic bath (40 kHz, 1 W/cm^2) for 1 h. The slurry solution, which contained unsupported MoS_2 particles, was filtered using filter paper of 20 μm pores. The unsupported MoS_2, which was dispersed in the solution due to added oleylamine and therefore passed through the filter paper, could be separated from the supported catalysts, which were in the size range of 150-180 μm. The powders remaining on the filter paper, i.e., Al_2O_3-supported catalysts, were recovered after washing with *n*-hexane.

For comparison, the prepared MoS_2/Al_2O_3 sample catalyst was also recovered without separating the unsupported MoS_2, followed by filtration and washing with *n*-hexane in the absence of oleylamine.

Both catalysts were calcined in air at 773 K for 6 h prior to measuring their Mo content. Fig. 1 shows a schematic diagram for the separation of the unsupported MoS_2 by oleylamine addition.

3. Characterizations

Thermogravimetric analysis (TGA) was performed with the MoS_2/Al_2O_3 sample, from which the unsupported MoS_2 was removed by oleylamine addition, to determine the proper condition for the calcination of the catalyst. The temperature of a sample holder containing 0.03 g of the sample was raised from room temperature to 973 K at a ramping rate of 5 K/min, while air was flowed through the sample holder at a rate of 30 sccm. The weight change of the catalyst was monitored.

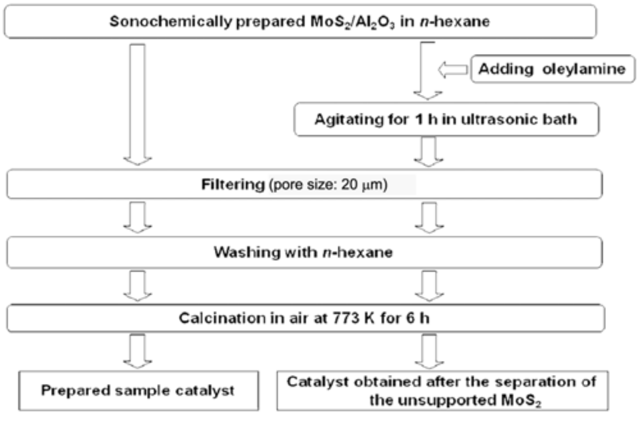

Fig. 1. Schematic diagram for the separation of the unsupported MoS_2.

The Mo and S contents of the calcined catalysts were measured by ICP-AES, and the contents of carbon, nitrogen and hydrogen were measured by elemental analysis (EA). Based on the Mo content of the calcined catalysts, the fractions of the unsupported MoS_2 in the prepared sample catalysts were calculated from the following equation.

$$\begin{aligned}&\text{Fraction of the unsupported MoS}_2\\&\quad=1-(\text{Mo content of the catalyst after the separation}\\&\qquad\text{of the unsupported MoS}_2)\\&\qquad/(\text{Mo content of the prepared catalyst})\end{aligned} \tag{1}$$

4. Evaluation of the HDS Activity

The activity of the catalyst for the HDS of DBT was examined by the same method as reported previously [3-8]. The reaction was carried out in a 100 cm^3 autoclave reactor at 573 K and an H_2 pressure of 4.0 MPa of H_2 pressure for 2 h. The temperature of the reactor, which contained 0.1 g catalyst, 0.03 g DBT and 30 ml *n*-pentadecane, was raised from room temperature to 573 K at a rate of 5 K/min and then from 573 K to 593 K at a rate of 2 K/min under an H_2 pressure of 0.6 MPa. At 593 K, 4.0 MPa H_2 was introduced into the reactor and the reaction started as the solution was vigorously stirred. Samples of the liquid product were obtained through a 1/16-inch stainless-steel tube every 30 minutes after starting the reaction, and the composition of the sample was analyzed by gas chromatography (GC) using a silicone capillary column (HP1; 0.53 mm in diameter and 30 m long) equipped with a flame-ionization detector (FID).

RESULTS AND DISCUSSIONS

1. Separation of the Unsupported MoS_2

We used various surfactants in order to disperse and selectively remove the unsupported MoS_2 from the sonochemically prepared catalysts. For example, oleylamine [12,13] and oleic acid [14,15], known surfactants for producing nanoparticles and dispersing agglomerates toward small particles, were added to the slurry solution containing the sonochemically prepared supported and unsupported MoS_2 or pure Al_2O_3 in *n*-hexane solvent, and the solution was subsequently agitated in an ultrasonic bath for 1 h. By adding oleylamine, agglomerates of the unsupported MoS_2, which were initially located at the bottom of the container due to their specific density larger than that of *n*-hexane, were disintegrated into smaller particles and suspended in the solution. On the other hand, no change was observed by adding oleic acid to the solution. In the case of the solution containing Al_2O_3, the addition of both surfactants did not make any change in the solution. The above results indicated that the unsupported MoS_2 could be dispersed by the addition of oleylamine, which was finally decided as a dispersing agent in this study.

The pore size of the filter paper was another important parameter for the separation of unsupported MoS_2 particles, which were supposed to be removed from the catalyst by filtration. Two kinds of filter paper, the pore sizes of which were 0.2 and 20 μm, respectively, were tested for the above purpose. The unsupported MoS_2 that was dispersed in the solution by the addition of oleylamine suc-

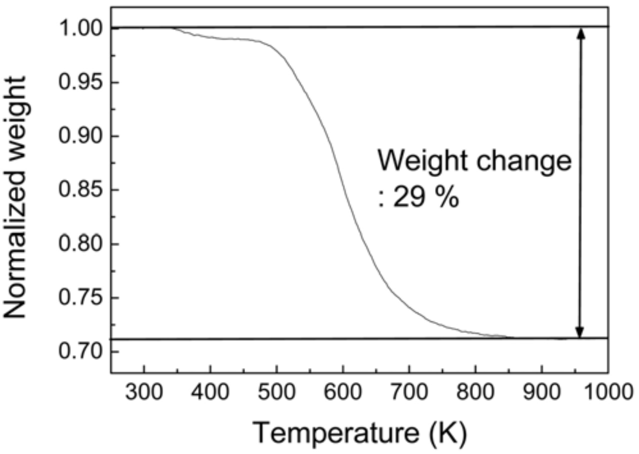

Fig. 2. Thermogravimetric analysis (TGA) of the catalyst obtained after the separation of the unsupported MoS_2.

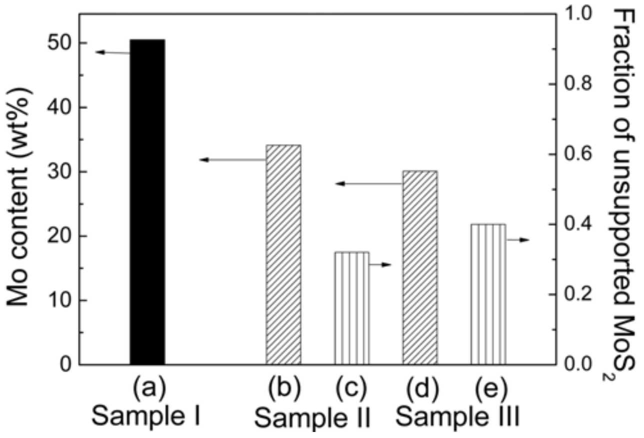

Fig. 3. Mo content and fraction of the unsupported MoS_2 for the prepared sample catalyst (a) and the catalysts obtained after the separation of the unsupported MoS_2 ((b), (c), (d), (e)).

cessfully passed through the 20 μm-size paper but not through the 0.2 μm-size paper. On the other hand, none of the unsupported MoS_2 passed through either of the two kinds of filter paper when oleylamine was not added. Al_2O_3, the size of which was larger than 150 μm, did not pass through neither of the paper independent of the oleylamine addition. Based on the above results, the 20 μm-size paper was finally selected for the filtration.

2. Determination of Calcination Condition

The sonochemically prepared MoS_2/Al_2O_3 contained a small amount of carbon, which originated from the decomposition of alkane solvent and/or carbon monoxide from the Mo precursor, in the form of molybdenum carbides [11]. The catalyst also included sulfur in excess of the amount required for producing MoS_2 species because additional amounts of sulfur were chemisorbed at the vacancy sites of the MoS_2 edges [16]. The catalyst obtained after oleylamine addition was found to have more carbon, nitrogen and hydrogen than without oleylamine addition, obviously due to the deposition of oleylamine on the catalyst surface. Therefore, the Mo content of the sample catalysts obtained after adding oleylamine was measured after the calcination of the sample in air to completely remove carbon, sulfur, nitrogen, and hydrogen from the sample.

Fig. 2 shows changes in the weight of the supported catalyst, which was separated from the prepared sample by adding oleylamine, during the TGA experiment. The sample weight slightly decreased at temperatures below 473 K due to the removal of water, and then sharply decreased until the temperature increased up to 773 K, beyond which the weight loss was negligible. The sample finally lost 29 wt% of the initial weight, which was close to the summed amount of carbon, sulfur, nitrogen, and hydrogen in the initial sample, 30 wt%, as analyzed by EA. This result indicated that the four elements could be completely removed from the catalyst without losing the Mo content by calcination in air. Accordingly, the calcination of the catalysts was performed in air at 773 K for 6 h.

3. Uncertainties Involved in the Separation Process

The first task in this study was to confirm the reproducibility of the separation process. Accordingly, we investigated errors involved in the estimated fractional amounts of the unsupported MoS_2 obtained in the repeated separation processes under the identical condition. A MoS_2/Al_2O_3 sample catalyst, which was obtained from a single batch preparation, was divided into three smaller samples. Sample I was obtained without the addition of oleylamine, and samples II and III were obtained after removing the unsupported MoS_2 under the identical condition. Fig. 3 shows the Mo content and the fraction of unsupported MoS_2 for the three samples. The Mo content of sample I was 50.1 wt% (Fig. 3(a)), whereas that of samples II and III was 34.1 and 30.1 wt%, respectively (Fig. 3(b) and 3(d)). Accordingly, it is apparent that fractional amounts of MoS_2, about 16-20 wt%, were produced as the unsupported species in the sonochemical preparation of MoS_2/Al_2O_3. However, it is also noteworthy that samples II and III showed different Mo content, although the separation procedure was carried out under the identical condition. As the difference in the Mo content was 4 wt%, the fraction of the unsupported MoS_2, defined by equation 1, was 0.32 and 0.40 for samples II and III, respectively. Considering that errors involved in the estimation of the Mo content by ICP-AES were ca. ±1 wt%, the above results indicated that errors in the estimated fractions of the unsupported MoS_2, obtained by the separation process of this study, were ca. ±0.08.

4. Uncertainties Involved in the Catalyst Preparation Process

Fig. 4 shows the Mo content and the fraction of the unsupported

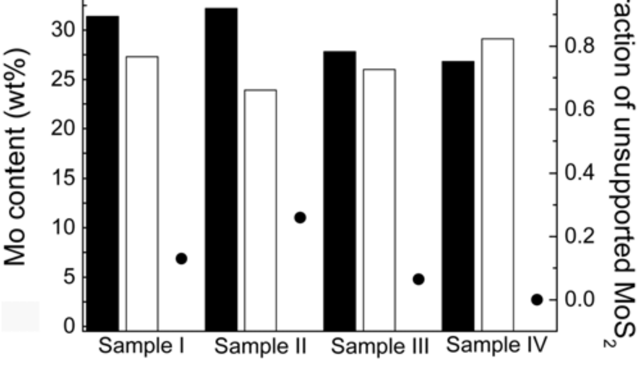

Fig. 4. Mo content of the prepared sample catalysts (■) and the catalysts obtained after the separation of the unsupported MoS_2 (□), and fractions of the unsupported MoS_2 (●).

MoS_2 for four MoS_2/Al_2O_3 sample catalysts, which were prepared in four different batches but under the identical condition. The Mo content of the prepared sample catalysts, prior to the separation of the unsupported MoS_2, was in the range of 27 to 32 wt%, indicating that the catalyst preparation process was subject to certain extents of errors in their Mo content, about 5 wt% in this case.

Suslick [9] reported that the first step in the sonochemistry of the volatile metal carbonyls, e.g., $Mo(CO)_6$, was unimolecular dissociation to remove carbonyl ligands. The intermediate, $Mo(CO)_x$ (x=1-6), could react with sulfur atoms to produce MoS_2 particles as well as with other intermediates. Accordingly, the Mo content of the prepared sample catalysts could be affected by numerous reactions that proceeded in the sonochemical preparation step.

However, additional experiments in this laboratory indicated that the Mo content of the prepared catalysts increased with an increase in the amount of added Mo precursor. For example, the Mo content increased from 7 to 21 wt% with an increase in the added amount of the Mo precursor from 1 to 5 mmol while the amount of Al_2O_3 was fixed at 1.0 g.

The samples obtained after the separation of the unsupported MoS_2 showed the Mo content in the range of 24-29%. Large deviations were observed in the amount of the unsupported MoS_2 among four samples. For instance, the amount was the largest, 8 wt%, for sample II but was a negative value for sample IV, suggesting that the latter sample contained a negligible amount of the unsupported MoS_2. As a result of the above large deviations, the fractions of the unsupported MoS_2 also varied in a wide range, from 0 to 0.26. Consequently, it can be concluded that the amount of the unsupported MoS_2 was subject to significant errors even when the catalyst was prepared under the identical condition. As mentioned in the introduction section, the unsupported MoS_2 could be produced when local hot spots, at which the sonochemical reaction proceeded, were not located near Al_2O_3 powder. The agglomeration of MoS_2 particles could be another reason for producing the unsupported species because the agglomerates with the size larger than that of the pore mouth of Al_2O_3 were prevented from penetration into the internal pores of the support. The large deviations in the fraction of the unsupported MoS_2 among the above samples were attributed to the complicated mechanism of MoS_2 formation in the catalyst preparation step.

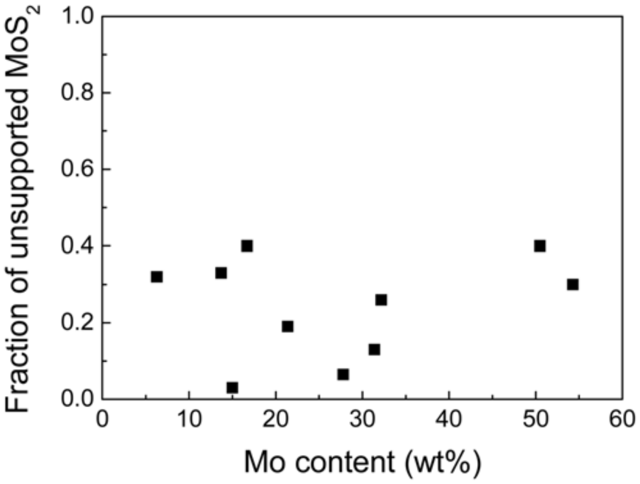

Fig. 5. Fractions of the unsupported MoS_2 in the catalysts prepared under different conditions.

Table 1. DBT HDS of Al_2O_3-supported and unsupported MoS_2 catalysts

	Mo content (wt%)	Activity (1/h-g Mo)
Al_2O_3-supported MoS_2	30	0.97
Unsupported MoS_2	40	1.03

5. Effect of the Catalyst Preparation Condition on the Fraction of the Unsupported MoS_2

The fractions of the unsupported MoS_2 in the catalysts prepared under different conditions are plotted in Fig. 5 versus the Mo content of the prepared catalysts. A specific correlation between the fraction of the unsupported MoS_2 and the Mo content was not observed. However, the data remained in a range of less than 0.4 irrespective of the Mo content that varied between 6 and 54 wt%. Accordingly, it can be concluded that the fractions of the unsupported MoS_2 were determined by the process parameters other than the Mo content of the prepared catalysts. The above results demonstrate that the sonochemical synthesis is a complicated process affected by numerous parameters, requiring further investigation based on systematic diagnoses.

6. Activity of the Unsupported MoS_2

The activity of the unsupported MoS_2 for the HDS of DBT was compared with that of the Al_2O_3-supported MoS_2. Both catalysts exhibited nearly the same activity, as shown in Table 1, indicating that the produced MoS_2 particles had similar surface characteristics regardless of whether they were supported or not. Unsupported MoS_2 catalysts that were prepared by a conventional precipitation method, followed by sulfidation at a typical temperature of 673 K, frequently lost their initial activity due to the sintering of the MoS_2 particles. Contrary to the above case, the MoS_2 particles prepared using a sonochemical method at 333 K, followed by thermal treatment at 473 K, did not undergo sintering and consequently maintained a high initial activity in the HDS process.

Previous studies reported that the activity of the sonochemically prepared MoS_2/Al_2O_3, which was supposed to contain a certain amount of the unsupported MoS_2, for the HDS of DBT and 4,6-dimethyldibenzothiophene increased with an increase in the Mo loading [3-5]. The above result was obtained because the activity of the unsupported MoS_2 was nearly the same as that of the supported MoS_2, as demonstrated in this study. However, it should be pointed out here that the presence of the unsupported MoS_2 in the prepared catalyst would eventually reduce the activity due to the sintering of the MoS_2 during HDS for an extended period and also due to the wash-out of the unsupported MoS_2 particles in the trickled-bed operation of the process. Therefore, efforts to minimize the amounts of the unsupported MoS_2 are still necessary in the preparation of the catalyst using a sonochemical method.

CONCLUSIONS

Unsupported MoS_2 particles produced in the sonochemical preparation of MoS_2/Al_2O_3 were successfully separated from the prepared catalyst by using oleylamine as a dispersing agent, and the fractions of the unsupported MoS_2 obtained under various conditions of the catalyst preparation were measured together with the activity of the MoS_2 for the HDS of DBT. Based on the experimental results, the following conclusions can be made.

A relationship between the fraction of the unsupported MoS_2 and the Mo content of the prepared catalyst was not observed, but the fractions were in the range of less than 0.4 irrespective of the Mo content of the catalysts. The activity of the unsupported MoS_2 was nearly the same as that of the Al_2O_3-supported MoS_2 in the HDS of DBT. Accordingly, the performance of the sonochemically prepared MoS_2/Al_2O_3 catalyst was not affected by the presence of the unsupported MoS_2.

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