Study on the Hydrodesulfurization Catalyst of Residual Fuel (Part 4)

— Improvement of Catalyst Support* —

by Masao Inoguchi*¹, Kazuhito Tate*², Yoshito Kaneko*³, Yoshihito Satomi*⁴,
Kiyohiko Inaba*⁵, Takehiko Mizutori*⁶, Harumi Kagaya*⁷,
Reijiro Nishiyama*⁸, Saburo Onishi*⁹ and Tamotsu Nagai*¹⁰

Summary: The control methods of pore properties of catalyst supports and the manufacturing methods of their desirable pore size distribution for hydrodesulfurization catalyst of residual fuel were studied. Namely, the correlations between pore properties of γ -alumina and preparation and calcination condition of alumina hydrates, especially boehmite gel, were investigated. From the experimental results, the following were obtained.

- 1) With higher hydrolysis temperature, the crystallites became larger, the specific surface area decreased and the pore volume of the pore having diameter less than 600 Å increased. When aging period of boehmite gel was prolonged, the degree of crystallinity advanced along with the crystal growth of bayerite and consequently, the specific surface area and the pore volume decreased.
- 2) When the alumina hydrates were washed in water, the pore volume and the specific surface area decreased. When they were washed in alcohol, the pore volume and the specific surface area increased on the contrary.
- 3) As the calcination temperature was raised higher, the specific surface area decreased and, in reverse, the pore volume increased.
- 4) The most important effect on the pore structure of the alumina as catalyst support was the permeation of alcohols into the interstice of crystallites of alumina. Also, selecting the preparation conditions of alumina hydrates adequately, the diameter of crystallites could be changed markedly and, consequently, the pore structure could be controlled.
- 5) When the suitable kind of acid was added to alumina hydrates and they were calcined to make alumina supports, the specific surface area was constant independent of the acid concentration, while the pore volume and the mean pore diameter decreased according to increase of the acid concentration.

1 Introduction

In connection with the activity of hydrodesulfurization catalysts for residual fuel, kinds of

catalysts, their physical properties and preparation methods had been studied from various viewpoints^{1)~3)}. In consequence, it became clear that physical properties of catalysts, especially pore properties such as pore size distribution, pore volume and mean pore diameter governed greatly the activity and selectivity of desulfurization reaction. For the purpose of controlling pore properties of the supports, the authors investigated preparation methods of the supports from alumina hydrates which were obtained by hydrolysis of aluminum alcoholate. It is well known that the inorganic powder as alumina etc. possesses the structure sensitive property. For instance, its physical properties are remarkably variable depending on raw materials, impurities, conditions of hydrolysis, conditions of after-treatment of alumina hydrates etc..

In case of alumina, many papers⁴⁾ have dealt with preparation methods and physical properties of alumina hydrates and phase transformation of alumina hydrates and alumina. Also de

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*1 Central Research Laboratory, Showa Oil Co., Ltd. (1-2-22, Ariake, Koto-ku, Tokyo, Japan)

*2 Research Laboratory, Mitsubishi Oil Co., Ltd.

*3 Central Research Laboratory, Toa Nenryo Kogyo K. K.

*4 Central Research Laboratory, Nippon Mining Co., Ltd.

*5 Production & Refinery Co-ordination Dept., Daikyo Oil Co., Ltd.

*6 Research Section of Kawasaki Refinery, Asia Oil Co., Ltd.

*7 Research Section of Kawasaki Refinery, Toa Oil Co., Ltd.

*8 Research Laboratory of Osaka Refinery, Koa Oil Co., Ltd.

*9 Central Research Laboratory, Maruzen Oil Co., Ltd.

*10 Research Section of Kawasaki Refinery, General Oil Refining Co., Ltd.

Boer^{5),6)} and Johnson⁷⁾ reported about the effects of kinds of raw materials of alumina hydrates on pore size distribution. However, calcination condition of alumina hydrates etc., the correlations among pore properties of γ -alumina and, preparation methods of alumina hydrates, especially boehmite gel and, moreover, calcination conditions had not been studied sufficiently.

The authors investigated the methods to control the pore properties and also studied to obtain the supports whose large amount of pore was from 100 Å to 200 Å in diameter which would be appropriate for desulfurization catalyst support for residual fuel. Using alumina hydrates prepared by hydrolysis of aluminum isopropoxide and commercial alumina hydrates, we investigated the effects on supports of the following conditions: hydrolysis temperature, aging hour, aging temperature, washing conditions, drying and calcination temperature and period.

In this paper, the authors will describe the information derived from the above-mentioned investigation.

2 Experiments

2.1 Preparation of samples

Powder of commercial aluminum isopropoxide was further ground by the agate mortar into that of 50 to 100 mesh. 100 g of it was added into pure water of 300 ml, kept at a designated temperature for 10 minutes under stirring and left as it was for 30 minutes and then was stirred up well to complete hydrolysis. Further, it was aged under a given set of conditions and the precipitate was filtered and washed in 100 ml of isopropylalcohol to remove non-reacted materials. The alumina hydrates thus prepared was washed, dried and calcined under the designated conditions to make them suitable for measurements. Commercial alumina hydrate was one of the by-product when high molecular alcohol was made from tri-ethylaluminum (alfol aluminum). Observed impurities were as follows; SiO_2 0.01 wt% and Na_2O 0.01 wt%. The type of crystallinity was observed to be the same as that of boehmite by means of X-ray diffraction.

2.2 Measurement of Pore Properties

Measurement of specific surface area was made using the BET Method based on the adsorption of N_2 . As for pore size distribution, we investigated the adsorption isotherm of liq. N_2 at the boiling point -196°C and calculated the pore size distribution of pores having a diameter less than 300 Å using the method of Cranston and Inkley⁸⁾. From the relative pressure of 0.967, we determined the volume of the pores whose

diameters were below 600 Å. The mean pore diameter was calculated from the following equation.

$$D(\text{Å}) = \frac{\text{Pore volume (ml/g)}}{\text{Specific surface area (m}^2\text{/g)}} \times 4 \times 10^4$$

3 Results and Discussion

3.1 Effects of Hydrolysis Temperature and Aging Temperature

Each 100 g of powder of aluminum isopropoxide was added into 300 ml of pure water of (a) 43°C , (b) 60°C , (c) 85°C for the duration of 10 minutes with stirring for the while, and was hydrolysed. The alumina hydrates thus prepared were washed three times in 100 ml of isopropyl alcohol, dried at 120°C for 24 hours and calcined at 550°C in the air. The pore properties of the alumina were measured. The results are shown in **Table 1** (1). As seen in the Table, when the temperature of hydrolysis was high, specific surface area decreased. The pore volume indicated the largest figure when hydrolysis was carried out at 60°C . From this result, the following was observed: with higher hydrolysis temperature, crystallites grew larger and the specific surface area decreased. However, at the same time, pore volume of the pore having diameter less than 600 Å, though growing large accompanying the growth of crystallites, became small by sintering when the growth attained a certain degree and the large pores were supposed to be concentrated to a small number.

Then, to check the effects of aging, samples prepared by hydrolysis in pure water of 60°C , were aged for (a) 0 hour, (b) 5 hours, and (c) 24 hours separately. The alumina hydrates thus manufactured were turned to γ -alumina by the following treatment and their pore properties were measured. The results are shown on **Table 1** (2). From the above experimental results, the longer the aging time, the growth of bayerite proceeded in parallel with the growth of crystallinity of boehmite. This is supposed to be the reason that the specific surface area, pore volume etc. decreased.

3.2 Effects of Drying Conditions

Using the manufactured samples by hydrolysis of aluminum isopropoxide in pure water of 43°C , the effects of drying conditions on physical properties were studied. As for the effects of drying temperatures, the samples were dried in muffle furnace controlled at 80°C , 100°C , 120°C and 140°C , for 24 hours and the decrease rate in volume was measured. As it was assured that desorption of adsorbed water of the samples was almost complete and their weight became constant by drying at 120°C , for 24 hours, the effects of drying time on physical

Table 1 Effects of Preparation Conditions on Physical Properties of Carrier

Sample Number	Preparation Conditions								Pore Properties		Crystallite Size**	Crystal Phase
	Hydrolysis Temp. (°C)	Aging Time (hr)	Washing Sol. Number	Drying Temp. (°C)	Drying Time (hr)	Calcining Temp. (°C)	Calcining Time (hr)	Surface Area (m ² /g)	Pore Volume (ml/g)	Mean Pore Diameter (Å)		
(1)	(a) 43	0	IPA* 3	120	24	550	2	340	0.686	81	32.4	Boehmite
	(b) 60	0	IPA 3	120	24	550	2	295	1.011	137	32.4	"
	(c) 85	0	IPA 3	120	24	550	2	249	0.850	137	53.9	"
(2)	(a) 60	0	IPA 3	120	24	550	2	295	1.011	137	32.4	Boehmite
	(b) 60	5	IPA 3	120	24	550	2	306	0.985	129	40.3	Boch. + Bay. (very weak)
	(c) 60	24	IPA 3	120	24	550	2	267	0.670	100	81.5	Boch. + Bay. (weak)
(3)	(a) 43	0	IPA 3	120	2	550	2	288	0.822	114	30.0	Boehmite
	(b) 43	0	IPA 3	120	5	550	2	309	0.778	101	28.9	"
	(c) 43	0	IPA 3	120	24	550	2	340	0.686	81	32.4	"
(4)	(a) 43	0	Water 1	120	24	550	2	270	0.486	72	31.0	"
	(b) 43	0	Water 3	120	24	550	2	240	0.445	74	35.2	"
	(c) 43	0	Water 10	120	24	550	2	223	0.467	84	—	Boch. + Bay. (weak)

* IPA: Isopropylalcohol

** Crystallite size was calculated by the Sherrer's equation

$$\text{Sherrer's equation: } D_{hkl} = \frac{0.89\lambda}{\beta \cos \theta}$$

 D_{hkl} : mean dimension of crystallite λ : wave length of $\text{CuK}\alpha_1$ β : half maximum line breadth (radian) θ : diffraction angle

properties were investigated. As a result, it was found that when drying proceeded enough, specific surface area increased and pore volume decreased. This means that mean pore diameter became small. These results are supposed to occur owing to the facts that the volume of isopropylalcohol attached to the alumina hydrate decreased as the drying time became longer and the generation of pores having a large diameter was restrained, which would be mentioned later, and also the effect on the disappearance of pores of small diameter, which occurred when alumina hydrate had adsorbed water, was observed to decrease due to drying for long period of time. In order to make sure of this observation, the physical properties of alumina hydrate, which was washed in water to make it alcohol free, were measured. The results are shown on **Table 1** (4). It was observed that comparing with the results on **Table 1** (3), both pore volume and specific surface area decreased because of washing in water.

3.3 Effects of Calcining Conditions

To study the effects of calcining conditions on pore properties, commercial alumina hydrate (boehmite gel) was calcined at a certain temperature for a certain period of time in an electric furnace and their physical properties were measured. The results are shown on **Table 2**. From **Table 2** (1), it was observed that as the calcining temperature was raised higher, specific surface area tended to decrease, and in contrast, pore volume increased. From the experimental results, it was supposed that as the temperature

Table 2 Effects of Calcination on Pore Properties of Alumina

Sample	Calcination		Pore Properties		
	Temp. (°C)	Time (hr)	Surface Area (m ² /g)	Pore Volume (ml/g) <300 Å	Mean Pore Diameter (Å) 300 Å
(1)	(a) 400	2	388	0.535	55
	(b) 500	2	294	0.554	75
	(c) 600	2	315	0.574	73
	(d) 700	2	203	0.629	124
(2)	(a) 600	2	315	0.574	73
	(b) 600	10	304	0.580	76
	(c) 600	24	292	0.590	81

was raised higher, sintering proceeded, small pores disappeared and mean pore diameter became large. Also, the effects of calcining period at 600°C are shown on **Table 2** (2). As the calcining period was prolonged, pore volume increased a little and specific surface area decreased. It was supposed, however, that comparing with the effects of temperature, effects of the time was relatively small.

The effects of calcining temperature on pore size distribution curve are shown on **Fig. 1** and **Fig. 2**. Comparing with the results on **Table 2**, it is observed that the peak of the pore distribution curve transferred to pores of larger diameter.

3.4 Effects of Alcohol Treatment

Few papers had studied the controlling methods of pore size distribution of catalyst supports

Fig. 1 Pore Size Distribution of Calcined Alumina (1)

Fig. 2 Pore Size Distribution of Calcined Alumina (2)

which had micro pore under 300 Å in diameter suitable for hydrodesulfurization catalyst. Also, papers on formation mechanism of pores were found to be few. The authors investigated the effects of alcohol on pore properties and their mechanism using commercial alfol alumina gel. In **Table 3** and **Fig. 3**, changes of physical properties caused by alcohol treatment are shown. From the experimental results, the changes in pore size distribution were found according to the kinds of alcohol used. In the following experiment, the effects of some kinds of alcohol on alumina hydrates were studied. Alfol alumina hydrates have boehmite type crystallite structure, not having so good crystallinity as judged from the X-ray diffraction figures. Generally, in case of such compound of layer structure as alumina hydrates, water is

Fig. 3 Effects of Alcohol Washing on Pore Size Distribution

Table 3 Effects of Addition of Alcohols on Pore Properties of Alumina

Sample	Calcination		Pore Properties		
	Temp. (°C)	Time (hr)	Surface Area (m²/g)	Pore Volume (ml/g) < 300 Å	Mean Pore Diameter (Å) < 300 Å
a) Water	550	2	220	0.473	86
b) Methyl Alcohol	"	"	288	0.685	95
c) Ethyl Alcohol	"	"	251	0.852	136
d) Isopropyl Alcohol	"	"	276	1.037	151
e) n-Butyl Alcohol	"	"	299	1.017	136
f) Hexyl Alcohol	"	"	228	0.430	75
g) Octyl Alcohol	"	"	197	0.418	85
h) Decyl Alcohol	"	"	202	0.451	89

included between layers which is combined comparatively loosely in van der Waals bond. Also, it is known that this water is easily substituted by such polar organic compound as amine group, alcohol group, glycol group, etc.. The results of measurement of alfol alumina hydrates by the differential thermo balance are shown in **Fig. 4**. From this figure, two endothermic peaks were noticed; the first one was from normal temperature to 240°C and the second one was from 350°C to 530°C. The decreased volume at this time was calculated to be 2.06 mol H₂O per Al₂O₃ 1 mol as crystal water. From **Fig. 5**,

TGA: Thermogravimetric analysis
DTA: Differential thermal analysis

Fig. 4 Derivatogram of Boehmite Gel

Target : Cu
Filter : Ni
Voltage : 30 kV
Current : 20 mA
Full scale count: 800 cps
Scanning speed: 1/2° 2θ/min

Fig. 5 X-Ray Diffraction of Boehmite Gel

the value of inter planar spacing d_{020} was obtained as 6.23 Å. According to Lippens⁴⁾ report on the relationship between an inter planar spacing d_{020} and number of mol of crystal water, when the value of crystal water was 1.21 mol, the inter planar spacing d_{020} was 6.23 Å. Therefore, the water of 2.06 mol which was obtained in this study was supposed to include the adsorbed water besides the crystal water.

Judging from the two endothermic peaks in the differential thermo balance, existence of two kinds of water having clearly different combining powers was recognized. From these experimental results it was considered that in the alfol alumina hydrates, the first peak was the normal adsorbed water and the second one was the crystal water of 1.1 mol H_2O on measurement; that is, adsorbed water between layers. The size of the crystallite of the (020) reflection of boehmite was measured to be 27 Å. When this boehmite was added alcohol, the alcohol was considered to permeate into the following three kinds of interstice; among layers of the layer structure, among crystallites and among aggregates. At first among layers, no more than 1.1 mol of water from the differential thermo balance, and 1.2 mol of water from the X-ray diffraction was found. Therefore, it was supposed that the substitution by permeation was difficult. Indeed, very small changes were ascertained in an inter planar spacing d_{020} by X-ray diffraction after alcohol was added. As Johnson⁷⁾ mentioned, pores formed by dehydration of water among layers of boehmite were such small as could not be checked by measure-

ment of pore size distribution by the adsorption isotherm of N_2 . Also, summation of specific surface area calculated from pore size distribution agreed well with that measured using the BET Method and very small pores, namely pores having a diameter less than 20 Å were never found after alcohol was added (Fig. 3). From the above observations, it was supposed that in this study the permeation of alcohol into interstice among layers did not occur by the alcohol treatment of boehmite. Next, alcohol seemed to permeate into interstice among crystallite and into interstice among particles which were formed owing to aggrigation of crystallites. In the latter case, interstice among particles was considered relatively wide, namely an average size of particle aggrigated was about 40 μ. Therefore essential effects on pore size distribution of pores having diameter from 0 to 300 Å were supposed to occur by the alcohol permeation into interstice among crystallites.

Boehmite, after impregnated in Methylalcohol, Ethylalcohol, Isopropylalcohol and *n*-Butylalcohol respectively, was dried for 24 hours at 120°C, calcined for 2 hours at 550°C and its pore properties were measured by means of the adsorption isotherm of N_2 . The results are shown in Fig. 3 and Table 3. As seen in the figure and in the table, an increase in comparatively large pores was observed in the boehmite impregnated in Methylalcohol and while in the boehmite which was impregnated in Isopropylalcohol and *n*-Butylalcohol, an increase in large pores was found very remarkably. In consequence, pore volume and mean pore diameter became large and also specific surface area increased though not so much as pore volume. The reasons of these results are considered as follows: boehmite was dried and calcined, including alcohol among crystallites as mentioned before and contraction by surface tension of water and dessolution and subsequently crystallization of alumina hydrates to water vapour took place repeatedly during the calcination period. In other words, alcohol has the promotion effects on calcining crystallites; therefore the decrease in pore volume was supposed to be prevented by the alcohol. When the alcohols of rather large molecular weight were used, the pore volume was observed to become a little large. However, as seen in Table 3, when such alcohols abundant in carbon number as Hexylalcohol, Octylalcohol and Decylalcohol were used, the permeation of molecules did not take place easily and the effects on pore structure of alcohol were not observed.

3.5 Effects of Acid

To 100 g of alfol alumina hydrates dried at

120°C was added separately the following nitric acid solution a) no addition, b) 3.2×10^{-3} mol, c) 5.2×10^{-2} mol, d) 2.5×10^{-1} mol, e) 7.4×10^{-1} mol. The mixture was kneaded well, dried at 120°C for 5 hours and then calcined at 600°C for 5 hours. The physical properties of thus prepared samples are shown in **Table 4** and **Fig. 6**. Independent of the volume of acid added, pore volume and also mean pore diameter decreased greatly, though specific surface area was almost constant. These results were supposedly caused by the way the surface of alumina dissolved by acid little by little, which had effects to bind alumina particles and after all, to plug the pores. However, acid acted on pores larger than 50 Å in diameter and did not permeate into smaller pores and therefore it was assumed that the specific surface area was not changed by acid.

4 Conclusion

1) With higher the hydrolysis temperature, the crystallites became larger from 32.4 Å to

Table 4 Effect of Nitric Acid on Pore Properties

Sample No.	Concentration of Solution (mol)	Surface Area (m ² /g)	Pore Volume (ml/g)	Mean Pore Diameter (Å)
a	0	225	0.470	83.6
b	3.2×10^{-3}	226	0.474	83.9
c	5.2×10^{-2}	229	0.457	79.8
d	2.5×10^{-1}	201	0.377	75.0
e	7.4×10^{-1}	199	0.327	65.7

Fig. 6 Effect of Acid on Pore Properties

53.9 Å in diameter, the specific surface area decreased from 340 m²/g to 249 m²/g and the pore volume of the pores having diameter less than 600 Å increased. When aging period of boehmite gel was prolonged, the degree of crystallinity advanced along with the crystal growth of bayerite and consequently, the specific surface area and the pore volume decreased.

2) When the alumina hydrates were washed in water, pore volume and specific surface area decreased. When they were washed in such particular alcohol as Methylalcohol, Ethylalcohol, Isopropylalcohol and *n*-Butylalcohol, the pore volume and the specific surface area increased on the contrary.

3) As the calcination temperature was raised higher, the specific surface area decreased rapidly and in reverse, the pore volume increased.

4) The most important effect on the pore structure of the alumina as catalyst support was the permeation of alcohols into the interstice of crystallites of alumina. Also, selecting the preparation conditions of alumina hydrates adequately, the diameter of crystallites could be changed markedly and, consequently, the pore structure could be controlled.

5) When nitric acid was added to alumina hydrates and they were calcined to make alumina supports, the specific surface area was constant independent of the acid concentration, while the pore volume and the mean pore diameter decreased according to increase of the acid concentration.

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