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.

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 boron5). The use of other active phases such as WS26), CrSx7),8), noble metals9) and other carriers such as TiO2 or mixed oxides10) and zeolites11) has also been investigated.

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).

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

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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 boron5). The use of other active phases such as WS26), CrSx7),8), noble metals9) and other carriers such as TiO2 or mixed oxides10) and zeolites11) 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 method12), 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.
2. Experimental

2.1. Catalyst Preparation

Sol-gelCoMo/Al2O3 catalyst was prepared as follows. Aluminium tri-sec-butoxide (Al(O-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 CuKα2 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 Minill (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):

\[
\text{Conversion} = \frac{1 - (\text{a peak area of DBT in product})}{(\text{a peak area of DBT in feed})} \times 100(\%)
\]  

3. Results and Discussion


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
Co-Mo/Al₂O₃ catalyst at lower temperatures.

Co and Mo species were supported on sol-gel Al₂O₃ by the impregnation method to prepare CoMo/sol-gel Al₂O₃, Co-Mo/sol-gel Al₂O₃ and Mo-Co/sol-gel Al₂O₃ catalysts. CoMo/sol-gel Al₂O₃ contained Mo and Co components simultaneously supported by impregnation. Co-Mo/sol-gel Al₂O₃ and Mo-Co/sol-gel Al₂O₃ 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-gel Al₂O₃ > Mo-Co/sol-gel Al₂O₃ > CoMo/sol-gel Al₂O₃. Catalysts with active components Co and Mo separately supported on sol-gel Al₂O₃ showed the higher activity.

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

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-gel Al₂O₃, showed the lowest activity. These findings may be related to the high stability of ref. Al₂O₃ compared with sol-gel Al₂O₃ and sol-gel catalysts. The structures of the Mo species and Co species on Al₂O₃...
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 HDS 25 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 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 adsorptions 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 adsorptions at
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-gelAl₂O₃ were higher than the peaks at 1854 cm⁻¹ and 1794 cm⁻¹ for CoMo/sol-gelAl₂O₃ and the peaks at 1858 cm⁻¹ and 1792 cm⁻¹ for Mo-Co/sol-gelAl₂O₃, compared to the peaks near 1700 cm⁻¹ for each catalyst. These findings may be related to the higher activity for Co-Mo/sol-gelAl₂O₃ 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-TCD as shown in Table 1. Sol-gelCoMo/Al₂O₃ adsorbed the highest amount of NO after initial sulfiding, but this value halved after second sulfiding. Sol-gelCoMo/Al₂O₃ has very high surface area and pore volume which may easily decrease as the surface area and pore volume of sol-gel Al₂O₃ 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/Al₂O₃, Mo-Co/Al₂O₃ 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/Al₂O₃ showed higher activity than sol-gel CoMo/Al₂O₃.

Calculation of the amount of NO adsorbed per BET surface area found Mo-Co/Al₂O₃ exhibited the highest value among Co-Mo/Al₂O₃, Mo-Co/Al₂O₃ and sol-gel CoMo/Al₂O₃ (Table 1), which may be related to the relatively high activity of Mo-Co/Al₂O₃. Sol-gel Al₂O₃ supported catalysts showed higher values than Co-Mo/Al₂O₃, Mo-Co/Al₂O₃ and sol-gelCoMo/Al₂O₃, indicating that Al₂O₃-supported CoMo catalysts have
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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References


要 旨

ソル-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 Al(O-(C4H9)3 と Mo を担持たる Al2O3 調製時に (NH4)6Mo7O24·4H2O, Co(NO3)2·6H2O の水溶液を加えるソル-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製造した。触媒のキャラクタリゼーションを XRD, N2 吸脱着、NO 吸着量、NO 吸着種の FT-IR 測定により行った。ソル-ゲル法によって（1）Al2O3 調製時に Mo を担持焼成後、もう一度 Co を担持して焼成した Co-Mo/Al2O3, および（2）Al2O3 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/Al2O3, 触媒は、Co と Mo の間成分を Al2O3 調製時に加えた触媒（sol-gelCoMo/Al2O3 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ピ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/Al2O3 触媒は 2 度硫黄化しても NO 吸着量に大きな変化はなかったが、sol-gelCoMo/ Al2O3 触媒では 2 度硫黄化しても NO 吸着量の大きな低下が観られ、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。触媒の物性ではソル-ゲル法を用いて調製した Al2O3 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 m2/g）であったが、細孔径は比較的小さかった（3.7 〜 6.3 nm）。