JOURNAL OF CATALYSIS 72, 255–265 (1981)

Preparation of Bimodal Aluminas and Molybdena/Alumina Extrudates

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Received January 20, 1981; revised July 23, 1981

Methods for preparing bimodal alumina supports and molybdena/alumina catalysts by extrusion techniques were examined. The methods used to produce bimodal pore structure in the extrudates were (1) partial peptization, (2) coextrusion of salt/boehmite mixtures, and (3) incorporation of combustible fiber such as Avicel or filter pulp. The study was limited to Conoco's Catapal SB alumina. The effects of solid content of the mixture, pH of the peptizing solution, and degree of mixing on the consistency of the extrusion mixture and the pore size distribution of the resulting extrudates were examined. The type of cellulose fiber and its loading was found to affect the nature of the macropores produced in the extrudates. The extrudates were thermally treated to develop mesopores in the range needed for coal liquefaction catalysts (80–180 Å with an average pore diameter of 120 Å).

INTRODUCTION

Several liquefaction processes are currently under development to produce clean fuels from coal. New catalysts and supports are needed because of the unique chemical nature of coal, which contains fairly large aromatic molecules, relatively high quantities of heteroatoms, and significant quantities of mineral matter. Recent work at both Hydrocarbon Research Inc. and Amoco Oil Company suggests that bimodal catalysts with mesopores in the range 80–180 Å and macropores in the range 1000–6000 Å are required to prevent rapid deactivation of liquefaction catalysts (*1*). A preferred form of the catalyst for the H-coal process is cobalt molybdate/alumina as $\frac{1}{16}$-in. extrudates. In addition, nickel molybdate/alumina and molybdena/alumina are also under consideration. A survey of the literature reveals no systematic information on the preparation of such bimodal/alumina supports or catalysts. The work in this paper describes the variables that affect the preparation of such bimodal alumina or molybdena/alumina extrudates.

METHODS

All of the extrudates described in this paper were prepared from Conoco's Catapal SB. This is high-purity boehmite, which has excellent extrusion characteristics and converts to a medium-density, high-surface-area γ-alumina on calcination. The extrusion batches were mixed in a Haake Rheocord torque rheometer equipped with a model 410-spec Rheomix mixer. This mixer was fitted with cam-type blades and had a usable volume of 275 ml. The extrusion batch was mixed at 32 rpm. The torque necessary to maintain this constant mixing speed is recorded as a function of time, which enables one to determine when complete peptization of the batch is achieved. The rheometer also measures the total energy utilized by the mixer. This energy input, rather than total mixing time, was used as the process variable to control the mixing process. The mixed batch was then extruded by a Hydromet model HEB-50 hydraulic extrusion press equipped with a $\frac{1}{16}$-in. die. The extrudates were dried overnight at room temperature, broken into

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small lengths, and calcined in a box furnace at temperatures between 500 and 1000°C. The furnace was purged with dry air at a rate of 1000 cm^3/min.

The extrusion mixes were prepared from boehmite, peptizing agent, molybdenum salt, combustible fiber, and deionized water. The peptizing agent consisted of reagent-grade acetic, formic, oxalic, or tartaric acid. The molybdenum salts were Fisher reagent-grade molybdic acid or ammonium heptamolybdate. The combustible fillers were FMC's microcrystalline cellulose (Avicel-pH-101) or Fishers' ash-free analytical filter pulp. The batches were always prepared to have a total volume of 260 ml.

Thermal sintering was chosen as the method for obtaining the desired mesopore range. Table 1 shows the pore size and chemical characteristics of Catapal SB calcined at various temperatures. BET data were measured on a Micrometrics Digisorb 2500 for these calcined powders and selected extrudates. The pore size distribution of the extrudates was measured on an American Instrument model J5-7125D 60,000-psi porosimeter. In general, pore distribution curves calculated for mercury penetration data yield distributions located at a 20–30% lower level of pore radii than those calculated from nitrogen capillary condensation, and the reason for this disagreement is not known (*2*). The pore distributions were based on the porosimeter data, since this method covers a wider range of distributions and is a more rapid method of analysis than the nitrogen condensation method. The crystallographic phases present in the sintered supports and catalysts were determined by XRD measurements. Also, laser Raman spectroscopic characterization of the Mo/Al_2O_3 catalysts was obtained.

TABLE 1

Surface Properties for Catapal SB Powder[a]

	Treatment		
	As received	500°C/4 hr	1000°C/4 hr
SA (m^2/g)	241	192	95
PV (cm^3/g)	0.340	0.453	0.337
APD (Å)	56	94	142
Pore Vol distribution			
20–60 Å	0.188	0.099	0.035
60–100 Å	0.102	0.173	0.045
100–400 Å	0.047	0.179	0.254
400–600 Å	0.002	0.002	0.003
SA distribution			
20–60 Å	181.8	81.6	30.6
60–100 Å	46.6	67.1	16.5
100–400 Å	12.5	42.9	47.7
400–600 Å	0.1	0.2	0.2
XRD	γ-AlOOH	γ-Al_2O_3	δ-, θ-Al_2O_3

[a] Abbreviations: SA, surface area; PV, pore volume; APD, apparent pore diameter; XRD, X-ray diffraction.

RESULTS AND DISCUSSION

A. Effect of Process Variables on Extrusion Characteristics

The main variables that affect the extrusion characteristics of boehmite and the pore size distribution of the extrudates are solid content, pH of the peptizing solution, and degree of mixing of the extrusion batch. With our extruder, we had little effective control over the extrusion pressure and rate. The effect of these three variables was examined for well-peptized batches of boehmite, which give monodispersed extrudates. Figure 1 shows a typical mixing curve for Catapal SB. There is a large increase in the torque necessary to drive the mixer at constant speed as the boehmite

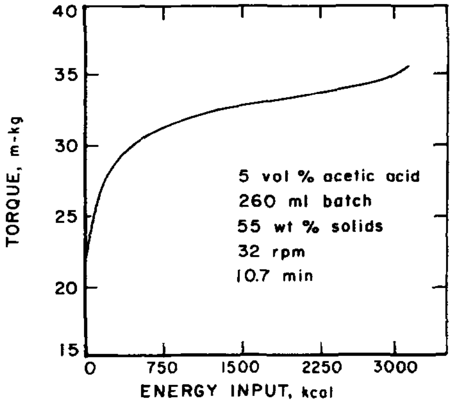

FIG. 1. Mixing characteristics for Catapal SB.

aggregates are peptized into a gel structure. The consistency of the batch is defined in terms of this torque, and its numerical value will depend on the volume of the batch and on the mixer configuration. The consistency correlates with the extrusion characteristics of the batch. With our extruder, good extrudates were obtained for batches having a consistency between 1.0 and 6.0 m-kg. At the lower end of the consistency range, the extrudates are very sticky and deform easily, while at the higher end of the consistency range the extrudates tend to flake on exiting from the die.

Figure 1 shows that the consistency of the batch reaches a relatively level plateau region as the degree of mixing increases. When the plateau is reached, the batch has been completely peptized, and little change in consistency of the batch is accomplished with increased mixing time. The consistency of these well-peptized batches is a strong function of the solid content of the batch (see Table 2). Indeed, the consistency increases exponentially with the solid content. A typical pore size distribution (see Fig. 2) shows that Catapal SB extrudates have a very narrow pore size distribution. The data in Table 2 also show that in the range where good extrusion properties are obtained, the solid content of the batch has only a very small effect on the pore volume or average pore diameter of the extrudates.

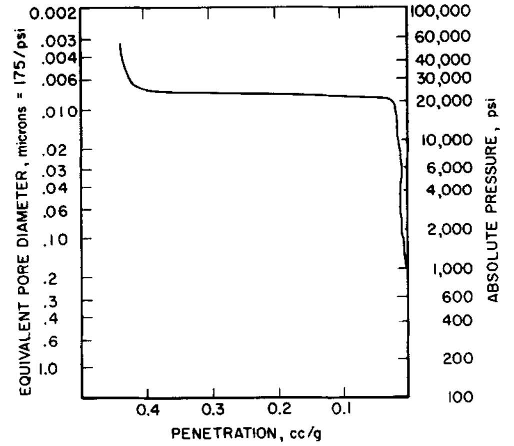

FIG. 2. Porosity determination; typical pore size distribution for Catapal SB.

A peptizing agent must be used to obtain extrudates with good crushing strengths and attrition resistance. The peptizing agent converts the "as received" aggregate structure of the spray-dried boehmite powder into a gel-type structure during the mixing process. The manufacturer recommends 5% acetic or nitric acid for this purpose. Use of nitric acid was rejected because of the presence of cellulose fibers in the extrusion batches. In addition to acetic acid, a series of organic acids were tried

TABLE 2

Effect of Solid Content of Extrusion Batch on Extrudate Properties[a]

	Sample No.				
	30020	21700	21701	21710	21712
Weight percentage AlOOH	30[b]	40	46	55	59
Torque (m-kg)	—	0.48	1.24	4.70	10.5
Energy input (kcal)	—	375	750	1875	1235
Pore vol (cm^3/g)	0.403	0.347	0.398	0.412	0.417
APD (Å)	56	39	51	55	56
SA (m^2/g)[c]	279	320	296	293	283
Pellet density (g/cm^3)	1.36	1.35	1.35	1.35	1.35

[a] Acetic acid, 5 vol%, used as peptizing agent in extrusion batch; $\frac{1}{16}$-in. extrudates calcined at 600°C/4 hr.

[b] Formed as gel.

[c] Surface area estimated from mercury porosimetry data.

to determine if the initial pH of the peptizing solution has any effect on the pore size of the extrudates. The acid concentrations were chosen so that all the peptizing solutions would have the same molar concentration. However, reaction of the acids with the boehmite component of the batch will cause the pH of the system to increase. Its value will depend on the extent of reaction, which will vary in a complex way with time, temperature, and extent of mixing of the batch. Table 3 shows that the consistency of the batch and, to a lesser extent, the pore volume of the extrudate are affected. However, the average pore diameter is nearly independent of the initial pH of the peptizing solution. All of the peptizing agents yielded strong extrudates.

The degree of peptization of the batch will depend not only on the type and amount of peptizing agent present in the batch but also on its degree of mixing. The torque necessary to drive the mixer at constant speed increases rapidly at the beginning of the mixing process due to peptization of the batch. After this initial rise, a relatively flat plateau region exists. Data obtained on the properties of extrudates prepared from batches mixed in this plateau region (see Table 4) show that both the pore volume and the average pore diameter of the extrudates increase slightly with increased degree of mixing. However, the effect is too small to prepare large-pore-diameter aluminas by this method, if reasonable mixing times are used.

TABLE 3

Effect of pH of Extrusion Batch on Extrudate Properties[a]

	Sample No.			
	31340	31360	31300	31320
Acid	Oxalic	Tartaric	Formic	Acetic
Weight percentage[b]	10.9	13.0	4.0	5.2
pH	0.61	1.52	1.91	2.41
Torque (m-kg)	4.40	3.17	7.40	3.48
Pore vol (cm^3/g)	0.373	0.386	0.452	0.434
APD (Å)	62	66	69	66
SA (m^2/g)[c]	238	233	258	258
Pellet density (g/cm^3)	1.40	1.42	1.28	1.33

[a] Extrusion batch contained 55 wt% AlOOH and was mixed to an energy input of 3000 kcal; $\frac{1}{16}$-in. extrudates calcined at 600°C/4 hr.

[b] Acid concentration chosen to yield 0.868 *M* solution.

[c] Surface area estimated from mercury porosimetry data.

TABLE 4

Effect of Degree of Mixing on Extrudate Properties[a]

	Sample No.		
	31621	31641	31320
Torque (m-kg)	3.00	3.35	3.48
Energy input (kcal)	750	1875	3000
Pore vol (cm^3/g)	0.375	0.394	0.434
APD (Å)	59	62	66
SA (m^2/g)[b]	250	251	258
Pellet density (g/cm^3)	1.43	1.44	1.33

[a] Extrusion batch contained 55 wt% AlOOH, and 5 vol% acetic acid as peptizing agent; $\frac{1}{16}$-in. extrudates calcined at 600°C/4 hr.

[b] Surface area estimated from mercury porosimetry data.

B. Preparation of Bimodal Supports

When the amount of acetic acid added to the extrusion batch is decreased, it takes a longer mixing time to completely peptize the batches. Bimodal supports can be obtained by extruding incompletely peptized batches. Figure 3 shows a typical pore size distribution for extrudates prepared by this method. The macropores are associated with the voids present between nonpeptized aggregates in the batch. The average pore size of the mesopores in the extrudates is again not dependent on the solid content of the batch (see Table 5) and the macropores tend to be quite large. However, the extrudates do have good strength. This method was not pursued because of the

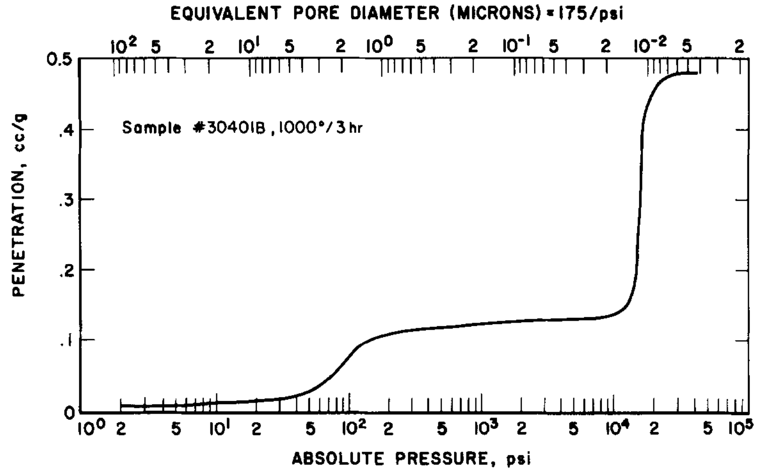

FIG. 3. Typical pore size distribution for extrudates produced from incompletely peptized extrusion batch.

large size of the macropores and because it was felt that it would be difficult to obtain reproducible results by this method.

A preferred method for producing bimodal supports involves the incorporation of a combustible fiber into a well-peptized extrusion batch. A typical pore size distribution for extrudates prepared by this second method is shown in Fig. 4. Since the development of the macroporosity is primarily regulated by the amount and type of cellulose fiber added to the extrusion batch and depends only slightly on mixing effects, the method is easily controlled and gives good reproducibility. The pore volume and average pore diameter of the macroporosity increase as the amount of fiber added to the batch is increased. For microcrystalline Avicel (see Table 6 and Fig. 5), the added porosity is in the range 50–80 Å at low loadings of Avicel. This indicates that the purified cellulose crystalline aggregates are separated into extremely small and well-dispersed pieces of fibril. As the cellulose loading is increased, these fibrils group into bundles and macroporosity is developed in the extrudates. Relatively high loadings (near 40 wt%) are required to produce macropores with an average pore diameter in the range of 1000 Å.

A somewhat different behavior is observed with the addition of the low-ash Fisher filter pulp. Macroporosity is observed at low loading with these cellulose fibers (see Table 7), since the fibers are not dispersed into fibrils as occurs with the depolymerized Avicel cellulose (*3*). Again, the average pore diameter of the macropores increases with fiber loading due to the fibers grouping into bundles. Since all of the cellulose in the pulp goes toward producing macroporosity, a lower loading is needed to

TABLE 5

Preparation of Bimodal Supports by Use of Insufficient Peptizing Agent[a]

	Sample No.		
	30392	30401	30400
Weight percentage AlOOH	65.0	62.5	60.0
Torque (m-kg)	6.50	3.10	1.25
Energy input (kcal)	750	750	750
Pore vol (cm^3/g)	0.533	0.539	0.529
APD (Å)	67	66	65
APD′ (Å)[b]	19,800	22,400	21,300
SA (m^2/g)[c]	240	250	242
Pellet density (g/cm^3)	1.20	1.18	1.20

[a] Acetic acid, 2.5 vol%, used as peptizing agent.

[b] Apparent pore diameter of macropores.

[c] Surface area estimated from mercury porosimetry data.

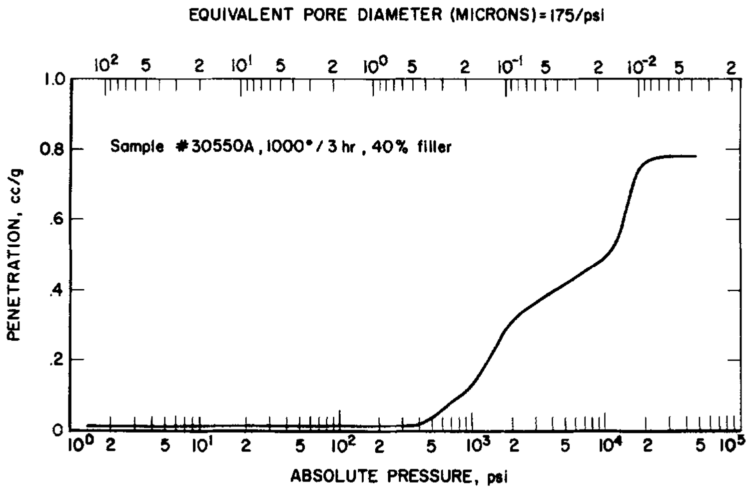

FIG. 4. Typical pore size distribution for extrudates (bimodal supports) prepared by addition of microcrystalline cellulose filler to completely peptized extrusion batch.

produce pores in the range 1000–10,000 Å.

The bimodal supports produced by the burnout of cellulose fibers at 600°C contain mesopores in the range 50–80 Å. Thermal sintering was used to increase the average pore diameter of these mesopores to 120 Å. For Catapal SB, temperatures in the order of 1000°C are needed. The range of pore size distributions for supports calcined at 1000°C/3 hr that can be obtained by this method are shown in Fig. 6. Table 8 gives the pore distribution characteristics that can be obtained by varying the sintering temperature between 800 and 1000°C. Supports sintered at 800°C contain only γ-alumina. At 900°C the supports consist of mixtures of γ-, θ-, and δ-alumina, with the amount of γ-alumina decreasing with increasing calcination temperature. The last three supports listed in Table 8 show the reproducibility that can be achieved by this method. Preliminary experiments showed

TABLE 6

Effect of Addition of Avicel to Extrusion Batch on Extrudate Properties[a]

	Sample No.				
	31621	30490[b]	30491[b]	30530	30550
Weight percentage Avicel	0	10	20	30	40
Torque (m-kg)	3.00	1.12	0.90	1.78	1.68
Pore Vol (cm^3/g)	0.375	0.480	0.555	0.675	0.819
APD (Å)	59	60	60	65	67
APD′ (Å)[c]	—	—	168	768	1108
SA (m^2/g)[d]	250	303	295	254	243
Pellet density (g/cm^3)	1.43	1.28	1.17	1.02	0.90

[a] Extrusion batch contained 55 wt% AlOOH (5 vol% acetic acid used as peptizing agent) and was mixed to an energy input of 750 kcal; $\frac{1}{16}$-in. extrudates calcined at 600°C/4 hr.

[b] Extrusion batch contained only 50 wt% AlOOH.

[c] Apparent pore diameter of macropores.

[d] Surface area estimated from mercury porosimetry data.

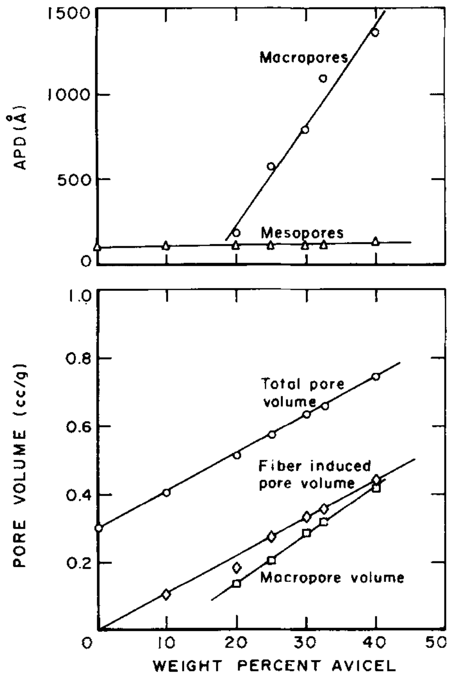

FIG. 5. Pore volume and apparent pore diameter characteristics of Catapal/Avicel supports calcined at 1000°C/3 hr.

that similar results could be obtained by steaming these supports at temperatures between 750 and 800°C. However, this alternate sintering technique was not explored in any detail.

C. Preparation of Coextruded Molybdena/Alumina Catalysts

The pore structure produced in γ-aluminas obtained from boehmite comes from the gel-like pore structure present in the original boehmite material (*4*). Calcining converts the boehmite to γ-alumina, reduces the surface area from the maximum value in the original boehmite, and increases the average pore diameter. Ammonium heptamolybdate can be added to the boehmite extrusion batch and mixed to give a homogeneous mixture. This mixture can be extruded and calcined to produce very uniform molybdena/alumina catalysts. Also, Srinvasan and Weller (*5*) have shown that molybdena enhances the sintering of alumina. Hence it seems possible that molybdena/alumina catalysts with 120-Å average pore size can be produced by the calcination of coextruded catalysts at a much lower temperature than that required for the alumina supports.

Both monodispersed and bimodal molybdena/alumina catalysts were prepared by the coextrusion method. The addition of a soluble molybdenum salt has a large effect on the peptization process. If the molybdenum salt is dissolved in the acetic acid solution used to peptize the batch prior to the

TABLE 7

Comparison of Supports Prepared Using Different Cellulose Fibers[a]

	Sample No.						
	30490C	30491C	30530C	30550C	31681	31671	31661
Type fiber	Avicel	Avicel	Avicel	Avicel	Fisher	Fisher	Fisher
Weight percentage fiber	10	20	30	40	5	10	15
Pore vol (cm^3/g)	0.401	0.486	0.636	0.770	0.427	0.453	0.491
APD (Å)	104	108	117	129	103	103	103
APD′ (Å)	—	184	795	1287	2500	4000	9000
SA (m^2/g)	148	153	137	123	141	141	141
Pellet density (g/cm^3)	1.47	1.27	1.08	0.99	1.40	1.34	1.28

[a] Extrusion batch contained 55 wt% AlOOH (5 vol% acetic acid used as peptizing agent) and was mixed to an energy input of 750 kcal for batches containing Avicel and 3000 kcal for batches containing Fisher filter pulp; $\frac{1}{16}$-in. extrudates calcined at 1000°C/3 hr.

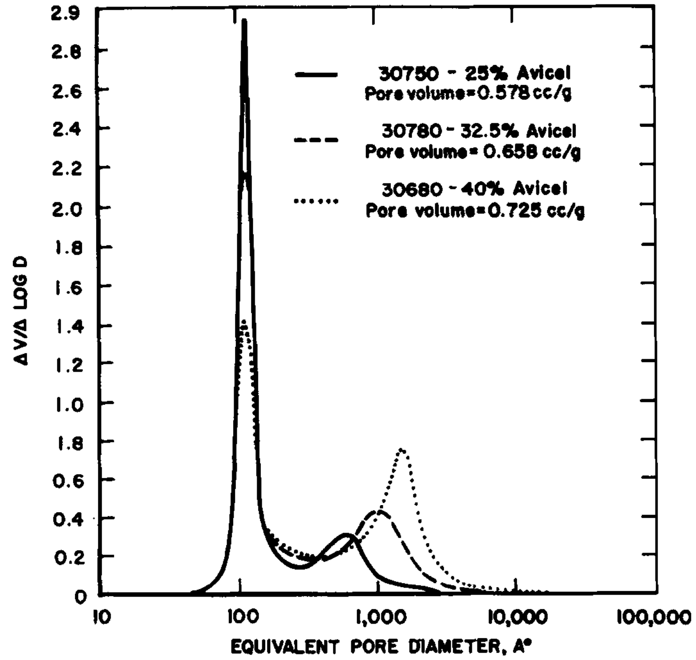

FIG. 6. Bimodal supports prepared by Avicel addition and calcined at 1000°C/3 hr.

addition of the solution to the Catapal SB powder, the batch does not peptize to any significant degree. This results in very weak extrudates. However, extrudates of good strength can be prepared by adding the acetic acid solution to a mixture of Catapal SB and molybdenum salt. Apparently the acid solution is imbibed by the porous boehmite

TABLE 8

Physical Characteristics of Extruded Bimodal Alumina Supports[a]

Sample No.	Treatment	Percentage Avicel	Pore vol (cm^3/g)	PV > 1000 Å (%)	APD (Å)	APD'[b] (Å)	SA[c] (m^2/g)	Pellet density (g/cm^3)
30770	800°C/3 hr	25	0.656	17.8	85	290	214	1.05
30760	900°C/3 hr	25	0.619	13.5	92	330	198	1.10
30750	1000°C/3 hr	25	0.578	11.4	115	580	144	1.15
30800	800°C/3 hr	32.5	0.731	23.8	85	1200	207	1.00
30790	900°C/3 hr	32.5	0.713	21.5	89	1000	188	0.99
30780	1000°C/3 hr	32.5	0.658	20.2	115	1000	129	1.11
30740	800°C/3 hr	40	0.869	33.6	92	1550	199	0.86
30710	900°C/3 hr	40	0.856	33.2	100	1450	175	0.87
30680	1000°C/3 hr	40	0.725	34.6	121	1550	149	1.01
30550A	1000°C/3 hr	40	0.770	37.0	129	1450	122	0.99
30660	1000°C/3 hr	40	0.740	33.2	122	1440	NA	0.97

[a] Extrusion batch contains 55 wt% solids, mixed to energy input of 3000 kcal, and 5 vol% acetic acid used as a peptizing agent.

[b] Apparent pore volume of macropores.

[c] Surface area estimated from mercury porosimetry data.

TABLE 9

Physical Characteristics of Coextruded Monodispersed MoO_3/Al_2O_3 Catalysts[a]

Sample No.	Mo salt	Torque (m/g)	Treatment	Pore vol (cm^3/g)	APD (Å)	SA[b] (m^2/g)	Pellet density (g/cm^3)
31440	MA	5700	600°C/4 hr	0.407	72	238	1.39
31141	MA	—	700°C/4 hr	0.418	85	201	1.44
31142	MA	—	750°C/4 hr	0.413	167	88	1.43
31180	AHM	4150	600°C/4 hr	0.392	72	235	1.44
31181	AHM	—	700°C/4 hr	0.404	85	196	1.41
31182	AHM	—	750°C/4 hr	0.418	139	110	1.42
31320[c]	AHM	3480	600°C/4 hr	0.434	66	258	1.33

[a] Extrusion batch contains 55% Solids as Catapal SB and molybdic acid or ammonium heptamolybdate. Acetic acid, 7.5 vol%, used as a peptizing agent and batch mixed to an energy input of 3000 kcal. Batch composition: 15 wt% MoO_3.

[b] Surface area estimated from mercury porosimetry data.

[c] Acetic acid, 5.0 vol%, used as a peptizing agent.

aggregates before any appreciable amount of molybdenum salt dissolves into the solution. This allows the batch to peptize before the molybdenum anions can interfere. This is reflected in the torque rheometer tracing, which shows a maximum after the very rapid rise characteristic of the peptization process. The mixing torque then slowly declines as the molybdenum salt dissolves and makes its influence felt.

Both molybdic acid (MA) and ammonium heptamolybdate (AHM) were tried as the source of molybdenum. Molybdic acid interferes less with the peptization process. However, laser Raman spectroscopic characterization of samples calcined at 600°C/4 hr shows that extrudates prepared from molybdic acid-containing batches have both molybdenum trioxide and molybdenum-support interaction species present, while those prepared from AHM-containing batches have only the interaction species. Also, the extrudates prepared from MA-containing batches convert to alumi-

TABLE 10

Physical Characteristics of Coextruded Bimodal MoO_3/Al_2O_3 Catalysts[a]

	Sample No.				
	31200	31201	31202	31240	31241
Treatment	600°C/4 hr	725°C/3 hr	725°C/6 hr	600°C/4 hr	725°C/6 hr
Percentage Avicel	32.5	32.5	32.5	—	—
Percentage Fisher pulp	—	—	—	10	10
Pore Vol (cm^3/g)	0.690	0.711	0.726	0.471	0.506
PV > 1000 Å (%)	4.2	6.3	19.0	23.4	21.3
APD (Å)	70	100	140	69	140
APD′ (Å)[b]	610	740	1000	7000	12,000
SA (m^2/g)[c]	220	162	116	200	110
Pellet density (g/cm^3)	0.99	0.99	1.02	1.30	1.30

[a] Extrusion batch contains 55% Solids as Catapal SB, ammonium heptamolybdate, and filler; 7.5 vol% acetic acid used as a peptizing agent.

[b] Apparent pore diameter of macropores.

[c] Surface area estimated from mercury porosimetry data.

num molybdate when calcined at 750°C/4 hr, while the other extrudates do not.

A calcination temperature between 700 and 750°C is required to produce mesopores with an average pore diameter of 120 Å (see Table 9). This temperature is almost 300°C lower than that required to produce a similar pore size distribution in the alumina support. Because of this lower temperature, transformation of the support to θ- or δ-alumina does not occur. In this calcination range, the molybdenum remains as an interaction species and the surface area of the catalyst is similar to those of catalysts prepared by impregnation of thermally sintered supports. Whether or not the molybdenum–alumina interaction that promotes this sintering at lower temperatures is beneficial or detrimental to the ultimate catalyst performance remains to be determined.

Bimodal molybdena/alumina catalysts were prepared by the incorporation of Avicel or Fisher filter pulp into the extrusion batches. The pore size distributions obtained in these coextruded supports are very similar to those obtained in the alumina supports. The data in Table 10 show that a thermal treatment of 725°C for about 4½ hr is required to produce mesopores with an average pore diameter of 120 Å. These extrudates have good strength. However, increasing the calcination temperature to 750°C causes the extrudates to lose this physical integrity. This is probably due to the formation of aluminum molybdate at this temperature.

CONCLUSIONS

The pore structure of extruded alumina supports prepared from boehmite powders was found to be dependent on the extent to which the original aggregate structure of the powder is converted into a "gel-type" structure during the mixing process. For incompletely peptized batches, a bimodal pore size distribution is obtained, consisting of mesopores in a range characteristic of the starting boehmite powder and very large macropores made up of the remnant void spaces between the unpeptized aggregates. For completely peptized batches, a single pore size distribution is obtained. The pore size of the mesopores produced in completely peptized batches is nearly independent of the type of acid used to peptize the batch and the pH of the peptizing solution. It varies only slightly with the solid content of the batch in the range of solid contents where extrudable batches are obtained. There does seem to be a small increase in average pore diameter with increasing mixing time or energy input. It appears that in these completely peptized batches, the pore size of the mesopores is primarily a property of the starting alumina powder and not of the processing conditions.

The degree of peptization of an extrusion batch can be correlated with the torque necessary to drive a mixer at a constant speed. This is defined as the consistency of the batch, and its numerical value will depend on the volume of the batch and on the mixer configuration. The consistency was found to depend very strongly on the solid content, pH, type of peptizing agent present in the batch, and the degree of mixing. Indeed, the consistency increases exponentially with the solid content of the batch.

Bimodal aluminas and coextruded catalysts can be prepared by incorporation of cellulose fibers into well-peptized extrusion batches. The types of macropores produced depends on the loading and nature of the cellulose fibers. Microcrystalline cellulose, such as Avicel, disperses in the gel structure to produce pores in the range 50–80 Å until the loading is high enough for the fibrils to group into bundles. High loadings are therefore required to produce macropores in the range of 1000 Å. Ordinary cellulose fibers, such as Fisher filter pulp, disperse to produce large macropores even at small loadings. Like the microcrystalline cellulose at high loadings, they group into bundles to produce very large macropores.

For coextruded molybdena/alumina catalysts, the order of mixing the batch is important. To obtain strong extrudates it is necessary to add the acetic acid peptizing solution to the physical mixture of the boehmite, molybdenum salt, and cellulose filter. Dissolution of the molybdenum salt in the peptizing solution before adding the solution to the mix interferes with the peptization process and yields extrudates of unacceptable strength.

Thermal sintering can be used to increase the average pore diameter of the mesopores to the desired 120-Å average pore diameter. For the alumina supports, a 1000°C/3-hr treatment is required, which reduces the surface area of the support to 100 m^2/g and causes the transformation of the support into a mixture of θ- and δ-aluminas. For the coextruded molybdena/alumina catalysts, the sintering treatment required to produce an equivalent 120-Å average pore diameter is reduced to 725°C/6 hr. At this milder condition, the support remains as γ-alumina, but again the surface area is reduced to 100 m^2/g. No crystalline molybdenum-containing phases are detected in these catalysts.

ACKNOWLEDGMENTS

I would like to acknowledge help received from Sidney S. Pollack, Edward L. Wetzel, and Christine A. Spitler of the Surface Analysis Branch, Pittsburgh Energy Technology Center, for the XRD and BET characterizations of the supports and catalysts. Also to be acknowledged is Leo E. Makovsky of the Surface Analysis Branch for his characterization of the molybdena/alumina catalysts using laser Raman spectroscopic techniques.

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