

PREPARATION OF ALUMINA CATALYST SUPPORTS AND NiMo/Al₂O₃ CATALYSTS

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Abstract—Several alumina catalysts were prepared to investigate effects of catalyst preparation variables on pore structure, including sintering time and temperature, acid type, and fiber type and loading. Each catalyst was characterized with a porosimeter and sorptometer in terms of pore size distribution, average pore diameters, pore volumes, densities and surface area. Bimodal NiMo catalysts were effectively prepared without losing surface area by using a combined method of coextrusion and fiber incorporation.

INTRODUCTION

Catalyst supports, in the form of extrudate pellets, can be prepared from an alumina gel using an acid and boehmite, followed by calcination to γ -alumina. Boehmite particles are chemically dispersed, i.e. peptized in the acid solution to form a viscous matter which can be easily extruded through a press die [1]. The term peptization was introduced by T. Graham, based on a similar phenomenon of the peptization method with the protein dissolution by the pepsin [2]. Chemical peptization occurs when a substance, such as acid, added to a system, reacts with a precipitate, such as boehmite; consequently an electrolyte which gives stability to the particles of the dispersed phase is formed. In other words, boehmite is chemically broken down to subagglomerates or ultimate crystallites by acid [3]. When an acid is added to boehmite, two possible reactions generally occur. The hydrogen ions of the acid will react with the hydroxo groups of boehmite forming aquo groups. Also deolation (dehydroxylation) may occur. As deolation occurs, OH groups of boehmite become free hydroxo groups. Finally aluminum ionic micelles are formed when enough acid is added. If the ratio of acid to alumina is low, the acid will be removed from the solution without dispersing the alumina. The peptizing order has been reported to be trichloroacetic > dichloroacetic > nitric > hydrochloric > monochloroacetic > formic > acetic > oxalic > tartar-

ic > sulfuric. More extensive discussion on the peptization is given in the literature [4].

Pore structure of the extrudates may be controlled either by a sintering technique or by using combustible fibers. Macropores (greater than 500Å in diameter) can be produced by incorporation of combustible agents such as natural or synthetic fibers, e.g. cellulose, rayon, and/or other materials, which are removed during calcination. Variables affecting the pore structure include acid type, pH, mixing time, drying and calcining temperatures and times, and combustible material loading.

Several methods are available for producing the bimodal (macro-micropore) catalyst supports. Basma-djian et al. [5] used water soluble organic polymers for the control of the pore volume and pore size distribution in alumina and silica gels. They found that the methyl cellulose compounds form mainly large pores.

Tischer [6] examined methods for preparing bimodal alumina supports and molybdena/alumina catalysts by extrusion techniques. Several methods including partial peptization, coextrusion of salt/boehmite mixtures, and incorporation of combustible fibers such as Avicel or filter pulp were examined. He found that the type of cellulose fiber and its loading affected the nature of the macropores produced in the extrudates. Thermal treatments of the extrudates were used to develop mesopores in the range of 80 to 180Å with an average pore diameter of 120Å. He and his coworkers also developed another method to produce the larger-diameter pores, without using a steaming or

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sintering process and resulted in higher surface areas of about 350 m²/g [7].

Ternan et al. [8] have prepared highly porous catalyst supports from dilute alumina gels. They found that high acid concentrations and very high fluid concentrations favored the preparation of highly porous solids. Attempts were made to dry the gel without collapsing the pore structure between the alumina particles.

Marcelin et al. [9] observed that surface areas and pore size distributions could be controlled by varying the stoichiometry of the precipitates. High alumina contents invariably yielded materials with high surface area and small pores while high aluminum phosphate contents resulted in smaller surface area and larger pores.

Jiratova et al. [10] reported the effect of different peptizing acids on the physical properties of extrudates. Their results were generalized by using the Hammett acidity function of the peptization solution. The size of primary aluminum hydroxide particles substantially influenced the physical properties of extrudates prepared from it.

Snell [11] achieved a desired mean pore size in the range of 75 to 400 angstroms by selecting appropriate pore regulation reagents which affected the porous structure of silica-rich silica-alumina gels because of their charge density and intensity. Pore-regulating molecules containing nitrogen had a particularly strong effect.

Vogel et al. [12] examined the effect of ammonium bicarbonate as a precipitant upon the physical properties of activated alumina. The surface area, pore volume, and pore radius of the resulting activated alumina depended upon the post-precipitation treatment given to the ammonium aluminum carbonate hydroxy hydrate. In order to obtain maximum control of the pore properties, a cycle of calcination-hydration-calcination was employed.

According to Belding and Rigge [13], both the forming techniques employed and the properties of the particular alumina had significant effects on control of the pore volume distribution in an alumina catalyst support. They found that catalyst supports with bi- or multimodal pore volume distributions were produced when aluminas were broken down to larger subagglomerates. Also the incorporation of alumina powder, calcined at high temperatures, into peptizable alumina produced pellets of multimodal volume distributions. The mean pore sizes were shifted by varying calcination conditions due to crystallite growth resulting in collapse of pore walls.

Table 1. Typical chemical composition of Catapal alumina^a

Chemical composition	wt%
Al ₂ O ₃ content	70.0
Total ignition loss	30.0
SiO ₂	0.005
Fe ₂ O ₃	0.005
Na ₂ O	0.004
Sulfur	nil

a: From manufacturer (Vista Chemical Company)

NiMo catalysts can be prepared by two methods, namely, impregnation and coextrusion. In the former method, active catalyst components are impregnated into the porous alumina extrudates using an incipient wetness technique where the solution volume containing the active catalyst components must be equivalent to pore volume. In the other method, a mixture of alumina gel and active catalyst components is extruded through a press die, followed by drying and calcining steps as in the impregnation method [14].

In this research several alumina extrudates were prepared to investigate the effects of catalyst preparation variables, such as sintering temperatures and times, acid types, and fiber types and loading, on pore structure. Also NiMo catalysts were prepared using the impregnation and coextrusion methods. Each catalyst was characterized in terms of macro- and micropore volumes, apparent and true densities, surface area, and average macro- and micropore diameters.

EXPERIMENTAL

1. Materials

Catapal alumina produced by the Vista Chemical Company was used as a raw material for making catalyst supports. This is a high purity boehmite alumina offered as a white, acid-dispersible spray-dried powder. Its typical chemical composition and properties are shown in Table 1 and Table 2. The combustible fiber utilized for introducing macroporosity was FMC's microcrystalline cellulose (Avicel-ph-101), with typical properties as given in Table 3. The peptizing agents were reagent grade 70 wt% nitric acid and 99.9 wt% acetic acid. The acetic acid peptizing agent (Fischer, reagent A.C.S.) was diluted to 5 vol% before use. Nitric acid (Fischer, reagent A.C.S.) was not used with cellulose because of safety concerns.

Nickel nitrate (Fischer, certified) and ammonium molybdate (Fischer, certified A.C.S.) were used as active catalytic agents; sodium lauryl sulfate (Fischer)

Table 2. Typical properties of Catapal alumina^a

Crystal structure ^c	Boehmite
Crystal structure ^b	γ -alumina
BET surface area ^b	270 m ² /g
Ultimate crystallite size (XRD)	
020 Refraction ^c	32 Å
021 Refraction ^c	45 Å
440 Refraction ^b	45 Å
Pore volume (mercury porosimeter)	
35-100 Å ^b	0.45 cc/g
35-10,000 Å ^b	0.50 cc/g
Loose bulk density ^c	0.71 g/cc
Particle size distribution ^c	43% <45 μ m 15% >90 μ m
Angle of repose ^c	33 degrees

a: As is.

b: After calcination for 3 hours at 483°C.

c: From manufacturer (Vista Chemical Company)

Table 3. Typical properties of Avicel PH-101^a

Retained on 400 mesh screen	>95%
pH	6.7
Loss on drying	4.1%
Residue on ignition	133 ppm
Water soluble substances	1.2 mg/g
Heavy metals	<10 ppm
Starch test	negative
Assay, % cellulose	98.7
Particle size	
+60 mesh	<0.1 wt%
+20 mesh	21 wt%
Average particle size	50 μ m

a: From manufacturer (FMC corporation)

as a surfactant; and potassium permanganate (Mallinckrodt) as a color indicator.

2. Preparation of Alumina Extrudates

When nitric acid was used as a peptizing reagent, initially, boehmite was well mixed with nitric acid and water using a Motomatic mixer (Electro Crat Co.), and then the mixture was dried at room temperature for one day. Finally, the mixture was calcined at 500°C for 6 hours using a Lindberg tubular muffle furnace.

When 5 vol% acetic acid was used as a peptizing reagent, the solid mixture of boehmite and fiber was well blended with the peptizing acid using a Hobart mixer (model N-50). The peptized mixture was then extruded using a Beckman spex hydraulic press and press die to produce cylindrical extrudates. Press dies with an 3.2 or 7.6 mm hole were used to produce 2.0 or 4.8 mm extrudates. The extrudates were dried

at room temperature for one day, and then calcined under the specific conditions. The size of the extrudates strongly depended on the manufacturing procedures such as calcining temperature and fiber loading. When the press die with an 7.6 mm hole was used to produce 4.8 mm extrudates, higher calcining temperature yielded larger shrinkage (0.34 mm at 1200°C) in diameter and higher fiber loading gave smaller shrinkage (0.48 mm at 40 wt% fiber loading) in diameter. A method of partial peptization was developed as an alternative to produce macroporous catalyst supports. When boehmite was sintered at 1000°C for 16 hours, it was not peptized by acetic acid and had larger pores than when it was not sintered. The emphasis of this technique was to produce extrudates from a mixture of raw and sintered boehmite and acetic acid.

3. Preparation of Ni/Mo Catalysts

After investigating several alternatives, the methods developed by Tischer [6] were determined to be most applicable for producing the catalysts needed for this study. Double impregnation by incipient wetness and coextrusion techniques were used in producing 4.8 mm diameter cylindrical catalyst extrudates. In both methods, combustible fibers were introduced to regulate an amount of macroporosity. The introduction of pre-calcined boehmite into the extrusion batch was also investigated as an alternative method for producing macropores.

In the impregnation method, a mixture of boehmite (Catapal alumina), acetic acid (5 or 7.5 vol%), and fiber (Avicel) was extruded when boehmite was fully peptized by acetic acid. It was found that a weight ratio of acetic acid to boehmite of approximately two was required to make an easily extrudable mixture. When this ratio was too small, the mixture was not fully peptized and yielded very weak extrudates. When the ratio was greater than two, the viscosity of the peptized mixture was too low to produce extrudates of cylindrical shape. The allowable ratio of acetic acid to boehmite was dictated by the acid concentration and fiber loading.

Using the impregnation technique, the active catalyst components (nickel nitrate and ammonium molybdate) were introduced into the catalyst support following calcination. Two separate aqueous solutions containing either Ni or Mo precursor were prepared, such that the amount of each active catalytic component would yield a catalyst of approximately 3 wt% NiO and 15 wt% MoO₃. Each solution volume was identical to the total pore volume of the catalyst support to be impregnated. Two stepwise impregnations were made, and impregnation of the Ni containing solution

always preceded that of the Mo containing solution. After each impregnation the catalyst was dried at 90°C with a nitrogen flow in a rotary evaporator. The catalyst was further dried with an air flow in a tubular muffle furnace where the temperature was raised very carefully to prevent any loss of the active component. Finally, the catalyst was calcined at 500°C for 16 hours.

The impregnation method was ineffective for the catalyst supports having very small micropores. When the solution was added to these extrudates, many of the extrudates fractured. In addition, an examination of the non-fractured extrudates revealed a nonuniform metals deposition, indicated by a white center in the (black) extrudates following sulfidation. Also, the degree of penetration of solution inside the extrudates could be seen by using potassium permanganate solution as a color indicator (violet). Addition of a surfactant (sodium lauryl sulfate) to the impregnating solution greatly reduced the fracturing phenomenon and aided the impregnation process by allowing the solution to reach the center of the extrudates. The addition of a surfactant was believed to reduce the surface tension between the solution and pore wall. The surfactant could also occupy adsorption sites and allow penetration of the other active ingredients to reach the center of the pellets. However, this method was later abandoned because of uncertain effects that the surfactant might have on the catalyst activity. Therefore, a more reliable coextrusion technique was used.

In the coextrusion technique, active catalytic agents were added directly into the peptized alumina batch prior to extrusion. As found by Tischer the sequence of adding materials into the mixing batch was crucial to the peptization process. The aqueous mixture of active catalyst components was added into the mixing batch after boehmite was peptized by acetic acid. When the solution of active components was added into the mixing batch, prior to fully peptization of boehmite by acid solution, a viscous and extrudable mixture was not formed. This behavior was presumed to come from a reaction between the acidic (acetic acid) and basic (active catalytic agents) solution and was also noted by Tischer [6]. After extrusion the catalyst extrudates were dried at room temperature for one day. Finally, calcination of the extrudates at 500°C for 16 hours followed a stepwise drying in a tubular muffle furnace. A slow heating rate and high air flow rate were sustained to prevent the extrudates from losing their active catalytic components and to completely remove all combustible materials without sintering the catalyst micro-structure.

4. Catalyst Characterization

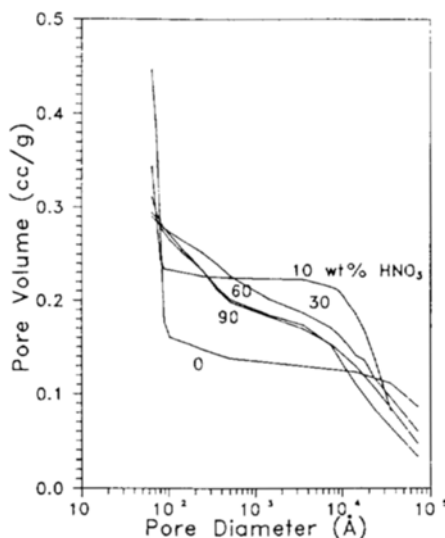


Fig. 1. Effect of nitric acid on pore structure of alumina aggregate.

In order to measure the pore size distribution and the apparent density of the extrudates, a Quantachrome Autoscan-33 porosimeter equipped with the Autoscan data reduction system was used. The maximum intrusion pressure of mercury into the pores was 33,000 psig, which corresponds to ca. 64 angstroms in pore diameter. All calculations were made assuming that the contact angle of mercury with catalyst surface is 140 degrees and the surface tension is 480 ergs/cm² [15, 16].

The surface areas of the extrudates were obtained from a Quantasorb sorption system, where four different gas mixtures of nitrogen and helium were used as adsorbents. The method of multipoint BET measurements [14] was applied to calculate a specific surface area of each extrudate. The pore volume of extrudates was measured from the water displacement in the pycnometer. A macropore was defined as the pore whose diameter is greater than 500 angstroms. For convenience pores less than 500 angstroms in diameter were treated as micropores. Average pore diameters were calculated from the pore volume and BET surface area data by assuming all pores have cylindrical shapes.

RESULTS AND DISCUSSION

1. Effect of Nitric Acid on Alumina Aggregates

The results of the effect of nitric acid on alumina aggregates are shown in Figure 1 and Table 4. As

Table 4. Effect of nitric acid on pore structure of alumina aggregates

Sample identification	Initial HNO ₃	Total	Macro-	Surface	Average pore diameter	
	content in sample (wt%)	pore volume (cc/g)	pore volume (cc/g)	area (m ² /g)	micro-	macro-
					(Å)	
a	90	0.29	0.20	29	138	5342
b	60	0.29	0.23	19	147	4465
c	30	0.31	0.20	37	124	5038
d	10	0.34	0.23	64	75	18242
e	0	0.45	0.14	155	78	8080

Note: (1) Each sample contains 10 wt% boehmite and 90 wt% liquid. For example, sample b was prepared by mixing 10 wt% boehmite, 60 wt% of 70% HNO₃, and 30 wt% water.

(2) Pore volume was measured by a mercury porosimeter which could scan pores larger than 64Å in diameter.

(3) Macropore volume = volume of pores larger than 500Å in diameter.

(4) Surface area = $0.0188 \sum p \Delta v$ (p in psia, v in cc) calculated from the porosimeter data.

(5) Average micropore diameter = $4 \times (\text{micropore volume}) / (\text{micropore surface area})$.

(6) Average macropore diameter = $4 \times (\text{macropore volume}) / (\text{macropore surface area})$.

Table 5. Effect of calcining time on characteristics of 2.0 mm alumina extrudates

Calcining time (hrs)	Total pore volume		Macropore volume (cc/g)	Surface area S _g		Density		Average pore diameter	
	Hg (cc/g)	H ₂ O (cc/g)		Hg (m ² /g)	BET (m ² /g)	ρ _a (g/cc)	ρ _s (g/cc)	micro-	macro-
								(Å)	
4	0.69	0.75	0.30	196	210	0.93	3.06	89	2748
8	0.69	0.75	0.30	195	209	0.93	3.04	88	2886
16	0.69	0.73	0.29	199	208	0.93	2.91	87	2675
32	0.72	0.75	0.30	201	205	0.94	3.15	89	2619

Note: (1) Compositions of solid mixture in the mixing batch: boehmite; 70 wt%, Avicel PH-101; 30 wt%. Solid wt% in the mixing batch: 52.5. Peptizing agent: 5 vol% acetic acid

(2) Calcining conditions: temperature = 600°C, initial sample weight = 6g with air flow

(3) Pore volume was measured using a porosimeter (Hg) or water displacement method (H₂O).

(4) Macropore volume was obtained from porosimeter data.

(5) Apparent density, ρ_a was calculated from porosimeter data.

(6) Solid density, ρ_s was calculated from porosimeter and water displacement data.

(7) Average micropore diameter was calculated based on water displacement data.

the amount of nitric acid in the original mixture preparation increased, surface area and Hg pore volume decreased while average mesopore diameter increased. These results are consistent with Ternan's [8]. As shown in Figure 1, the amount of nitric acid above about 30% (samples a, b, and c) did not greatly affect the shape of the intrusion curve.

Nitric acid, as a peptizing agent, seemed to have little advantage compared to acetic acid. First, nitric acid cannot be used with organic fibers such as Avicel because of safety concerns. Also the alumina gel formed with this acid rapidly became too viscous to make good extrudates. It may be noted that the alumina supports in Table 4 exist as aggregate rather than cylindrical pellets.

2. Effect of Calcining Time

As shown in Table 5 and Figure 2, effects of calcin-

ing time on characteristics of 2.0 mm alumina extrudates were negligible. This means that no problems were encountered in burning the combustible materials existing within the extrudates under the given conditions. The only difference observed was in the color of the extrudates; the longer the calcining time, the whiter the color of the extrudates. This indicates that very short times may not completely remove all organic material.

It was found that a slow heating rate with sufficient air flow was needed to keep the extrudates from cracking into pieces. Rapid heat-up without sufficient air flow seemed to make fibers inside the extrudates combust very rapidly, thereby resulting in breakage of pellet structure.

3. Effect of Calcining Temperature

Different calcining temperatures gave different mi-

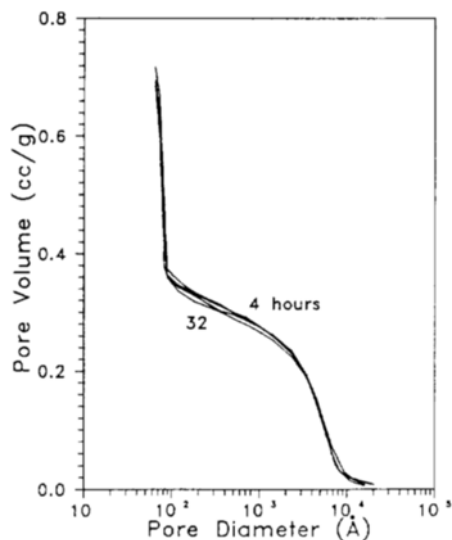


Fig. 2. Effect of calcining time on pore structure of 2.0 mm alumina extrudates.

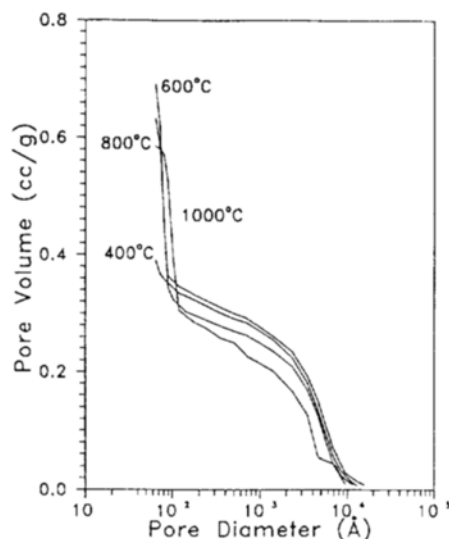


Fig. 3. Effect of calcining temperature on pore structure of 2.0 mm alumina extrudate.

Table 6. Effect of calcining temperature on characteristics of 2.0 mm alumina extrudates

Calcining temp. (°C)	Total pore volume		Macropore volume (cc/g)	Surface area S_g		Density		Average pore diameter	
	Hg (cc/g)	H ₂ O (cc/g)		Hg (m ² /g)	BET (m ² /g)	ρ_s (g/cc)	ρ_p (g/cc)	micro- (Å)	macro- (Å)
400	0.39	0.74	0.29	42	274	0.93	3.02	67	2693
600	0.69	0.75	0.30	195	209	0.93	3.04	88	2886
800	0.63	0.69	0.27	178	162	1.00	3.19	105	2681
1000	0.59	0.60	0.26	132	112	1.05	2.87	128	2730

Note: (1) Solid content in the mixing batch: 52.5 wt%. Peptizing agent: 5 vol% acetic acid, Combustible material: Avicel PH-101, 30 wt% of solid mixture

(2) Calcining conditions: time=8 hours with air flow

cropore structures of the 2.0 mm alumina extrudates as shown in Table 6 and Figure 3. The lowest temperature, e.g., 400°C, may not sufficiently remove the combustible materials, especially in the micropore region. The color of the extrudates calcined at 400°C was dark-grey. Also, the pore volume of these extrudates was much lower than that of the other extrudates. On the other hand, the highest temperature, 1000°C, was high enough to destroy some micropores. Due to this effect, the average mesopore diameter was increased and the surface area was decreased. The effect of the calcining conditions on the average macropore diameter was not great. As the calcining temperature was increased, the color of the extrudates changed from dark-grey to snow-white. It is recommended here that a calcining temperature of 600°C be used in order to obtain both high surface area and bimodality of extrudates.

Generally speaking, the BET surface area would be expected to be larger than the surface area measured using the Hg porosimeter since pores smaller than 64 angstroms in diameter cannot be detected by the porosimeter. As indicated in Table 10, this is true for all 4.8 mm NiMo/alumina catalysts. However, the alumina supports in Table 7 show the opposite behavior. To further investigate this behavior three independent measurements were performed using an alumina support calcined at 750°C. Values of 203, 196, and 190 m²/g were obtained by Hg porosimeter, while values of 161, 155, and 151, respectively, were obtained by BET analysis. The exact reason for this difference is not known; however, according to a review by Rootare [15, 16], who found some similar instances, variation in the contact angle (here assumed to be 140°) is the most likely source. He reported values as high as 160° for some solids as determined by equating

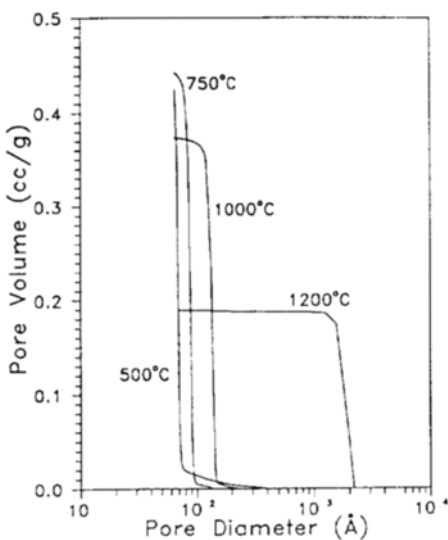
Table 7. Effect of calcining temperature on characteristics of 4.8 mm alumina extrudates

Calcining temp. (°C)	Total pore volume		Macropore volume (cc/g)	Surface area S_k		Density		Average pore diameter	
	Hg (cc/g)	H ₂ O (cc/g)		Hg (m ² /g)	BET (m ² /g)	ρ_v (g/cc)	ρ_s (g/cc)	micro- (Å)	macro- (Å)
500	0.43	0.45	a	240	220	1.30	3.09	81	a
750	0.44	0.43	a	196	156	1.29	2.86	106	a
1000	0.37	0.34	a	113	97	1.50	3.09	142	a
1200	0.24	0.24	0.24	5	3	2.27	3.32	b	1832

Note: (1) Extrudates were prepared by extruding mixture which contained same weight of boehmite and 5 vol% acetic acid.

a: No macropores

b: No micropores

**Fig. 4. Effect of calcining temperature on pore structure of 4.8 mm alumina extrudate.**

the BET and Hg surface areas; although Baiker and Reithaar [17] suggested that 130° is more reasonable for catalyst materials. Errors in the Hg surface areas can also be caused by the presence of so-called "ink bottle" pores. The BET surface area was retained as the more reliable value in this work.

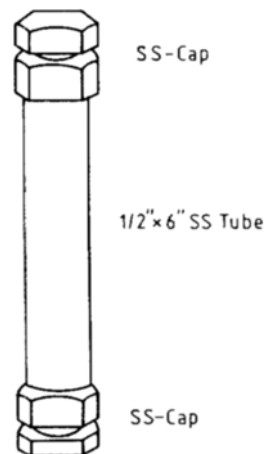
As shown in Table 7 and Figure 4, the pore distributions of unimodal 4.8 mm alumina supports were significantly dependent on the calcining temperatures. As the temperature increased, the apparent density average micropore diameter became larger but the surface area became smaller. This phenomenon may have resulted from a destruction of some small micropores and reconstruction of large macropores by the sintering process. Data of support sintered at 1200°C indicate that most micropores are destroyed and re-oriented at a high temperature.

Table 8. Results of attrition test using 2.0 mm alumina supports

Fiber loading (wt%)	Attrition (weight loss after 30 min. shaking, wt%)	
	800 cpm	1000 cpm
0	1.8	3.5 ^a
10	2.0	2.0
20	2.8	2.6
30	3.3	3.2
40	4.9(2.3) ^b	8.7(5.7) ^b
50	4.7	9.7

a: very brittle

b: shaking atmosphere = water
other cases = air

**Fig. 5. Diagram of attrition testing tube.**

4. Effect of Fiber Loading

Fiber loading had direct effects on the characteristics of the 2.0 mm extrudates as shown in Table 9 and Figure 6. Figure 7 shows that total pore volume and macropore volume increase as the fiber loading

Table 9. Effect of fiber loading on characteristics of 2.0 mm alumina extrudates

Fiber loading (wt%)	Total pore volume		Macropore volume (cc/g)	Surface area S _v		Density		Average pore diameter	
	Hg (cc/g)	H ₂ O (cc/g)		Hg (m ² /g)	BET (m ² /g)	ρ _v (g/cc)	ρ _s (g/cc)	micro- (Å)	macro- (Å)
0	0.30	0.43	0.00	175	214	1.34	3.19	81	a
10	0.50	0.49	0.01	251	217	1.21	2.93	87	b
20	0.59	0.55	0.05	241	222	1.06	2.59	95	1326
30	0.69	0.75	0.30	195	209	0.93	3.04	88	2886
40	0.79	0.89	0.45	157	226	0.83	3.20	78	3329
50	1.03	1.16	0.70	157	194	0.68	3.15	98	3781

Note: (1) Calcining conditions: temperature=600°C, time=8 hours with air flow

5 vol% acetic acid was used as a peptizing acid.

Solid content=52.5 wt%.

(2) Fiber loading values indicate wt% of fibers in the solid mixture.

a: No macropores

b: Amount of macropores is negligible

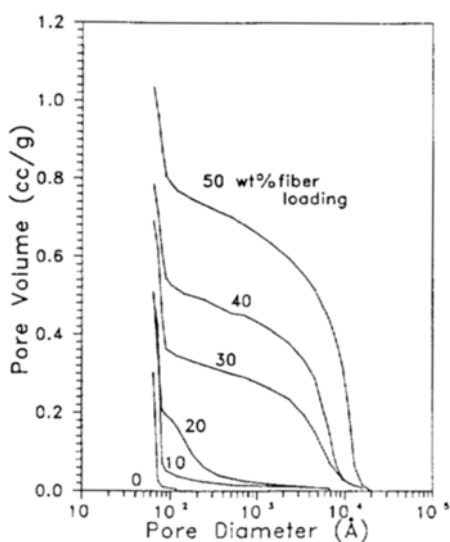


Fig. 6. Effect of fiber loading on pore structure of 2.0 mm alumina extrudates.

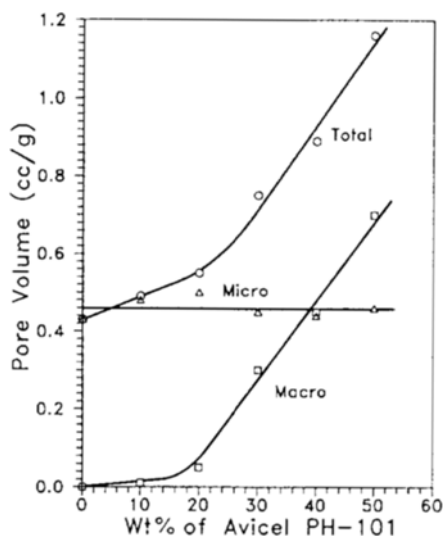


Fig. 7. Effect of fiber loading on pore volumes of 2.0 mm alumina extrudates.

increases. The macropore volume is not, however, directly proportional to the fiber loading, as might be expected. This nonlinear dependence of macropore volume on fiber loading possibly results from individual fibers grouping into agglomerates, as well as the hydrolytic action of the acetic acid upon the cellulose fibers. The effect of fiber loading on micropores was negligible as shown in Figure 8.

Attrition test may be used to measure the mechanical strength of pellet catalysts. Since the standard method (ASTM D4058-81) needs large amounts of catalysts, a modified tubing bomb microreactor was used as shown in Figure 5, where only one gram of pellet

catalysts was used. Table 8 shows the results of attrition test using 2.0 mm alumina supports. The degree of attrition was defined as the weight loss of pellets after 30 minutes shaking in the testing tube. As expected, the pellets with higher fiber loading were weaker as evidenced by higher values of attrition. Increasing the shaking speed from 800 to 1000 cpm had little effects on the attrition of pellets having low fiber loadings (up to less than 30 wt%); however, the shaking effects were noticeable for the pellets of high fiber loading (>40 wt%). The change of the shaking atmosphere from air to water reduced the attrition of the pellets of 40 wt% fiber loading by 3 wt%, possibly

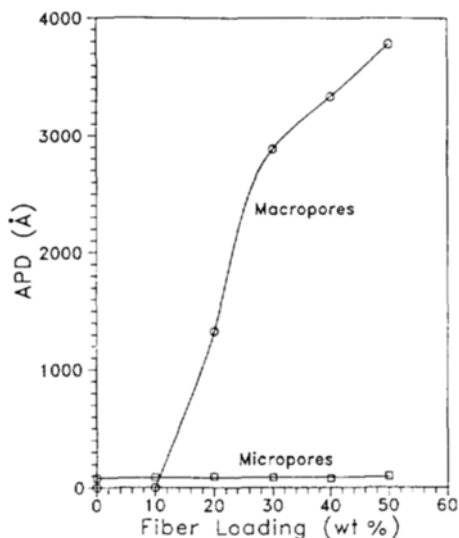


Fig. 8. Effect of fiber loading on pore diameter of 2.0 mm alumina extrudates.

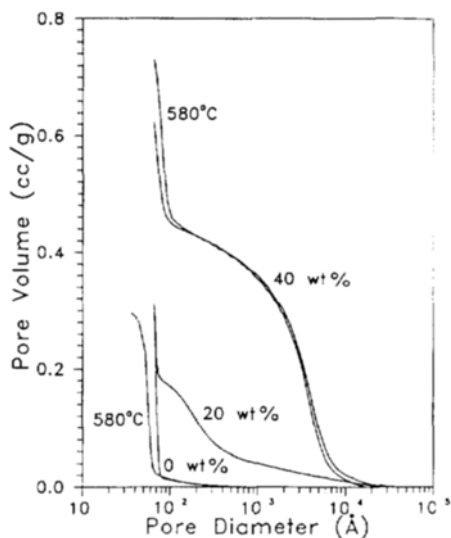


Fig. 9. Effect of fiber loading on pore structure of 4.8 mm coextruded NiMo catalysts.

Table 10. Effect of fiber loading on characteristics of 4.8 mm coextruded NiMo catalysts

Fiber loading (wt%)	Total pore volume		Macropore volume (cc/g)	Surface area S_g		Density		Average pore diameter	
	Hg (cc/g)	H ₂ O (cc/g)		Hg (m ² /g)	BET (m ² /g)	ρ_s (g/cc)	ρ_p (g/cc)	micro- (Å)	macro- (Å)
0 b	0.03	0.40	a	11	287	1.47	3.50	55	a
c	0.31	0.42	a	172	197	1.49	3.95	85	a
20 b	0.30	0.47	0.06	98	301	1.29	3.27	56	1560
40 b	0.62	0.80	0.40	110	272	0.90	3.19	61	2348
c	0.73	0.81	0.39	156	258	0.90	3.33	66	2253

Note: (1) Calcining conditions: temperature=500°C or 580°C, time=16 hours with air flow

(2) 5 vol% acetic acid was used as a peptizing acid.

Ratio of acetic acid to boehmite=2.

Fiber loading indicates wt% of fibers in the solid mixture of boehmite and fibers.

a: No macropores

b: Calcined at 500°C

c: Calcined at 580°C

due to lessening the abrasion between the pellets and the tube wall by more viscous medium. The mechanical strength of 2.0 mm alumina pellets was comparable to that of commercial catalysts. The attritions of commercial 1.6 mm unimodal catalysts, i.e. Shell-324 and Harshaw NiMo/ γ -Al₂O₃ were 1.0 and 2.7 wt% respectively at 1000 rpm.

The method of fiber incorporation turned out to be an effective way to produce the macroporous 4.8 mm extrudates without severely destroying micropores. As shown in Table 10 and Figure 9, the fiber loading increases the macropore volume and average macropore diameter. The BET surface area data were

useful for calculating an average micropore diameter when the extrudates had many small pores less than 64 angstroms since these pores could not be detected by the porosimeter used in this experiment. The average micropore size obtained from the porosimeter data should be similar to that obtained from BET data if those two surface areas are similar. Thus curve shape for catalysts calcined at 500°C would be much different in the micropore region from those of the other three catalysts.

Under the calcining condition of 500°C-16 hours fiber loading has little effect on the BET surface area and average micropore diameter. This negligible effect

Table 11. Effect of fiber particle size on characteristics of 2.0 mm alumina extrudates

Fiber name & size (μm)	Total pore volume		Macropore volume (cc/g)	Surface area S_x		Density		Average pore diameter	
	Hg (cc/g)	H ₂ O (cc/g)		Hg (m ² /g)	BET (m ² /g)	ρ_s (g/cc)	ρ_p (g/cc)	micro- (\AA)	macro-
PH-105 (20)	0.81	0.94	0.49	164	215	0.80	3.19	86	3289
PH-101 (50)	0.78	0.90	0.45	157	226	0.83	3.20	78	3329
PH-102 (90)	0.90	0.98	0.49	190	197	0.80	3.23	102	3470

Note: (1) Solid content in the mixing batch: 52.5 wt%

wt% of Avicel in the solid mixture: 40

Peptizing agent: 5 vol% acetic acid

Calcining conditions: temperature=600°C, time=8 hours with air flow

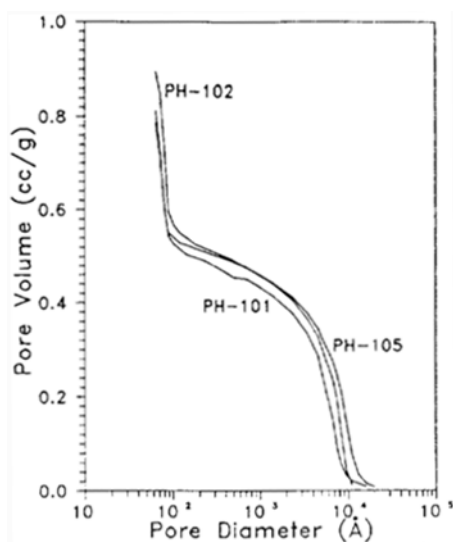


Fig. 10. Effects of fiber type on pore structure of 2.0 mm alumina extrudates.

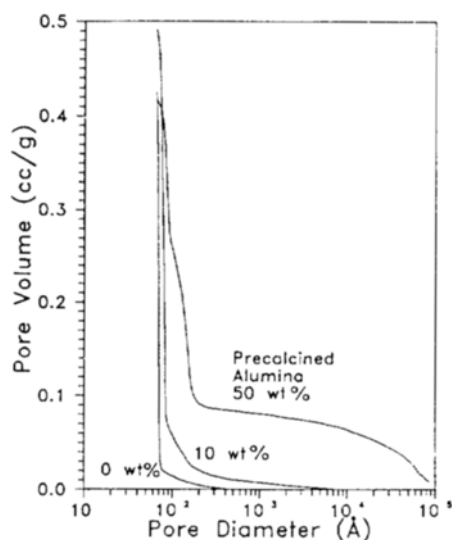


Fig. 11. Effect of precalcined alumina on pore structure of 4.8 mm alumina extrudate.

implies that the fiber incorporation method does not change the micropore structure, a result similar to Tischer's work [6]. However, the sintering temperature had another effect on the pore structure of coextruded catalysts. The average micropore diameter of catalysts calcined at 580°C for 16 hours was larger than that calcined at 500°C for 16 hours. This increase in the micropore size might cause higher catalytic activity by providing reactants with more accessibility to catalytic active sites.

5. Effect of Fiber Particle Size

As shown in Table 11 and Figure 10, the characteristics of the 2.0 mm alumina extrudates were almost independent of fiber particle size. This probably occurs because the Avicel fibers breakup into smaller fibrils during the mixing and extrusion process. Detailed examination of the particle size distribution of the Avicel, e.g., by microscopy, may be needed to fully

explain this effect.

6. Effect of Precalcined Alumina

The introduction of precalcined boehmite into the extrusion mixture was also investigated as an alternative way to introduce macroporosity into the pore structure. As shown in Table 12 and Figure 11, the addition of boehmite which had been precalcined at 1000°C increased the average micropore diameter and also produced some macropores.

Interestingly, compared to the combustible fiber incorporation method, this method produced a smaller macropore volume, but larger average macropore diameter. However, supports produced in this manner were too friable for use as catalyst supports in the shaking reactor and were not utilized in reactions. If a new technique to strengthen these supports is developed or if a less demanding type of reactor, e.g. trickle bed, is utilized, then this method may be useful

Table 12. Effect of precalcined alumina on characteristics of 4.8 mm alumina extrudate

Sintered alumina loading (wt%)	Total pore volume		Macropore volume (cc/g)	Surface area S_g		Density		Average pore diameter	
	Hg (cc/g)	H ₂ O (cc/g)		Hg (m ² /g)	BET (m ² /g)	ρ_p (g/cc)	ρ_s (g/cc)	micro- (Å)	macro- (Å)
0	0.43	0.45	a	240	220	1.30	3.09	81	a
10	0.49	0.47	0.01	230	203	1.21	2.74	92	1042
50	0.42	0.40	0.08	126	147	1.43	3.27	85	6766

Note: (1) Sintered alumina was prepared by sintering boehmite at 1000°C for 16 hours.

(2) Calcining conditions: temperature=500°C, time=16 hours with air flow

(3) Ratio of acetic acid to solid mixture=2

Sintered alumina loading means wt% of sintered alumina in solid mixture.

a: No macropores

Table 13. Properties of diffusion wafers prepared from boehmite

Wafer name	Pressing force (ton)	Fiber loading (wt%)	Total pore volume (cc/g)	Micropore volume (cc/g)	Surface area ^a (m ² /g)	Average pore diameter (Å)	
						micro-	macro-
1a	1	10	0.17	0.14	11	111	6686
1b	10	10	0.13	0.09	14	126	5188
2a	1	40	0.70	0.62	31	115	10216
2b	10	40	0.55	0.49	20	143	8476

Note: (1) Calcined at 600°C for 4 hours under air flow

(2) Weight of each wafer before calcination=0.26 g.

Sample for making wafer was prepared by drying the initial mixture which contained boehmite, fiber and 5 vol% acetic acid.

a: Measured using a porosimeter

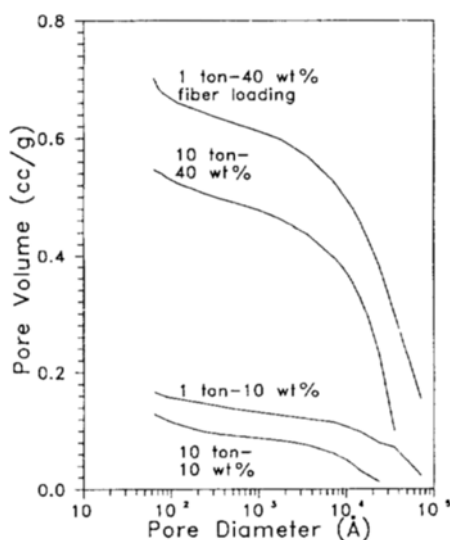


Fig. 12. Pore volume distribution of alumina wafers.

for production of macropore supports.

7. Preparation of Diffusion Wafers

In order to evaluate the diffusional characteristics

of the new supports, the preparation of alumina wafers was explored. Two kinds of approximately 2.5 mm diameter alumina wafers were prepared and characterized. As shown in Table 13 and Figure 12, the alumina wafer which was made under the higher pressure resulted in the higher density and strength, and lower pore volumes and pore sizes.

CONCLUSION

Among several experimental parameters, two factors, i.e. calcination temperature and fiber loading had substantial effects on the pore structure of catalyst supports. Macroporosity was directly proportional to the fiber loading and higher calcination temperature produced larger micropore diameters. However, calcination at high temperature caused a severe reduction in surface area.

The coextrusion method was more effective in producing uniform NiMo catalysts compared to the impregnation technique. Bimodal NiMo catalysts were effectively prepared without losing surface area by using a combined method of coextrusion and fiber incorporation. Also, alumina wafers having various pore struc-

tures were produced using the fiber incorporation technique.

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