[Regular Paper]

Preparation of Alumina-supported Cobalt–molybdenum Catalysts by Sol-gel Method and Hydrodesulfurization Activities

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Al₂O₃-supported Co and Mo catalysts were prepared by the sol-gel method, in which Co and/or Mo species were added at the hydrolysis of Al tri-*s*-butoxide. XRD patterns, N₂ adsorption and desorption, amounts of NO adsorption and NO species by FT-IR were measured to characterize the catalysts. Catalysts with active components Co and Mo separately supported by the sol-gel method had higher activity for hydrodesulfurization of dibenzothiophene. Mo–Co/Al₂O₃, in which Mo species was supported on Co/Al₂O₃ by the sol-gel method, showed the highest activities at lower temperature, indicating that the Co species was effectively dispersed on Al₂O₃ during the preparation of Co/Al₂O₃. Catalysts in which Co and Mo species were simultaneously supported had lower activity, indicating that both Co and Mo species were dispersed and reduced interaction between Co and Mo. Co–Mo/sol-gelAl₂O₃, with the Co species supported on Mo/sol-gelAl₂O₃, showed the highest activity among sol-gelAl₂O₃ supported CoMo catalysts, indicating that the Mo species was effectively dispersed during the preparation of Mo/sol-gelAl₂O₃. Biphenyl was selectively obtained. NO adsorption measurement showed that the amount of NO adsorbed was almost same for Mo–Co/Al₂O₃ sulfided once or twice. In contrast, sol-gel CoMo/Al₂O₃, with the Co and Mo added simultaneously by the sol-gel method, showed significant decrease in NO adsorption after second sulfiding, which would be related to the lower stability of sol-gelCoMo/Al₂O₃ prepared by the sol-gel method. Al₂O₃-supported Co–Mo catalysts prepared using the sol-gel method had relatively high surface areas (282–544 m²/g) and relatively smaller pore sizes (3.7–6.3 nm).

Keywords

Hydrodesulfurization, Dibenzothiophene, Alumina support, Cobalt–molybdenum catalyst, Sol-gel method

1. Introduction

Sulfur concentrations of gasoline and gas oil are now regulated to less than 10 ppm. However, stricter regulations are likely in the near future, so HDS catalysts must be further developed to reduce the cost of fuel production, and to provide ultra-deep desulfurized naphtha or kerosene for hydrogen production for use in fuel cells. In fact, the sulfur content of fuel oil for ships in the Baltic Sea and North Sea is already limited to 1.0 %. Similar regulations will soon be introduced in many other maritime areas, so hydrodesulfurization of gas oil, diesel oil and fuel oil for ships will become more and more important. Therefore, further development of hydrodesulfurization catalysts has continued, especially to identify more active and selective catalyst components^{1,2)}.

Conventional HDS catalysts consist of MoS₂ planes containing Ni or Co atoms ('NiMoS' or 'CoMoS' phase)

supported on a carrier, usually γ -alumina. The performance of these CoMo- and NiMo-based catalysts can be improved by adding further elements such as fluorine³⁾, phosphorus⁴⁾ or boron^{4),5)}. The use of other active phases such as WS₂⁶⁾, CrS_x^{7),8)}, noble metals^{9)–15)}, as well as other carriers such as TiO₂ or mixed oxides^{16)–21)} or carbon²²⁾ and zeolites²³⁾ has also been investigated.

The sol-gel method enables the preparation of porous materials with fine structure and polycrystalline materials with uniform composition from more than one component at low temperature. Active components Mo and Co in HDS catalysts supported on Al₂O₃ are usually prepared by an impregnation method. Using the sol-gel method, these active species can be added to an intermediate gel during preparation of the support, so very active catalysts with highly dispersed metals may be obtained. Mo/Al₂O₃ HDS catalysts have been prepared by the sol-gel method²⁴⁾, but examples for HDS application are rare.

The present study investigated the HDS properties of Al₂O₃-supported Co–Mo catalysts prepared by the sol-gel method, for comparison with catalysts prepared by conventional impregnation methods.

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2. Experimental

2.1. Catalyst Preparation

Sol-gelCoMo/Al₂O₃ catalyst was prepared as follows. Aluminium tri-*sec*-butoxide (Al(O-*s*-C₄H₉)₃, ASB, 9.86 g) was dissolved in anhydrous ethanol (27.60 g). Then, ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O, 0.62 g) and cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 0.40 g) were dissolved in water (6.48 g) and the obtained solution was added to the ASB solution at the rate of one drop per 5 s. The mixture (pH 7.5) was stirred at 25 °C for 18 h. The obtained gel was dried at 100 °C for 12 h and calcined at 500 °C for 3 h.

Sol-gelAl₂O₃ was prepared from ASB and water through drying and calcination. Sol-gelMo/Al₂O₃ was prepared from ASB and an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O through drying and calcination. Co-Mo/Al₂O₃ catalyst was prepared from an aqueous solution of Co(NO₃)₂·6H₂O and sol-gelMo/Al₂O₃ catalyst by the impregnation method followed by drying and calcination. Sol-gelCo/Al₂O₃ was prepared from ASB and an aqueous solution of Co(NO₃)₂·6H₂O through drying and calcination. Mo-Co/Al₂O₃ catalyst was prepared from an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O and the sol-gelCo/Al₂O₃ catalyst by the impregnation method followed by drying and calcination.

Sol-gelAl₂O₃-supported Co and Mo catalysts were prepared by incipient wetness impregnation using aqueous solutions of (NH₄)₆Mo₇O₂₄·4H₂O and Co(NO₃)₂·6H₂O. For Co-Mo/sol-gelAl₂O₃, Mo/sol-gelAl₂O₃ loaded with 20 wt% MoO₃ was prepared first as follows. Sol-gelAl₂O₃ was impregnated with an aqueous solution containing the desired amount of (NH₄)₆Mo₇O₂₄·4H₂O, followed by drying at 100 °C for 2 h and calcining in air at 500 °C for 3 h. Then, the Mo/sol-gelAl₂O₃ catalyst was impregnated with an aqueous solution containing a given amount of Co(NO₃)₂·6H₂O. The obtained solids were dried at 100 °C for 2 h and then calcined in air at 500 °C for 3 h. For Mo-Co/sol-gelAl₂O₃, cobalt was supported first. After calcination, Mo was supported similarly. For CoMo/sol-gelAl₂O₃, Co and Mo were supported simultaneously. The Co/Mo molar ratio was 0.4 for each catalyst.

X-ray diffraction (XRD) patterns of the samples (25 mg) were obtained using an Ultima IV (Rigaku Corp.) diffractometer equipped with a nickel-filtered CuKα₁ X-ray source (λ = 0.15405 nm) operated at 40 kV and 20 mA under the following conditions: scan mode CONTINUOUS, slit (SS) 1° (DS) 1° (RS) 0.3 mm, present time 1 s, scan speed 4°/min, measurement range 2θ = 10–70°.

N₂ adsorption was measured by Belsorp MiniIII (Bel Japan Inc.). NO adsorption was measured by a pulse

method using gas chromatograph thermal conductivity detector (GC-TCD, Shimadzu GC-8A) to determine the amount of coordinatively unsaturated sites. The calcined sample 0.04 g was packed into a fixed bed reactor, heated to 400 °C at 5 °C/min under 5 % H₂S/H₂ flow at 30 mL/min and maintained for 1.5 h. After purging with N₂, the reactor was held at 400 °C under He flow at 60 mL/min for 3 h and then cooled to 25 °C. NO pulses 1.0 mL were introduced at 25 °C using a six-way valve until the amount of NO detected became constant.

2.2. Apparatus and Procedure

The catalysts were packed in a fixed bed flow reactor (stainless tube, OD 10 mm, ID 8 mm) and presulfided under a flow of 5 % H₂S/95 % H₂ (1.8 L/h, 0.1 MPa, 5 °C/min, 400 °C, 3 h). After presulfiding, the reactor was cooled to room temperature and then pressurized with hydrogen. The reactant solution (DBT dissolved in decalin) was fed into the reactor after pre-heating to the desired reaction temperature using a high-pressure liquid pump (Nihon Seimitsu Kagaku NP-S-252). Typical HDS reaction conditions were as follows: H₂ flow rate 18 L h⁻¹, WHSV 28 h⁻¹, reaction pressure 5 MPa, reaction temperature 200–260 °C, and concentration of DBT in decalin 0.1 wt%. The liquid products were collected every 15 min and analyzed using a gas chromatograph equipped with a FID detector (sample 0.3 μL, INJ, COL, DET 240 °C, pressure 90 kPa, split ratio 1 : 50, Shimadzu-17A) and a commercial capillary column (DB-1).

Conversion was calculated according to the following Eq. (1):

$$\left(1 - \frac{\text{(a peak area of DBT in product)}}{\text{(a peak area of DBT in feed)}}\right) \times 100(\%) \quad (1)$$

3. Results and Discussion

3.1. Hydrodesulfurization of Dibenzothiophene Using Catalysts Prepared by the Sol-gel Method

All CoMo catalysts contained 20 wt% of MoO₃ with Co/Mo ratio 0.4. Catalytic activity for HDS was evaluated using a decalin solution of dibenzothiophene (DBT) (0.1 wt%) with products of biphenyl (BP) and cyclohexylbenzene (CHB). **Figure 1** shows the effect of temperature on the conversion and selectivity for CHB. The catalytic activity decreased in the order Co-Mo/Al₂O₃ = Mo-Co/Al₂O₃ > sol-gelCoMo/Al₂O₃. Catalysts with active components Co and Mo separately supported by the sol-gel method showed higher activity than catalysts with Co and Mo simultaneously supported. Biphenyl was selectively obtained. Reaction mainly proceeded by the direct desulfurization route. However, cyclohexylbenzene was also formed over each catalyst at the highest temperature examined. The Mo-Co/Al₂O₃ catalyst had higher activity than the

Fig. 1 Effect of Temperature on Conversion and Selectivity of CHB

Co-Mo/Al₂O₃ catalyst at lower temperatures.

Co and Mo species were supported on sol-gelAl₂O₃ by the impregnation method to prepare CoMo/sol-gelAl₂O₃, Co-Mo/sol-gelAl₂O₃ and Mo-Co/sol-gelAl₂O₃ catalysts. CoMo/sol-gelAl₂O₃ contained Mo and Co components simultaneously supported by impregnation. Co-Mo/sol-gelAl₂O₃ and Mo-Co/sol-gelAl₂O₃ contained Mo and Co components separately supported by impregnation. Mo was supported first for the former and Co was supported first for the latter. The catalytic activities for HDS of DBT are shown in Fig. 2. The catalytic activity decreased in the order Co-Mo/sol-gelAl₂O₃ > Mo-Co/sol-gelAl₂O₃ > CoMo/sol-gelAl₂O₃. Catalysts with active components Co and Mo separately supported on sol-gelAl₂O₃ showed the higher activity.

Fig. 2 Effect of Temperature on Conversion and Selectivity of CHB

Catalysts with active components simultaneously supported had lower activity. Biphenyl was selectively obtained but CHB was formed over Mo-Co/sol-gelAl₂O₃. In contrast to the case for Mo-Co/Al₂O₃ described above, the activity for Mo-Co/sol-gelAl₂O₃ was much lower than that for Co-Mo/sol-gelAl₂O₃.

Conventional Al₂O₃ support was not used in this study. However, use of a conventional Al₂O₃ support (ref. Al₂O₃) in dimethyl-DBT HDS in a preliminary experiment showed the effect of the preparation procedure on activity was very small. Nevertheless Mo-Co/ref. Al₂O₃, prepared with a similar method to Mo-Co/sol-gelAl₂O₃, showed the lowest activity. These findings may be related to the high stability of ref. Al₂O₃ compared with sol-gelAl₂O₃ and sol-gel catalysts. The structures of the Mo species and Co species on Al₂O₃

Table 1 Surface Area, Pore Volume and Pore Radius of Catalysts and NO Adsorption Measurement

Sample name	BET surface area [m ² g ⁻¹]	BET pore volume [cm ³ g ⁻¹]	BJH pore radius [nm]	NO adsorbed [mmol g-cat ⁻¹]	NO adsorbed [10 ⁻³ mmol m ⁻²]
Co-Mo/Al ₂ O ₃	323	0.85	2.4	0.45	1.39
Mo-Co/Al ₂ O ₃	235	0.57	2.7	0.36 (0.31) ^{a)}	1.53
Sol-gelCoMo/Al ₂ O ₃	521	1.28	2.4	0.74 (0.38) ^{a)}	1.42
Co-Mo/solgelAl ₂ O ₃	285	0.95	2.4	0.63	2.21
Mo-Co/solgelAl ₂ O ₃	196	0.48	2.4	0.35	1.79
CoMo/sol-gelAl ₂ O ₃	260	0.51	2.4	0.45	1.73
Sol-gelAl ₂ O ₃	385	1.87	6.1	-	-

a) Values in parenthesis were measured after second sulfiding.

were not much modified by the preparation method using conventional ref. Al₂O₃, but the structures of these species were significantly modified depending on the preparation procedure in the sol-gel method. Therefore, the sol-gel method has advantages to prepare various structures of alumina-supported CoMo catalysts, although variations in the stability of the catalysts may cause problems depending on the specific reactions.

3.2. Characterization of Catalysts by N₂ Adsorption and Desorption, XRD, NO Adsorption, and FT-IR Observation of Adsorbed NO Species

N₂ adsorption characterizations of the catalysts are shown in **Figs. 3** and **4**, and **Table 1**. All catalysts showed hysteresis in the adsorption-desorption isotherms (**Figs. 3(a)** and **4(a)**), indicating that these catalysts contained mesopores. BJH plots of the pore size distributions of these catalysts demonstrated the presence of similar sizes of mesopores as shown in **Figs. 3(b)** and **4(b)**. Comparisons of surface area, pore diameter and pore volume showed catalysts made by the sol-gel method had relatively higher surface area. Sol-gel CoMo/Al₂O₃ and Co-Mo/Al₂O₃ catalysts exhibited high surface areas of 521 m²/g and 323 m²/g, respectively. The lower activity of sol-gelCoMo/Al₂O₃ indicates that high surface area is not very significant for high activity. Sol-gelAl₂O₃ had higher surface area than Al₂O₃ (about 250 m²/g) commonly used for HDS²⁵⁾ and the surface area decreased after loading of Co and Mo species. Sol-gel catalysts had low pore radius (2.4–2.7 nm) (**Fig. 3(b)**). As shown in **Table 1**, sol-gelAl₂O₃ had higher pore radius of 6.1 nm. However, the pore radius decreased to 2.4 nm after loading of Co and Mo species (**Fig. 4(b)**), indicating that aggregation of alumina particles may occur using sol-gelAl₂O₃ with high porosity.

XRD revealed peaks of MoO₃ (2θ = 27°) (**Fig. 5**) for the CoMo/sol-gelAl₂O₃ catalyst, which had lower surface area. The reduced HDS activity was thought to result from the nonuniform support of the Mo species on CoMo/sol-gelAl₂O₃. XRD revealed a small peak of MoO₃ for Mo-Co/sol-gelAl₂O₃. Therefore, the lower activity compared to Mo-Co/Al₂O₃ was due to lower dispersion of Mo species. XRD found no peaks of

Fig. 3 (a) Adsorption Isotherms and (b) BJH-plots for Catalysts Prepared by the Sol-gel Method

MoO₃ for catalysts prepared by the sol-gel method in which active components were added during Al₂O₃ preparation. Therefore, catalysts prepared by the sol-gel method have higher dispersion of Mo species even at loadings as high as 20 wt% of MoO₃.

FT-IR of NO species adsorbed on alumina-supported CoMo catalysts with presulfiding detected three absorptions near 1860, 1790 and 1700 cm⁻¹, assigned to NO species adsorbed on Co sulfide and Mo sulfide (**Fig. 6**)²⁵⁾. The peak heights of the absorptions at

Fig. 4 (a) Adsorption Isotherms and (b) BJH-plots for Catalysts Using Al_2O_3 Prepared by the Sol-gel Method

1860 cm^{-1} and 1790 cm^{-1} were slightly higher than that at 1700 cm^{-1} , indicating that cobalt species were loaded on molybdenum species. Specifically, the peaks at 1860 cm^{-1} and 1798 cm^{-1} for Co-Mo/sol-gel Al_2O_3 were higher than the peaks at 1854 cm^{-1} and 1794 cm^{-1} for CoMo/sol-gel Al_2O_3 and the peaks at 1858 cm^{-1} and 1792 cm^{-1} for Mo-Co/sol-gel Al_2O_3 , compared to the peaks near 1700 cm^{-1} for each catalyst. These findings may be related to the higher activity for Co-Mo/sol-gel Al_2O_3 as shown in Fig. 2. All spectra were similar, indicating that the structures of the active species were very similar just after presulfiding. However, these structures changed after desulfurization because the structures of the alumina supports were different for each catalyst.

The amount of NO adsorbed was measured by the pulse method using GC-TCD²⁵⁾ as shown in Table 1. Sol-gelCoMo/ Al_2O_3 adsorbed the highest amount of NO after initial sulfiding, but this value halved after second sulfiding. Sol-gelCoMo/ Al_2O_3 has very high surface area and pore volume which may easily decrease as the surface area and pore volume of sol-gel

Fig. 5 XRD Patterns of CoMo/ Al_2O_3 Catalysts Prepared by the Sol-gel Method and the Impregnation Method

Al_2O_3 significantly decreased at loading of the metal species as shown above. Such a decrease must be a result of a change in the structure. In contrast to sol-gelCoMo/ Al_2O_3 , Mo-Co/ Al_2O_3 showed very low amount of NO adsorbed after initial sulfiding, and this value was little changed after second sulfiding, indicating minimum change in the structure. Consequently, Mo-Co/ Al_2O_3 showed higher activity than sol-gelCoMo/ Al_2O_3 .

Calculation of the amount of NO adsorbed per BET surface area found Mo-Co/ Al_2O_3 exhibited the highest value among Co-Mo/ Al_2O_3 , Mo-Co/ Al_2O_3 and sol-gelCoMo/ Al_2O_3 (Table 1), which may be related to the relatively high activity of Mo-Co/ Al_2O_3 . Sol-gel Al_2O_3 supported catalysts showed higher values than Co-Mo/ Al_2O_3 , Mo-Co/ Al_2O_3 and sol-gelCoMo/ Al_2O_3 , indicating that Al_2O_3 -supported CoMo catalysts have

Fig. 6 FT-IR Spectra of NO Species Adsorbed on Alumina-supported CoMo Catalysts

more coordinatively unsaturated sites of metal species, at least just after presulfiding. Co-Mo/sol-gelAl₂O₃ showed the highest values of NO adsorbed, which may be related to the highest activity among sol-gelAl₂O₃ supported catalysts.

CoMoS phase, which is regarded as the active phase, was not directly observed by any characterization method in this study. However, Co-Mo/Al₂O₃ and Mo-Co/Al₂O₃ in the sol-gel method and Co-Mo/sol-gelAl₂O₃, which showed relatively higher activities, were likely to include CoMoS phase in their structures. In these catalysts, Co or Mo species are first supported on Al₂O₃ and then another metal species is supported on the metal species supported on Al₂O₃. Therefore, CoMoS phase would be formed. In contrast, sol-gelCoMo/Al₂O₃ and CoMo/sol-gelAl₂O₃, which showed relatively lower activities, probably did not include CoMoS phase in their structures because both Co species and Mo species were separately supported due to the simultaneous addition and resulting extremely high dispersion of these metal species.

4. Conclusions

Catalysts with active components Co and Mo separately supported by the sol-gel method or the conventional impregnation method showed higher activity than catalysts prepared by simultaneous addition of active components. If Co was supported first, the activity for Mo-Co/sol-gelAl₂O₃ prepared by impregnation method was lower than that for Mo-Co/Al₂O₃ prepared by the sol-gel method. Measurement of surface area, pore diameter and pore volume for each catalyst showed that sol-gelAl₂O₃ had higher surface area than Al₂O₃ commonly used for HDS and its surface area decreased with the support of Co and Mo species. Catalysts made by the sol-gel method had relatively smaller pore diameter.

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要 旨

ゾル-ゲル法によるアルミナ担持コバルト-モリブデン触媒の調製と脱硫反応特性

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本研究では $\text{Al}(\text{O}-s-\text{C}_4\text{H}_9)_3$ を用いて Al_2O_3 調製時に $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ の水溶液を加えるゾル-ゲル法によって, Co および Mo の活性成分を担持させて脱硫触媒を調製した。触媒のキャラクタリゼーションを XRD, N_2 吸脱着, NO 吸着量, NO 吸着種の FT-IR 測定により行った。ゾル-ゲル法によって (1) Al_2O_3 調製時に Mo を加え焼成後, もう一度 Co を担持して焼成した Co-Mo/ Al_2O_3 触媒, および (2) Al_2O_3 調製時に Co を加え焼成後, もう一度 Mo を担持して焼成した Mo-Co/ Al_2O_3 触媒は, Co と Mo の両成分を Al_2O_3 調製時に同時に加えた触媒 (sol-gelCoMo/ Al_2O_3 触媒) と比較して高

活性であることが分かった。何れの触媒の生成物選択性でもほとんどの条件でビフェニルを選択的に生成しており, 分散度の高い触媒であることが示唆された。Mo-Co/ Al_2O_3 触媒は2度硫化しても NO 吸着量に大きな変化はなかったが, sol-gelCoMo/ Al_2O_3 触媒では2度硫化した後, NO 吸着量の大きな低下が見られ, このことがこの触媒の活性が低いことと関係している可能性がある。触媒の物性ではゾル-ゲル法を用いて調製した Al_2O_3 担持 Co-Mo 触媒は一般的な脱硫触媒と比較して高表面積 (282 ~ 544 m^2/g) であったが, 細孔径は比較的小さかった (3.7 ~ 6.3 nm)。