

Catalytic activity of molybdenum sulfide prepared by mechanical milling

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Molybdenum sulfide (MoS_2) powder comminuted under various conditions and exfoliated by use of n-butyllithium was characterized mainly from the standpoint of 1-methylnaphthalene hydrogenation (HY) activity. Comminuting conditions are found to give a significant effect on the HY activity. The activity increases in the order of dry comminution in air > wet comminution in water > wet comminution in alcohol. Exfoliation of molybdenum sulfide powder gives a slight effect on the activity, but the effect is not so large as dry comminution in air.

Key words: comminution, molybdenum sulfide, exfoliation, hydrogenation

1. INTRODUCTION

Molybdenum sulfide powder has been utilized as a hydrogenation (HY) and hydrodesulfurization (HDS) catalyst. Tanaka et al. [1] showed that MoS_2 edge planes were active sites for olefin hydrogenation (HY) and isomerization (ISOM) of olefins via alkyl intermediates and that basal planes were active sites for isomerization via tertiary carbonium cation. They also reported that HY correlated well with 3 and ISOM with 2 coordinatively unsaturated (cus) Mo ions. Jalowiecki et al. [2] who used isoprene HY and cis-1,3-pentadiene HY and ISOM found that the optimum S/Mo ratio existed for the highest HY. On unsupported MoS_2 , 3 cus edge Mo ions were reported to be active site in the HY, and 2 and/or 4 cus edge Mo ions in the ISOM. There are, however, still discussions on the catalytic mechanism. It is probable that edge planes of molybdenum sulfide powder are active catalytic sites.

Comminution which can easily produce edge planes of layered materials has been expected to produce highly active HY and HDS catalysts. We studied the effect of comminution on particle properties[3], comminuting such catalytic particles as MoS_2 , NiS and Co_9S_9 under wet conditions and showing that comminuted sulfide particles had higher the hydrogenation of 1-methylnaphthalene (1-MN HY) [4]. We also prepared molybdenum sulfide powder comminuted in wet and dry conditions, demonstrating comminution could make molybdenum sulfide more active hydrogenation catalysts[5]. The effect of various comminution atmospheres on the catalytic activity of molybdenum sulfide is not, however, investigated. On the other hand, specific surface area is usually considered to be one of the important parameters to determine catalytic activity. If the edge of molybdenum sulfide mainly acts as active sites for HY, only the increase of basal plane by exfoliation of molybdenum sulfide is considered not to be useful for

improving the HY catalytic activity.

In this paper, we comminute molybdenum sulfide under 3 different atmospheres, i.e. dry in air, wet in water and wet in alcohol, and also exfoliate and exfoliate, followed by comminuting molybdenum sulfide. The effects of comminution atmospheres and exfoliation on catalytic activity of molybdenum sulfide are examined. The catalytic activity is evaluated from 1-MN HY.

2. EXPERIMENTAL

2.1 Comminution and exfoliation

Comminuting machine The planetary ball mill (Seishin Enterprise, Japan) used has a rotating disk on which we place 3 sample containers 0.12 m in diameter and 0.09 m high. The container rotates around the center of the disk at 420 rpm and on its own axis at 525 rpm in the opposite direction. The centers of the disk and container are 0.115 m apart. Commercially available MoS_2 powder (Aldrich Chemical Company, Inc., USA, 5 g) was charged in the container with 216 g of zirconia balls (0.005 m in diameter). Comminution time is 1,800 s (0.5 h) to 14,400 s (4 h).

Comminution atmosphere MoS_2 was comminuted under 3 different atmospheres; (1) dry in air, (2) wet in water and (3) wet in alcohol (methanol, ethanol, butanol and decanol).

Exfoliation Molybdenum sulfide was first intercalated by mixing with n-butyllithium in hexane for a week after which it was filtered and dried. As soon as water was poured in the intercalated powder, hydrogen gas was evolved by the reaction of butyllithium with water. The pressure of evolved gas exfoliated MoS_2 particles.

2.2 Characterization

Particle characterization BET one-point method (Coulter, USA, SA3100) was used to measure specific surface area. Samples were dried at 573 K for 7,200 s

(2 h) before measurement. X-ray diffraction (XRD) was used to measure the crystallinity of sample powders (Phillips, Netherlands PW1800, Cu K α , 40 kV, 40 mA) at 0.02 deg $\cdot$ s $^{-1}$ and 2θ of 5-80 degree.

Samples were observed by scanning electron microscope (SEM, Hitachi, Japan S-800). X-ray photoelectron spectroscopy (XPS) was conducted using a PHI 5500 (ULVAC-PHI Inc., USA) at AlK α (1486.6 eV). Surface S/Mo and O/Mo ratios were calculated by integrating Mo $3d$, S $2p$ and O $1s$ profiles.

Catalytic activity 1-MN HY with as-received and comminuted MoS $_2$ was used to evaluate catalytic activity. All reactions were conducted at 623 K for 3,600 s (1 h) in a batch reactor with an inner volume of 50 ml. 1-MN of 5 g was charged in the reactor with MoS $_2$ of 0.15 g. The feed and product were analyzed by gas chromatography-mass spectroscopy (GC-MS HP 5970, Hewlett-Packard, USA: column OV-101, 0.25 mm x 50 m) and GC-FID (HP5890: OV-1, 0.32 m x 50 m). 1-MN conversion X was defined as $1 - C/C_0$, where C is the weight of 1-MN after the reaction and C_0 the weight before the reaction. 1-MN HY was a pseudo-first-order reaction[3]. Reaction rate constant per weight of catalyst and per surface area of catalyst are here described by k_w and k_s , respectively. They are calculated by eqs. (2) and (3). Here, t is the reaction time, S the surface area, and W the weight of the catalyst.

$$-dC/dt = k_w WC = k_s SC \quad (1)$$

$$k_w = (Wt)^{-1} \ln(C_0/C) = -(Wt)^{-1} \ln(1-X) \quad (2)$$

$$k_s = (St)^{-1} \ln(C_0/C) = -(St)^{-1} \ln(1-X) \quad (3)$$

3. RESULTS AND DISCUSSION

3.1 Characteristics of comminuted powder

Fig.1 shows specific surface area of MoS $_2$ comminuted under various conditions and exfoliated. Specific surface area of exfoliated powder was almost equal to that of the as-received one, although hydrogen gas was evolved in the exfoliation and the XRD profiles of exfoliated MoS $_2$ significantly broadened as shown in **Fig.2**. Bockrath et al. [6] also exfoliated MoS $_2$ by the same technique, showing that exfoliated sample had a slightly larger specific surface area than as-received one. These results indicate that the exfoliation technique is not strong enough to isolate each S-Mo-S layer and that the exfoliated sample is restacked in drying process. Comminuting the exfoliated sample not only dry in air but also wet in water did not increase specific surface area, whereas comminuting as-received powder under the same atmosphere provided 4 – 6 times larger specific surface area than the as-received one. We do not know the exact reason. MoS $_2$ comminuted in water had larger specific surface area than both as-received one and

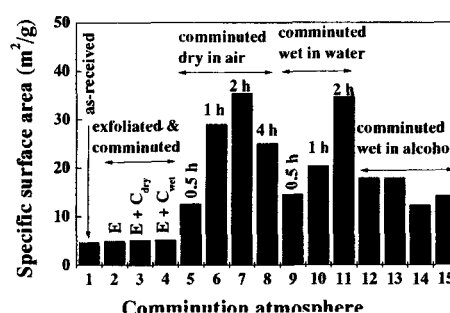


Fig.1 Specific surface area of MoS $_2$ comminuted in various atmospheres

(1. as-received, 2. exfoliated 3. exfoliated, followed by dry comminution in air (3,600s (1h)), 4. exfoliated, followed by wet comminution in water (3,600s (1h)), 5-8. dry comminution in air, (5. for 1,800s (0.5h)), 6. for 3,600s (1h), 7. for 7,200s (2h) and 8. for 14,400s (4h)), 9-11. wet comminution in water, (9. for 1,800s (0.5h), 10. for 3,600s (1h) and 11. for 3,600s (2h)), 12-15. wet comminution in alcohol; (12. in methanol, 13. in ethanol, 14. in butanol and 15. in decanol)

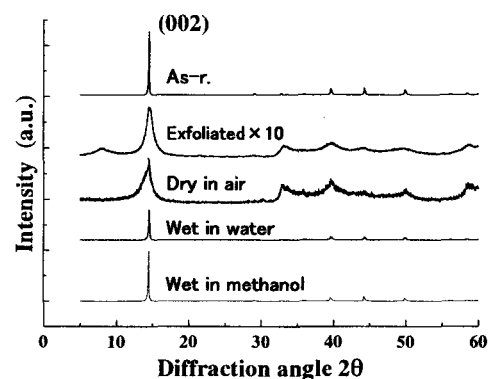


Fig.2 XRD profiles of MoS $_2$ comminuted for 3,600s (1 h) and exfoliated.

powder comminuted in alcohol, but had about the same as dry comminuted sample.

The XRD profiles of exfoliated sample magnified by the factor of 10 has the broad (002) reflection peak at $2\theta = 14.6^\circ$ ($d = 0.62$ nm) and a small peak at $2\theta = 8.0^\circ$ ($d = 1.13$ nm) as shown in Fig.2. This indicates that the exfoliated one is very low crystallinity and partly has a longer lattice distance. The XRD profiles of MoS $_2$ comminuted in air more broaden than those of MoS $_2$ comminuted in water and alcohol, probably because of low friction factor in the liquid between powder and grinding media, and high viscosity of the liquid.

3.2 Catalytic activity

Fig.3 depicts the conversion X of 1-MN with comminuted and exfoliated samples. The conversion

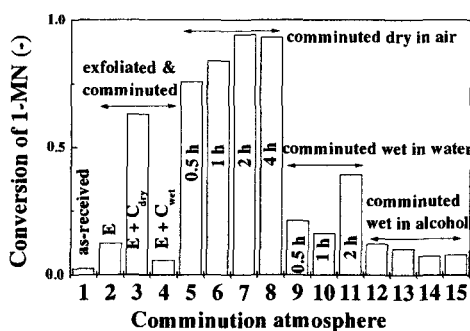


Fig.3 Effect of comminution atmosphere on conversion of 1-MN.

(Figures in x-axis are the same in Fig.1)

was especially improved in the case of comminuting MoS₂ in air. The conversion increased with the increase of the comminution time. A small decrease of the conversion (8 in Fig.3) at comminution time of 14.4 ks (4 h) is partly due to inverse comminution of MoS₂, i.e. decrease in specific surface area. The conversion with MoS₂ comminuted in water was higher than that with MoS₂ comminuted in alcohol. The kind of alcohol did not give little difference in the conversion.

Exfoliation of MoS₂ slightly increased the conversion. Exfoliating, followed by comminuting it in air provided much higher conversion than the exfoliated sample.

Fig.4 shows hydrogenation (HY) activity evaluated both from k_w and k_s . These values were respectively normalized by the reaction rate constant k_{wa} and k_{sa} for as-received MoS₂. The comminuted and exfoliated MoS₂ showed higher HY activity than the as-received one. Exfoliation increased the rate constant, but did not give so much effect on 1-MN HY as dry comminution in air.

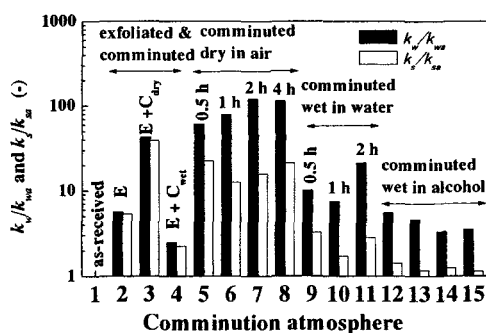


Fig.4 Relation between reaction rate constant ratios and comminution atmosphere

(Figures in x-axis are the same in Fig.1)

The hydrogenation activity of exfoliated MoS₂ became 5 times higher than the as-received one, although its specific surface area was not so much changed by the exfoliation. Iwata et al. [7] showed that unsupported MoS₂ prepared from ammonium heptamolybdate and ammonium tetrathiomolybdate

differed the catalytic activity for 1-MN HY. They concluded that the high activity was due to large numbers of active sites formed on highly bent basal planes in the layered crystalline structure. The highly bent structure was indicated by the broad XRD profile. In the exfoliation the crystal structure was highly distorted and crystal lattice distance was partly increased by hydrogen gas evolved between basal planes. One of the reasons why the exfoliation increased the HY activity was considered to be highly bent basal planes. Exfoliated MoS₂, followed by dry comminution had a significant high hydrogenation activity which was 40 times higher than k_{wa} and k_{sa} .

Comminution atmosphere gave a significant influence on the HY activity. The activity increased in the order of wet comminution in alcohol < wet comminution in water < dry comminution in air for both k_w and k_s . The value of k_s in exfoliating, followed by comminuting MoS₂ dry in air was higher than that in comminuting as-received MoS₂ dry in air, because the specific surface area of the former was almost unchanged, but that of the latter significantly increased, compared to the as-received.

Fig.5 shows the relation between surface area of catalyst and conversion of 1-MN, i.e. $-\ln(1-X)$, where $X=1-C/C_0$. Data for as-received MoS₂ were partly quoted from Kuriki[4]. The slope of data in Fig.5 is proportional to k_s as described in eq.(3). The value of $-\ln(1-X)$ increased with the increase in surface area of molybdenum sulfide depending on the comminution atmosphere. Fine dotted line corresponds to the data for as-received MoS₂, fine solid line for MoS₂ comminuted in alcohol, bold dotted line for MoS₂ comminuted in water and bold solid line for MoS₂ comminuted in air.

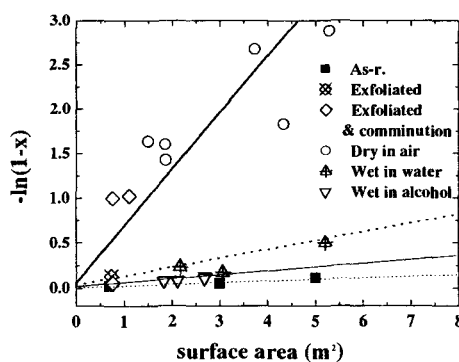


Fig.5 Relation between $-\ln(1-X)$ and surface area of catalyst (fine dotted line for as-received, fine solid line for comminuting wet in alcohol, bold dotted line for comminuting wet in water and bold solid line for comminuting dry in air)

MoS₂ had higher 1-MN HY activity in the order of comminution in air > wet in water > wet in alcohol,

which appears that comminution in oxidation condition seemed to be better for producing high 1-MN HY catalysts. No reasonable correlation is not, however, obtained between k_s and O/Mo calculated from XPS. The relation is now under consideration between 1-MN HY activity and characteristics of MoS₂ comminuted in various conditions.

4. CONCLUSION

MoS₂ was comminuted in various conditions, exfoliated and exfoliated, followed by being comminuted. Comminuted MoS₂ was characterized using hydrogenation of 1-methylnaphthalene (1-MN HY). Followings are the findings in the experiment.

(1) All comminuted MoS₂ powders have higher 1-MN HY activity than as-received one. Exfoliated MoS₂ has a slightly higher catalytic activity than as-received one, but lower than MoS₂ comminuted dry in air. MoS₂ comminuted dry in air has drastically higher HY activity.

(2) Comminution conditions give a significant effect on the catalytic activity. HY activity of comminuted MoS₂ increases in the order of dry comminution in air > wet comminution in water > wet comminution in alcohol.

Factors responsible for 1-MN HY activity are not clear and have to be investigated.

Acknowledgement

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