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Characterization of Alumina Prepared by Sol–Gel Methods and Its Application to MoO_3–CoO–Al_2O_3 Catalyst

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Alumina powder was prepared by hydrolysis of aluminum isopropoxide (AIP) by two different methods: (1) AIP was poured directly into hot water to form fibrillar sols of aluminum hydroxide; (2) AIP was dissolved in butanol and then hydrolyzed with a small amount of water. The physical properties of these two alumina powders were compared. Alumina-supported molybdenum–cobalt catalysts were prepared by these two different hydrolysis methods and the catalytic activities for the desulfurization of thiophene were studied and discussed in terms of the surface concentrations of Mo and Co in the catalyst particles.

INTRODUCTION

Alumina has generally been produced by pyrolysis of aluminum hydroxide prepared from various aluminum salts such as sulfates, nitrates, and sodium aluminates. Alumina thus prepared is often contaminated with residual ions in spite of the repeated washing of the aluminum hydroxide. These impurities have undesirable effects of catalytic activities when the alumina is used as a catalyst or a catalyst carrier. Feachem and Swallow (*1*) have reported that a decrease in sodium content enhances the catalytic activity of alumina for the dehydration of ethanol to ethylene. Based on this result, Adkins and Watkins (*2*) have prepared alumina from aluminum isopropoxide(AIP), since alumina thus formed has been considered to be free from any impurities. They may be the first who have employed alumina from AIP as a catalyst and reported superior activity for the dehydration of hexanol to hexene, compared to commercial alumina powders.

Alumina powder from AIP is not only free from any impurities but is considered to be composed of finely and uniformly divided particles and hence has often been employed for the production of densely sintered ceramics as well (*3*). Densely sintered ceramics are so important in the electronic device industry that the preparation techniques have been extensively investigated to develop a convenient method available at low temperatures. One of the promising techniques is the sol–gel method, studied first by Dislich (*4*) for the production of silica thin films, and then by Mazdiyasni *et al.* (*5*) and Adachi and Sakka (*6*) for the production of pure and dense bodies of $BaTiO_3$ and silica glass, respectively.

Although a detailed description of the preparation of alumina from AIP was not given in the original paper (*2*), two different methods have been independently developed for the hydrolysis of AIP, which is a principal step in the sol–gel process. Direct hydrolysis of AIP was performed in one method: AIP powder was poured into an excess amount of hot water. The hydrolysis was assisted by the addition of nitric or hydrochloric acid, resulting in the formation of fibrillar aluminum hydroxide. This method was developed by Yoldas (*7*) and extended to the production of transparent and porous alumina substrates (*8*). In the other method, hydrolysis was carried out

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using AIP dissolved in various organic solvents such as benzene (*9*) and isopropyl (*10*) and sec-butyl alcohols (*11*), where the hydrolysis of AIP proceeded to a greater extent than in the direct method. Astier *et al.* (*11*) and one of the authors (A.U.) (*12*) have applied the latter method to the preparation of Ni/Al_2O_3 catalysts to avoid the problems caused by impurities in commercial aluminas.

The differences in the physical and catalytic properties of aluminas and alumina-supported catalysts prepared by these two different hydrolysis methods have not been discussed. The purpose of this work is to characterize the alumina powders prepared by these two different hydrolysis techniques and to extend these techniques to the preparation of alumina-supported molybdenum–cobalt oxide catalysts for the desulfurization of thiophene.

EXPERIMENTAL

Catalyst Preparation

The catalysts employed here were Al_2O_3-supported MoO_3/CoO and were prepared by hydrolysis of AIP in two different ways:

1. Fibrillar aluminum hydroxide sols were prepared by addition of AIP to hot water (85°C) with a small amount of nitric acid, and then mixed with a solution of $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ and Co $(NO_3)_2 \cdot 6H_2O$ dissolved in 1,3-butanediol. After the sol solution was stirred for 1 day, the solvents were eliminated by heating them under reduced pressure, drying, and calcining at 500°C for 5 h. The catalyst thus formed was designated Alk-1. Bare alumina, without either Mo or Co ions, was also prepared from the fibrillar aluminum hydroxide sols in the same way. Note that the molar ratio of "nitric acid/AIP" was 0.195 (7) in all the experiments described here.

2. AIP dissolved in butanol was added to a solution of $(NH_4)_6 Mo_7O_{24} \cdot 4H_2O$, and $Co(NO_3)_2 \cdot 6H_2O$ dissolved in 1,3-butanediol at 85°C with vigorous stirring. Hydrolysis was performed by addition of a small amount of water to the mixed solution at 85°C. The solution became a rigid and transparent gel immediately after addition of water. The gel was dried and calcined at 500°C for 5 h to form the Al_2O_3-supported MoO_3/CoO catalyst. The catalyst thus formed was called Alk-2. Bare alumina was also prepared by a similar procedure. The preparation procedures are summarized in Tables 1 and 2.

Shape and Size of Fibrillar Sols Observed by TEM and SAXS

Aluminum hydroxide sols, prepared by addition of AIP to hot water with a small amount of nitric acid (*7*), were observed under a TEM transmission electron microscope (TEM, Hitachi-800) operating at an accelerating voltage of 200 kV with a magnification of 5×10^4. By measurement of the length and thickness of fibrils, the size distribution curve and, hence, the mean size were obtained. The changes in mean size with stirring time of the sol solution were also measured by TEM.

TABLE 1

Procedure for Preparation of Alk-1 Catalyst[a]

$Al(OC_3H_7)_3$
↓ ← H_2O
Heat at 85°C with stirring
↓ ← HNO_3
Formation of clear sol
↓ ← $(NH_4)_6Mo_7O_{24}$ and $Co(NO_3)_2$ in 1,3-butanediol
Dry under reduced pressure
↓
Dry at 110°C for 24 h
↓
Calcine at 500°C for 5 h
↓
MoO_3–CoO/Al_2O_3 catalyst

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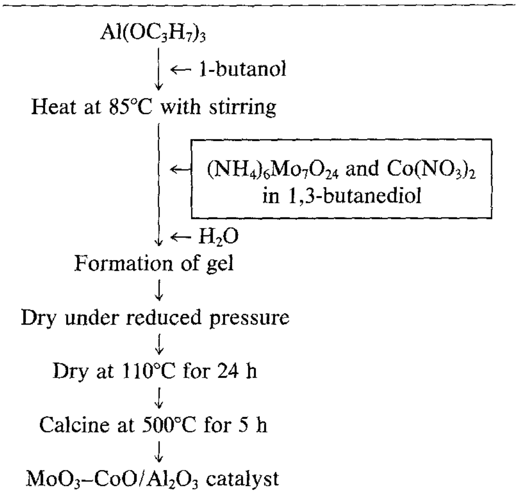
[a] For preparation of Alk-1 alumina, steps concerning Mo and Co compounds are omitted.

TABLE 2

Procedure for Preparation of Alk-2 Catalyst[a]



[a] For preparation of Alk-2 alumina, steps concerning Mo and Co compounds are omitted.

The size of aluminum hydroxide sols was monitored by a small-angle X-ray scattering device (SAXS, Rigakudenki Geigerflex), equipped with a scintillation counter fitted with a line focused Cu X-ray tube (60 kV, 200 mA) using a Ni filter (*13*). The scattered X-rays were scanned at a 2θ per minute rate of 0.025 over the range $0.1 < 2\theta < 3.5$. From the plots of intensity against diffraction angle, the Guinier (R_g) and Porod (R_p) radii were calculated according to the equations given by Whyte *et al.* (*14*). R_g and R_p were converted to H_g and H_p using $H_x = \sqrt{3}R_x$ (*15*), since the scattering substrates are in linearly growing fibrils. The length of the sols is distributed between H_g and H_p.

Surface Area and Pore Volume Measurements

Surface area, pore volume, and pore size distributions of Al_2O_3 and Al_2O_3-supported 15 wt% MoO_3/5 wt% CoO catalysts were examined by isothermal desorption in adsorption/desorption measurements at −196°C using nitrogen (Shimazu Co., Sorptomatic-1800). This is applicable to micropores less than 150 Å in diameter. For volume measurements of pores less than 10^5 Å in diameter, a mercury penetration porosimeter (Carlo Erba Co., Porosimeter-220) was employed. A scanning electron microscope (SEM, Hitachi X-650) was operated at an accelerating voltage of 10 kV with a magnification of 3×10^3 to observe the surface structures of both aluminas and alumina-supported catalysts calcined at 500°C for 5 h. A decrease in the surface area of both Alk-1 and Alk-2 aluminas with an elevation in calcination temperature was observed, powders being calcined at temperatures between 500 and 1200°C for 4 h.

Activity Measurements for Desulfurization of Thiophene

Catalytic activities for desulfurization were measured using a flow-type reactor packed with 0.5 g of catalysts. The catalysts were first treated with 4.4 vol% H_2S/H_2 at a flow rate of 80 ml/min at 400°C for 2 h and then submitted to desulfurization tests using 6.5 vol% C_4H_4S/H_2 at a rate of 80 ml/min at 315°C under a pressure of 3 kg/cm^2. Catalytic activities were estimated from thiophene concentrations at the outlet of the reactor, measured by gas chromatography using a column packed with 2.2 wt% Triton on Chromosorb 103. A commercial catalyst (KF-742, Sumitomo Metal Mining Co., 280 m^2/g surface area) containing 15 wt% MoO_3 and 5 wt% CoO was also employed for the activity test.

AES Measurements of Mo and Co in Catalysts

The concentration ratios of Mo/Al and Co/Al at the surface of catalyst particles were measured by Auger electron spectroscopy (AES, JEOL, Jamp-10), at an accelerating voltage of 10 kV with sample currents of ca. 10^{-6} A. Change in the ratios with the depth from surface was also monitored by AES with sputtering techniques using Ar at an acceleration voltage of 3 kV.

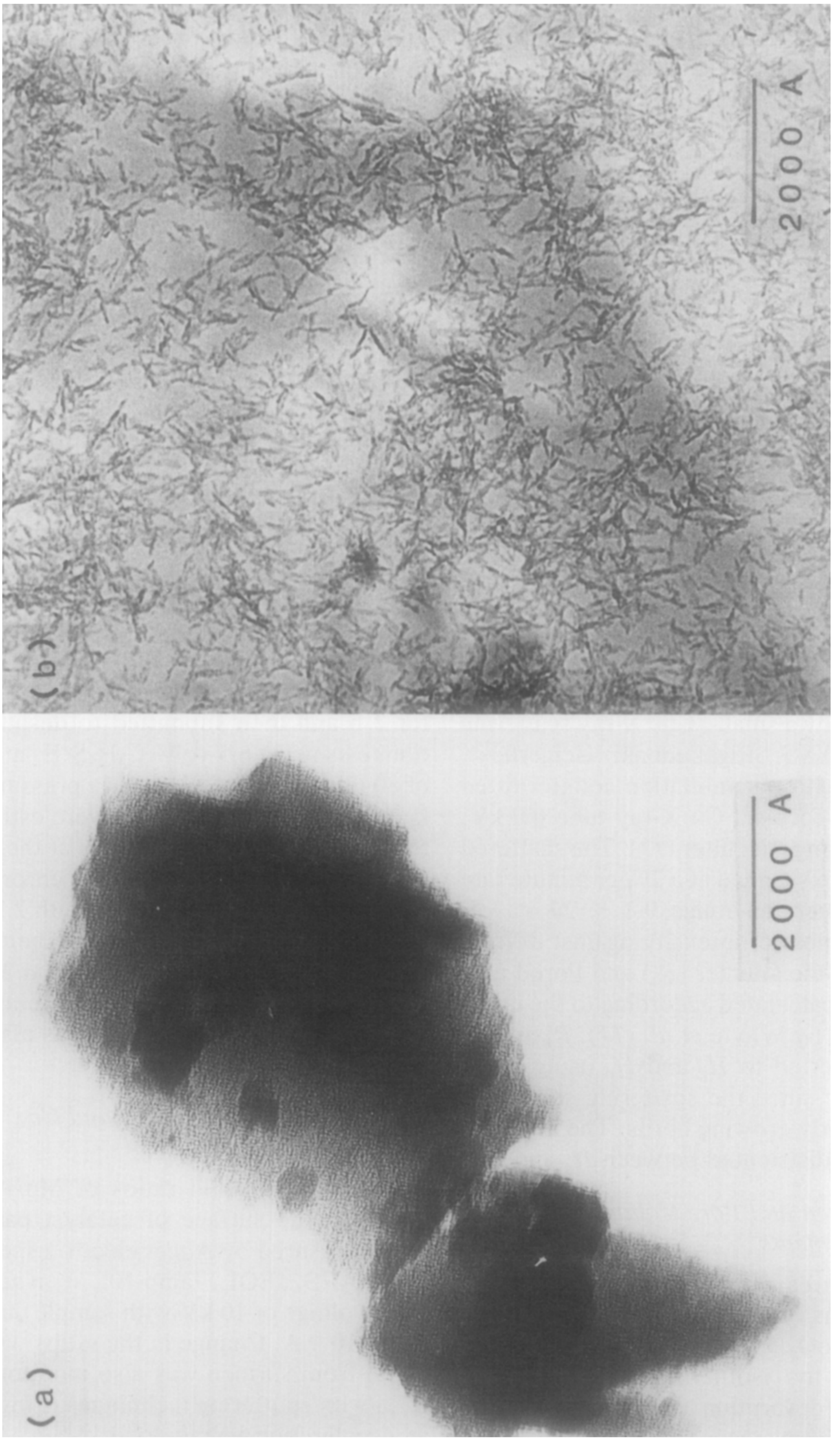


FIG. 1. TEM photographs of (a) block-like gels and (b) fibrillar sols formed during hydrolysis of AIP, pH 1.

RESULTS

Shape and Size of Aluminum Hydroxide Sol

Figure 1 shows a TEM photograph of fibrillar sols produced by the addition of AIP to hot water with a small amount of nitric acid. By measurement of the length and thickness of more than 300 fibrils, a size distribution curve was obtained (Fig. 2), indicating that the length of fibrils is dispersed between 400 and 800 Å and the thickness is around 100 Å. The length observed by TEM is in good accordance with that estimated by SAX, as summarized in Table 2. Change in the mean length of fibrils with stirring time of the sol solution is given in Fig. 3.

Physical Properties of Alumina from AIP

In Table 3 are also given the surface area and pore volume of the alumina and Al_2O_3-supported 15 wt% MoO_3/5 wt% CoO catalysts. Pore size distribution curves for the aluminas and the supported catalysts are illustrated in Figs. 4 and 5, and significant differences in the surface structures of these alumina powders and catalysts are demonstrated in Fig. 6. Since it was found that the Alk-1 alumina calcined at 500°C had a high surface area (264 m^2/g), changes in the surface area with elevation of calcination temperature were studied (Fig. 7).

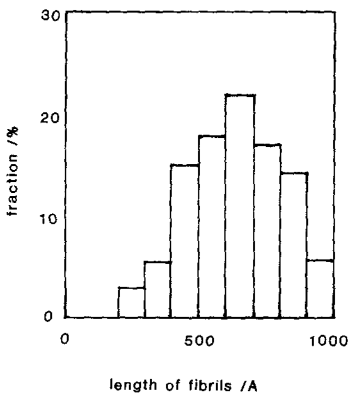


FIG. 2. Size (length) distribution curve of fibrillar sols, prepared by stirring the sol solution 7 days.

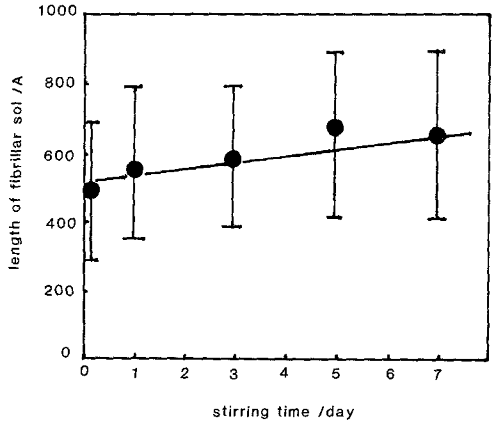


FIG. 3. Change in the length of fibrillar sols with stirring time of the sol suspension solution of pH 1.

Activities for Desulfurization of Thiophene

Figure 8 depicts the activities of MoO_3/(CoO)/Al_2O_3 catalysts for desulfurization of thiophene at 315°C, where the catalysts of Alk-1 exhibited activities much higher than the catalysts of Alk-2. (The activity of the commercial catalyst is also depicted for comparison.) Especially in Alk-1 catalysts, the activities were extremely enhanced by addition of Co, whose effect was studied by monitoring AES peaks at 187, 779, and 1400 eV, assigned to Mo, Co, and Al, respectively. In Fig. 9 are shown the changes in peak intensity ratios of Mo/Al and Co/Al with sputtering time, i.e., distance from the catalyst surface. The ratios were normalized by those obtained before sputtering.

DISCUSSION

Characterization of Fibrillar Sols

As has been already reported by Yoldas (*7*), the addition of AIP to hot water yields cloudy precipitates composed of boehmite and pseudoboehmite gels (*16*). The gels are peptidized to fibrillar sols by the presence of a small amount of nitric acid. Thus, the role of additional nitric acid is to peptidize the gel-like precipitates to their constituents, the fibrillar sols. The sols consist of aluminum monohydroxide associated to some extent, $(AlO(OH))_n$ (*7*). Accordingly,

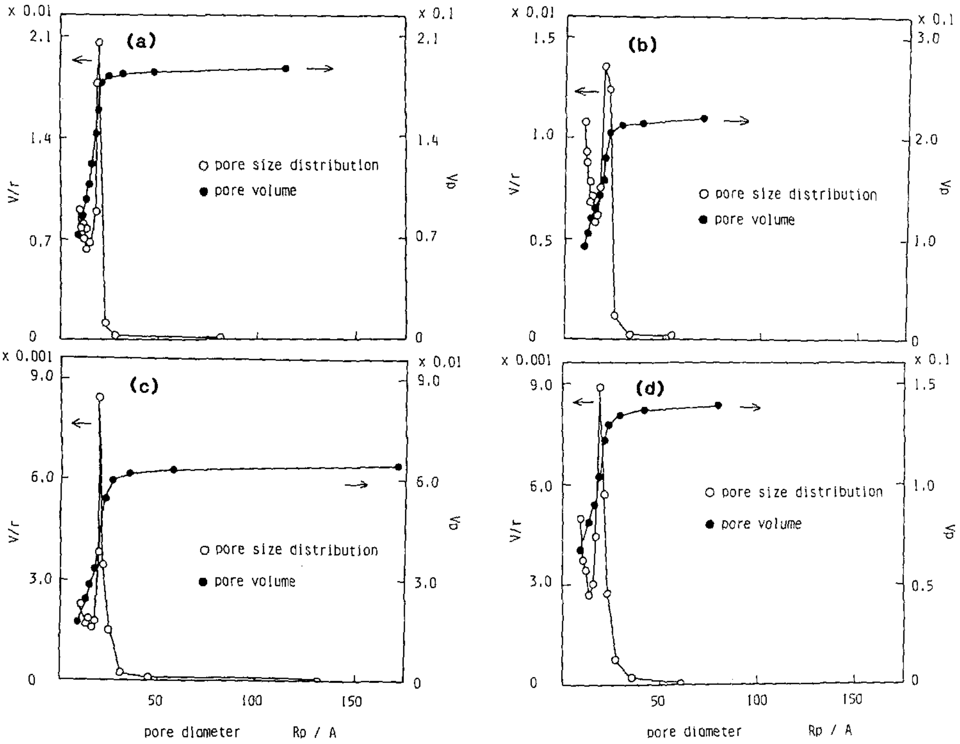


FIG. 4. Pore size and pore volume distribution curves for (a) Alk-1 alumina ($d < 150$ Å), (b) Alk-2 alumina ($d < 150$ Å), (c) Alk-1 catalyst ($d < 150$ Å), and (d) Alk-2 catalyst ($d < 150$ Å). All the samples were calcined at 500°C for 5 h.

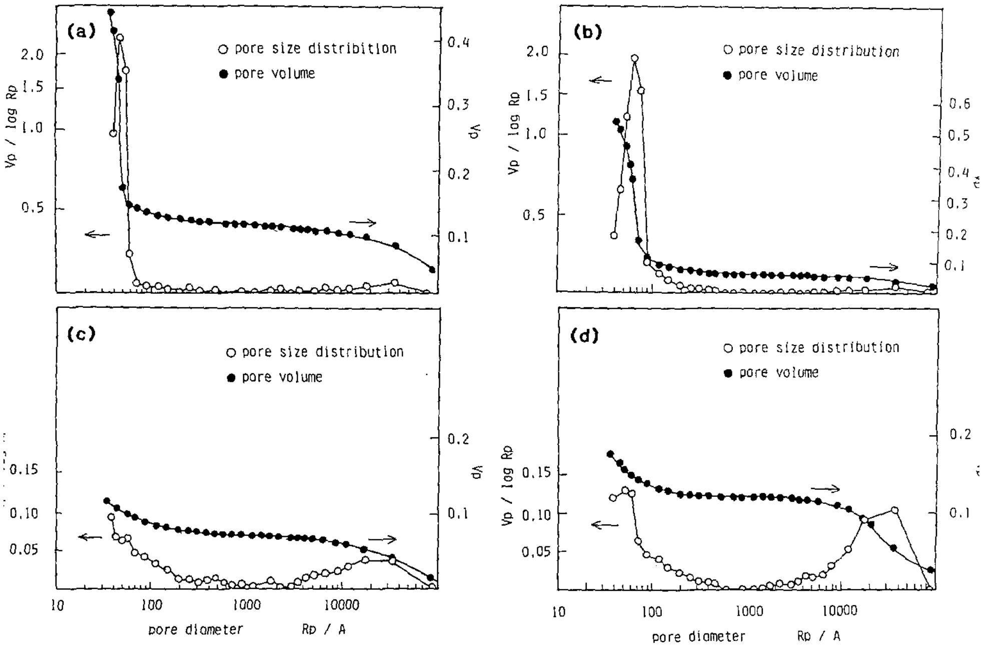


FIG. 5. Pore size and poor volume distribution curves for (a) Alk-1 alumina ($d < 10^5$ Å), (b) Alk-2 alumina ($d < 10^5$ Å), (c) Alk-1 catalyst ($d < 10^5$ Å), and (d) Alk-2 catalyst ($d < 10^5$ Å). All the samples were calcined at 500°C for 5 h.

FIG. 6. SEM photographs of (a) Alk-1 alumina, (b) Alk-2 alumina, (c) Alk-1 catalyst, and (d) Alk-2 catalyst. All the samples were calcined at 500°C for 5 h.

the size of the fibrillar sol is determined by "n," the extent of the association. Yoldas reported that (*7*) the shape and size of fibrillar sols varies with the amount of acid added to the gel suspension solution, but in our preliminary experiments no significant changes in shape and size of the fibrillar sols were observed. The sols range from 400 to 900 Å in length and are about 100 Å in thick even when the pH values of the gel suspension are varied from 1 to 3. The TEM photograph of fibrillar sols shown in Fig. 1a was obtained for sols formed at pH 1. Not only the pH but also the stirring time of the solution after addition of acid did not change the size and shape of the fibrillar sols. Even with prolonged stirring for 7 days, the length was still in the range of 400

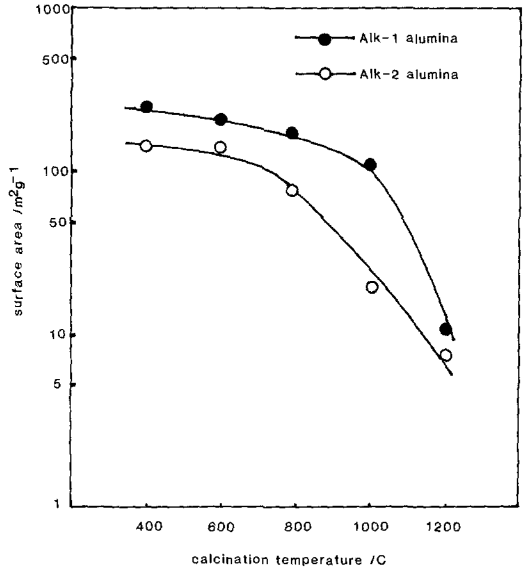


FIG. 7. Change in the surface areas of Alk-1 and Alk-2 aluminas with increasing calcination temperature. All the samples were calcined at each temperature for 5 h.

to 900 Å with a broad distribution curve (see Fig. 3). The sizes monitored by SAXS are also given in Table 3.

Consequently, the peptidization of cloudy gels is completed with a small amount of nitric acid (pH of the solution being less than 3) and with a short stirring of about 1 day. The extent of association, i.e., the *n* value, might be characteristic of the aluminum monohydroxides formed during hydrolysis of AIP with hot water.

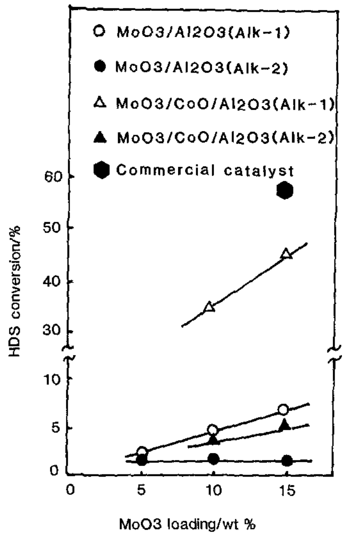


FIG. 8. Activities of Alk-1, Alk-2, and the commercial (KF-742) catalysts for desulfurization of thiophene at 315°C.

Block-like particles were observed for gels formed by the hydrolysis of AIP dissolved in butanol (see Fig. 1b), suggesting three-dimensional growth of gels during the hydrolysis. This is the most important difference from the direct hydrolysis of AIP with hot water, which results in the formation of fibrillar sols. This structural difference between fibrillar sols and block-like gels caused a significant different in the physical properties of the resulting alumina powders and in the activities of alumina-supported catalysts, as is described below.

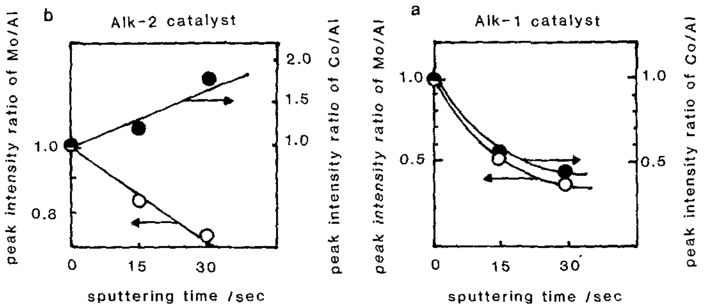


FIG. 9. Changes in the peak intensity ratios of Mo/Al and Co/Al for (a) Alk-1 catalyst and (b) Alk-2 catalyst.

TABLE 3

Characterization of Aluminas and Alumina-Supported Catalysts[a]

Catalyst	Surface area (m^2/g)	Sol or gel size		Pore volume (ml/g)		Mean pore size (Å)
		TEM	SAXS	$d = 150$ Å	$d = 10^5$ Å	
Alk-1 alumina	264	400–800 Å	112–732 Å	0.202	0.438	20
Alk-2 alumina	135	0.1–5.0 μm	—	0.072	0.114	20
Alk-1 catalyst	295	—	—	0.232	0.554	20
Alk-2 catalyst	150	—	—	0.144	0.177	25

[a] Mean pore size represents pore diameter, where the peak intensity in Figs. 4 and 5 is at a maximum.

Physical Properties of the Alumina Powders

Two kinds of alumina powders, Alk-1 and 2 aluminas, were prepared by drying and calcining at 500°C the fibrillar sols and the block-like gels, respectively. The surface structures of these alumina powders are given in Figs. 6a and b, indicating glassy and sintered surfaces for alumina prepared from block-like gels and rather porous structures for alumina from fibrillar sols. As can be expected from the photographs, the surface area of the alumina from fibrillar sols is about twice that of the alumina from block-like gels (see Table 3). The difference in their pore volumes is also given in Table 3 and seems to be acceptable, considering the surface structures shown in Figs. 6a and b. The mean pore sizes are, however, almost the same (20 Å) in these aluminas, which is due to the evaporation of organic solvents such as butanol and isopropyl alcohol, formed during the hydrolysis (see Fig. 4).

The alumina from fibrillar sols was found to have a relatively high surface area (264 m^2/g); thus, its thermal resistance was studied in the temperature range 500 to 1200°C. The thermal resistance of alumina is of great interest (*17*), and in recent work (*18*) an alumina with a surface area of about 20 m^2/g, even after calcination at 1200°C for 5 h, has been developed by addition of BaO to alumina. The thermal resistances of the present aluminas are depicted in Fig. 7, where a gradual decrease from 264 to 108 m^2/g was observed when the Alk-1 alumina was calcinated at 1000°C for 5 h; this was followed by a rapid decrease to 12 m^2/g after calcination at 1200°C, because of the formation of α-Al_2O_3 at 1100°C. Since the aluminas prepared here were never mixed with other metal ions, it is excellent to have a surface area as high as 12 m^2/g after calcination at 1200°C for 5 h.

Characterization of the Alumina-Supported Catalysts

The surface structures of alumina-supported MoO_3/CoO catalysts calcined at 500°C are also given in Figs. 6c and d, being similar to the structures shown in Figs. 6a and b, respectively. This means that the mechanisms for the preparation of alumina from fibrillar sols and from block-like gels are the same as the mechanisms for preparation of the respective alumina-supported catalysts.

The surface area and the pore volume of Alk-1 and 2 catalysts are considerably greater than those of Alk-1 and 2 aluminas, as summarized in Table 3. The increments in surface area and pore volume of the supported catalysts are explained by the deposition of MoO_3 and CoO crystallites on the alumina particles. Fine crystallites of both MoO_3 and CoO are deposited on the surface of the alumina in the Alk-1 catalyst, since this catalyst was prepared by immersing the fibrillar sol in a solution of

$(NH_4)_6Mo_7O_{24}$ and $Co(NO_3)_2$ dissolved in 1,3-butanediol. Accordingly, both Mo and Co ions are adsorbed on the surface of the fibrillar sols and deposited as fine crystallites of MoO_3 and CoO when calcined at 500°C. For the Alk-2 catalyst, on the other hand, Co ions are incorporated into the alumina matrix, forming Co–O–Al bonds, since it is well known that Ni and Co ions can easily substitute for Al ions at tetrahedral sites in an alumina matrix (*19*), recently confirmed by extended X-ray absorption fine structure (EXAFS) (*20*). Molybdenum ions, however, have never been reported to substitute for the Al ions in Al_2O_3 crystallites. Thus, only particles of MoO_3 are formed on the surface of the Alk-2 alumina when the catalyst is calcined at 500°C.

The above discussion is clearly demonstrated in Fig. 9, where Mo and Co concentrations, normalized by Mo/Al and Co/Al ratios at the surface of the catalysts, are plotted against sputtering time, i.e., the distance from the catalyst surface. Both Mo and Co ions simultaneously disappeared as distance from surface of the Alk-1 catalyst increased, while the opposite changes were observed for Mo and Co concentrations of Alk-2 catalyst with sputtering time. Because of some matrix effects during sputtering, the peak intensities in the AES spectra of the Alk-1 catalyst could not be compared precisely with those of the Alk-2 catalyst. The Mo/Co ratio at the surface of the Alk-1 catalyst is, however, clearly different from that of the Alk-2 catalyst, resulting in a difference in desulfurization activities of these two catalysts.

Activities for Desulfurization of Thiophene

As has been already proposed by Delmon *et al.* (*21*), the catalytic activities of alumina-supported MoO_3/CoO for desulfurization are strongly dependent on the surface concentrations of Mo and Co, and the most effective catalyst is considered to be 15 wt% MoO_3/5 wt% CoO dispersed on alumina supports. Activities of the present catalysts for the desulfurization of thiophene are shown in Fig. 8, indicating a large effect of additional CoO in Alk-1 catalysts; from 6.7% conversion for 15 wt% MoO_3/Al_2O_3 to 43.0% for 5 wt% CoO/15 wt% MoO_3/Al_2O_3. In the Alk-2 catalysts, the effect of CoO addition was less pronounced, probably because incorporation of the Co ions into the alumina matrix leads to an undesirable Mo/Co concentration ratio at the surface of the Alk-2 catalysts. In other words, the surface concentration ratio of Mo/Co in Alk-1 is the same as that in the solution into which the fibrillar sols were immersed, 15/5, which is the most desirable ratio for a desulfurization catalyst (*21*). The surface Mo/Co ratio in Alk-2 catalyst is greater than that in the solution in which AIP was dissolved because the Co ions are trapped in the alumina matrix. It is also shown in Fig. 8 that the MoO_3/Alk-1 alumina showed higher activity for desulfurization of thiophene than the MoO_3/Alk-2 alumina. This is ascribed to higher dispersion of MoO_3 on Alk-1 alumina than on Alk-2 alumina because the surface area of Alk-1 alumina is much greater than that of Alk-2.

The catalyst preparation methods employed in the present work used a coprecipitation route and it is fair to compare their catalytic activities with that of a commercial catalyst (KF-742, Sumitomo Metal Mining Co.) prepared by conventional impregnation. As is seen in Fig. 8, the commercial one exhibited higher activity (58%) for desulfurization of thiophene than the Alk-1 catalyst (43%), although the surface area of the commercial catalyst (280 m^2/g) is less than that of the Alk-2 (380 m^2/g). This might be ascribed to higher dispersions of MoO_3 and CoO on the commercial catalyst, probably by well-devised techniques for the catalyst preparation, than the present catalysts. Moreover, the commercial catalyst has been improved by small amounts of other additives such as NiO and P_2O_5, which affect dispersions of MoO_3 and CoO to enhance the catalytic activities.

It is concluded that alumina-supported

catalysts prepared from fibrillar sols of alumina monohydroxide have a high surface area and a large pore volume. Moreover, metal ions supported are concentrated at the surface of the alumina particles, which enhances the efficiencies of the metal ions employed for catalysis.

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