JOURNAL OF MATERIALS SCIENCE 22 (1987) 2549–2556

Variables in the synthesis of unusually high pore volume aluminas

J. N. ARMOR*, E. J. CARLSON
Allied-Signal Inc., Corporate Technology Research Laboratories, PO Box 1021R, Morristown, New Jersey 07960, USA

This paper summarizes our successful efforts to obtain high pore volume aluminas ($> 5.0\,\mathrm{cm^3\,g^{-1}}$). The pore volumes of these aerogels, prepared by the hydrolysis of aluminium isopropoxide (AIP) in alcoholic media, are very sensitive to the amounts of water and alcohol employed in the synthesis. An unexpectedly large ratio of water to alkoxide yields the highest pore volumes. By suitable selection of initial levels of aluminium alkoxide, methanol and water, one obtains average pore volumes of $8.6\,\mathrm{cm^3\,g^{-1}}$. A two-step formulation of AIP, methanol, and water followed by hypercritical solvent removal to form the alumina aerogel yields the highest pore volumes. Other alternative approaches also increase the yield of aerogel produced within the autoclave. Pore volumes of about $7\,\mathrm{cm^3\,g^{-1}}$ result if the premix is concentrated twofold after formulation and before autoclave processing. Lower pore volumes result if the reactant charge is increased directly by simply increasing the concentration of AIP. It appears that the reduction in pore volume results in part from the higher isopropanol content in the final reaction mixture (isopropanol is a co-product from AIP hydrolysis).

1. Introduction

Aerogels are unique, highly porous solids prepared by the removal of solvent from a wet gel at a temperature above the critical temperature of the solvent. Over the past four years. Allied-Signal Inc. has built up a strong technical background in such materials [1–5]. Aerogels possess unusual properties of high pore volume (with predominantly large pores) and high surface area, as well as low bulk density. These properties result from the unique methods of preparation that obviate the inherent shrinkage or structural collapse that occurs when precursor gels are conventionally dried to a solid form. Such shrinkage or compaction results from the surface tension of residual liquid trapped within the fragile gel structure. The most common method of preparation involves a fluid medium containing water as a minor component. One procedure is to raise the temperature of the wet gel (under its autogeneous pressure) to or above the critical point of the fluid medium, and to vent off the bulk of the fluid above the critical temperature to leave a porous solid residue, or aerogel. The product is not a true "gel", and in fact "aerogel" materials are quite thermally and mechanically stable.

Early investigators [6] prepared aerogels in stages. First, an aquagel, such as a SiO_2 gel from the acidification of a sodium silicate solution, was washed free of by-product salts. Then the aqueous phase was displaced with methanol, and the latter removed as a hypercritical vapour, leaving an aerogel of silica as a bulky residue. More recently, Teichner [7–11] pioneered a more direct route by hydrolysing and gelling pure, soluble alkoxides (or acetates) in an aqueous alcohol medium and then hypercritically removing the fluid phase along with the alcohol (or esters) co-products. We have expanded considerably on Teichners' approach in much of our work on aerogels.

Aerogels have been evaluated as catalysts [1, 2, 4], catalyst supports [5], precursors for monolitics glasses [12] Cerenkov detectors [13], solar plate collectors [14], insulators [15, 16], and for a number of other applications [17]. Zarzycki and co-workers recently described the details for the preparation of crack-free, transparent silica aerogels [18]. The synthesis conditions vary for each oxide system. The large number of variables in the synthesis of the gel prohibit a clear understanding of the conditions required to consistently obtain high pore volume materials. During the course of our work with alumina aerogels, we occasionally observed some alumina aerogels with pore volumes much greater than the traditional values of 1.5 to $5.0\,\mathrm{cm^3\,g^{-1}}$. In order to understand this unusual phenomenon, we examined a large number of variables critical to the synthesis of extremely porous alumina aerogels.

2. Experimental techniques

In general, the alumina pregel was prepared from aluminium isopropoxide (AIP), methanol, and water. This mixture was contained within a $225\,\mathrm{cm^3}$ (3.5×25 cm) Pyrex liner tube, in a $300\,\mathrm{cm^3}$, unstirred autoclave (rated for more than 27.2 MPa). The fluid phase was removed hypercritically within a 3 to 5 h cycle, thus generating the alumina aerogel. Final temperatures were typically 280 to 310° C. Detailed discussions of the "aerogel technique" were provided in earlier

---

* *Present address*: Air Products and Chemicals Inc., PO Box 538, Allentown, Pennsylvania, 18105, USA.

0022–2461/87 \$03.00 + .12

TABLE I Order of addition of reactants

Sample no.	H_2O/AIP* (mole ratio)	Order of addition and digestion	Ageing (stirred continuously)	Nature of pregel†	Nature of aerogel‡	Maximum autoclave temperature (° C)	Maximum pressing psig	pore volume ($cm^3 g^{-1}$)	surface area ($mg^2 g^{-1}$)
7742	3.0	AIP, MeOH (2.5 h, 60° C); then add H_2O for 1 h at 60° C	overnight 35–40° C	TV	SL + pd	290–295	2220	4.3 4.5§	327 297
7741	3.0	AIP, MeOH (1 h, 60° C); then add H_2O for 1 h at 60° C	None	M	SL + pd	290–295	2140	4.6 3.9§	288 262§ –
7743	3.0	as in 7742	overnight 50° C	TV	SL + pd	290–295	2190	4.1	268
7744	3.0	[AIP + (MeOH, H_2O)] + 1 h at 60° C all at once	5 days 50–60° C	P	HL + pd	285–290	2190	3.8	226
7745	3.0	as in 7744, at room temperature	5 days room temperature	M	HL + pd	285–290	2280	4.2	236
7747	3.0	as in 7742	as in 7742	TV	SL + pd	265–270	1760	4.0	215
7748	2.0	as in 7741	as in 7741	TV/P	SL + pd	290	2310	3.8	273
7749	6.0	as in 7741	as in 7741	M/TV	SL	290	–	5.6	387

*AIP = aluminium isopropoxide (Ayers, lot 282, 17 g, 90 g MeOH, 4.6 g H_2O (for 3/1 ratio). Prior to sealing for autoclave, all samples were maintained with MeOH to a height of 9 to 9.5 cm from the top of the glass liner; all runs were heated for 4 h from room temperature to maximum temperature prior to venting.

†TV = thick/viscous, but will settle on standing; M = milky suspension; P = paste-like suspension; M/TV = milky with some thickening; TV/P = thick paste.

‡SL = soft lumps; HL = hard lumps; pd = powder.

§PV of product heated in air at 125° C for 2 h.

reports [1, 2, 5]. Methanol (MeOH), not isopropanol was the preferred solvent, because the methanol solvent produced higher pore volumes as well as being a superior alumina catalyst [4]. Initially, AIP was chosen because it represented an inexpensive source for aluminium alkoxides; however, attempts to use other aluminium alkoxides, such as aluminium secondary butoxide, produced aerogels with much lower pore volumes.

2.1. General procedure for preparing alumina aerogel (pore volume $8.5\,cm^3\,g^{-1}$) from AIP

A 2 l beaker of water was preheated to 40 to 45° C on a stirrer-hotplate. To the Pyrex autoclave liner tube, 90 g ($115\,cm^3$) dry methanol was added along with a magnetic stir bar, and the tube was placed in a water bath at 40–45° C. A freshly weighed (17 g) portion of AIP (J. Ayers, Inc., Bethlehem, Pennsylvania, USA) was added with stirring to maintain the Al_2O_3 in suspension. The bath temperature was raised to 60° C and stirring continued for at least 1 h as the batch thickened and became "creamy". Water (14.1 g) was added with stirring. The batch temporarily thickened and required vigorous manual stirring (with a long glass rod) for several minutes until the batch again thinned out, when magnetic stirring was continued for at least one additional hour at bath temperature of 60° C. After the batch was cooled to 40 to 45° C (followed by 1 to 24 h of continued stirring), the stir bar was removed and the tube containing this alumina pregel inserted into the autoclave. The autoclave was purged several times with nitrogen and then heated to raise the internal temperature to 285 to 300° C over about 2 to 2.5 h. The internal temperature was recorded using a thermocouple linked to a strip chart recorder. (The external jacket temperature was thermostatically controlled to avoid exceeding the desired internal temperature.) There were two external thermocouples, one leading to the controller, the other to an indicator readout. Heating was continued (with thermostat control) at peak temperature for an additional 1.5 h. The pressure (which had built up to about 13.6 MPa) was slowly released over 20 to 30 min, without allowing the temperature to drop (adiabatic cooling effect from the pressure release) below 270° C. (The vented vapours of methanol, isopropanol, and water were cooled and continuously collected as a liquid, according to our standard practice.) The contents of the Pyrex tube were purged several times with nitrogen, and then allowed to cool to room temperature overnight. The aerogel was removed from the glass liner and dried overnight at 120° C.

Surface areas were measured on a Quantasorb surface area analyser (Quantachrome Corporation, Syosset, New York) using the single point BET approach. Using a Quantachrome Autoscan Porosimeter, pore volumes were calculated from the net change in pore volume (ignoring the initial surge in pore volume due to crushing by the column of mercury) against pressure (to 408.6 MPa) divided by the mass of material used.

3. Results and discussion

3.1. Initial studies at a "low" fixed H_2O/AIP mole/mole ratio of 3.1/1

At the onset of the investigation, a fixed ratio of 3.1/1 (mole/mole) H_2O/AIP (a slight excess of water) [7] was chosen, and the reaction time, temperature and sequencing of reactants were varied.

$$Al(OR)_3 + 3H_2O \;=\; Al(OH)_3 + 3ROH$$

(Medium of methanol and water; R is isopropyl)

During this study, we found that, despite a wide variation in the nature of the pregel, extensive digestion (even at elevated temperatures) was unnecessary. Under the hypercritical conditions, remarkably similar products were obtained. Without any added methanol, the pore volumes were reduced to $\sim 2\,cm^3\,g^{-1}$. Also, the use of other alkoxides of alumina gave products having lower pore volumes.

Venting the fluid at 295 or 265° C had only a slight effect on the pore volume of the resulting aerogel. Analysis of the solvent collecting on venting indicated that it contained methanol with traces of water and dimethyl ether (Table I, sample no. 7741).

Since a number of aerogels analysed in the past seemed slightly damp, some of the "raw" aerogels were further dried at 125° C in air for ~ 2 h. Some small clumps were observed, but certainly no major morphological changes in pore volume (e.g., to $6\,cm^3\,g^{-1}$) were detected. Aerogel samples were heated in air at various temperatures for 8 h. For the alumina aerogels the high pore volumes and surface areas were maintained beyond 800° C (see Table II). In addition most of the organic residue within the aerogels was removed between 500 and 800° C.

Finally, the reduction of the molar ratio of H_2O/AIP from 3.1 to 2.0 had only a minimal effect on the pore volume, which suggested that some water was probably derived from the isopropanol. Addition of a large excess of water (sample no. 7749) produced a significant increase in pore volume (from 4.5 to $5.6\,cm^3\,g^{-1}$) and in surface area.

At first (we later learned this was not the optimum H_2O to AIP ratio) a slightly higher pore volume

TABLE II Calcination of alumina aerogels

Temperature* (°C)	Pore volume ($cm^3\,g^{-1}$)	Surface area ($m^2\,g^{-1}$)	Carbon (%)	Hydrogen (%)	Weight loss (%)
as isolated	8.1	589	3.22	2.01	–
800	7.0	482	0.25	0.90	14%
950	4.5	321	0.14	0.75	19%
1100	2.4	141	0.21	0.27	–

*Calcined 8 h in air.

TABLE III Order of additions at 3.1/1 H_2O/AIP (mole/mole) ratio

Sample no.	Procedure	Pore volume ($cm^3 g^{-1}$)	Surface area ($m^2 g^{-1}$)
7742	Step 1 (AIP + MeOH + hold 1 h, 60° C) Step 2 + (H_2O + hold 1 h, 60° C) and age overnight	4.3	327
7741	Step 1 as 7742 Step 2 as 7742 but omit overnight ageing	4.5	288
7744	Combined steps 1 and 2 [AIP + (MeOH + H_2O)] and age 5 days, 55° C	3.8	226
7745	Combined step as 7744 and age 5 days, 20–25° C	4.2	236

was obtained via a two-step pregelation procedure against a combined step, as shown in Table III. The two-step procedure involved first mixing the AIP and dry methanol, then later adding the water. In the combined step, AIP was mixed with the premixed methanol–H_2O. The runs of Table III were made at a maximum autoclave temperature of 280 to 295° C. When the temperature was lowered (sample no. 7747, Table I) to 265° C (closer to critical temperature), there was no improvement over sample no. 7741 (Table I) and, in fact, the surface area fell from 327 to $215 m^2 g^{-1}$.

3.2. Variation of H_2O/AIP molar ratio

Using the pregelation procedure described above for sample nos. 7741 and 7742 of Table I, the H_2O/AIP molar ratio was varied with striking results in pore volume. The AIP and methanol quantities were held essentially unchanged while the amount of water was varied. These points fell along a straight tie line when plotted on triangular plotting paper, as shown in Fig. 1, line 17g–B. The tie lines for different H_2O/AIP ratios are also indicated on the base line of Fig. 1 (for example, line 6/1–C).

The data show the pore volume peaked with a significantly higher value of $8.6 cm^3 g^{-1}$ at or close to an applied H_2O/AIP molar ratio of 9.4/1. This H_2O/AIP ratio was within a fairly narrow range as shown in Fig. 1 (line 17g–B) and outlined below in Table IV. Note that the highest pore volume was accompanied by the highest surface area.

Because of the limited time available, no extensive effort was made to pinpoint the optimum H_2O/AIP ratio. It is unlikely that the ratio of 9.4/1 represented the exact optimum. In later experiments wherein the procedures, capacity, and other factors were studied, the pore volume never exceeded $8.6 cm^3 g^{-1}$. However, the preferred H_2O/AIP molar ratio of about 9.4 did not apply to other AIP/MeOH ratios.

3.3. Effect of other variables at optimum feed composition ratio

A number of procedural variations at optimum compositions were studied and are summarized below. None of these approaches generated higher pore volumes.

3.3.1. Variation in the free volume above the liquid level in the autoclave

At a fixed ratio of AIP/MeOH/H_2O, the total amount of solution was varied over a broad range. Whether the $220 cm^3$ liner tube was filled to capacity or to

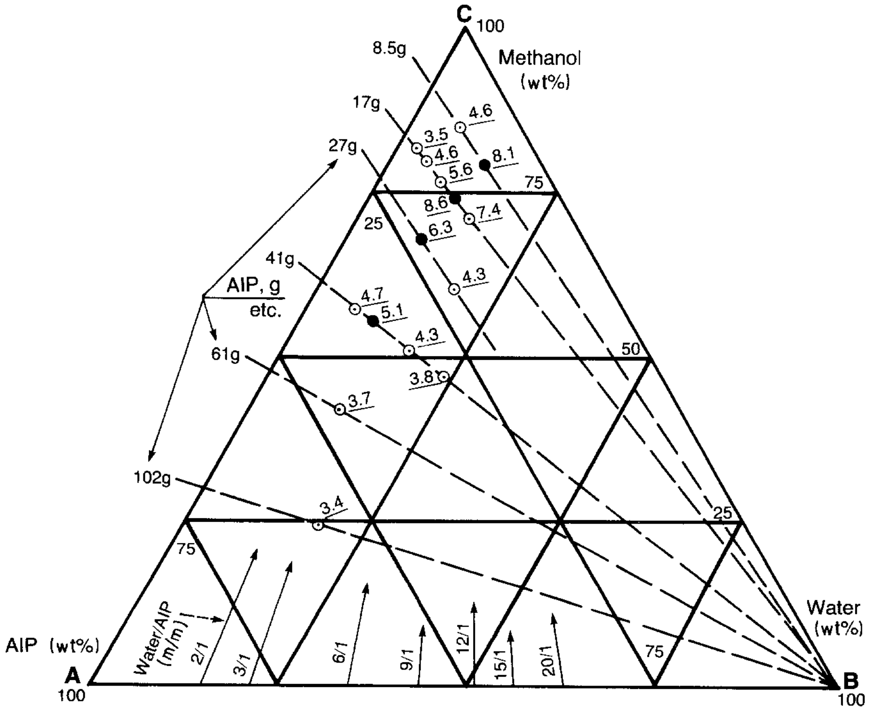

Figure 1 Alumina aerogels from AIP–methanol–water: pore volume against input composition. ⊙, Pore volume ($cm^3 g^{-1}$); ●, pore volume ($cm^3 g^{-1}$) peak at optimum water input. Autoclave, $300 cm^3$; liner, $220 cm^3$.

TABLE IV Effect of H_2O/AIP ratio*

Sample no.	Molar ratio of H_2O/AIP	Pore volume ($cm^3 g^{-1}$)	Surface area ($m^2 g^{-1}$)
7748	2.1	3.8	273
7742	3.1	4.3	327
7749	6.3	5.6	387
7750	9.4	8.6	438
7752†	9.4	8.6	436
7754	12.4	7.4	348

*17 g AIP throughout; procedure as described for sample no. 7742 (Table I).

†Duplicate of no. 7750 but without overnight ageing of the pregel.

a much lower level, pore volumes of 8.1 $cm^3 g^{-1}$ (or higher) were consistently obtained. Thus, it did not appear that the volume above the liquid level within the autoclave was a critical factor (Table V). The pore volumes were only slightly higher at the higher liquid loading in the autoclave.

3.3.2. *One-step pre-gelation*

The pregel was formulated in one step according to details given for sample nos. 7744 and 7745 (Table I) except without ageing. The pore volume of the product (sample no. 7772) fell to 5.9 $cm^3 g^{-1}$ with a surface area of 437 $m^2 g^{-1}$. These results showed the desirability of the two-step formulation route.

3.3.3. *Higher and lower autoclave temperature*

Changing the maximum temperature was ineffective, although there was apparently no harm in running at 325° C (see summary, Table VI and compare sample nos. 7772, 7773, and 7774).

3.3.4. *Flash evaporation instead of hypercritical solvent removal*

In this case the autoclave temperature was held to a maximum 217° C, well below the critical temperature of the fluid (critical temperature of methanol is 245° C; of isopropanol, 235° C). The fluid phase was flashed off at or below 217° C (there is an adiabatic cooling effect). This resulted in a substantial reduction in pore volume for run no. 7776 to 2.1 $cm^3 g^{-1}$ with a surface area of 317 $m^2 g^{-1}$.

3.3.5. *Unlined autoclave*

In this case the pregel of alumina was made in the preferred manner in a Pyrex tube, but the liner was not used in the stainless steel autoclave. Hypercritical solvent removal proceeded normally. The pore volume was still above 8 $cm^3 g^{-1}$ and the surface area for sample no. 7775 was 427 $m^2 g^{-1}$.

3.3.6. *Different solvent system*

Half the usual methanol was displaced by sec–butanol. The AIP was combined in three 1 h stages successively with butanol, methanol, and water, all at 60° C. The pore volume was lowered as a result. In the above solvent system some isopropanol was (as usual) also present (from the hydrolysis of AIP). For this run (sample no. 7779), the pore volume was 4.1 $cm^3 g^{-1}$ and the surface area was 339 $m^2 g^{-1}$.

TABLE V Freeboard experiment with 220 cm^3 tube at best AIP–MeOH–H_2O ratio

Sample no.	Total charge* (g)	Pore volume ($cm^3 g^{-1}$)	Surface area ($m^2 g^{-1}$)
7761	43	8.1	483
7768	90	8.2	359
7750, 7752	116	8.6	437
7762	166†	8.5	461

*Weight of individual components shown in Table VI. Charge volumes in cm^3 = wt/0.9.

†To prevent excessive autoclave pressures in the case of the largest 166 g (185 cm^3, cold) charge, the autoclave was partially vented approaching critical conditions so as not to exceed about 21.8 MPa. Once at about 290° C, above critical, the venting was completed in normal fashion.

3.4. Increased AIP throughput (without increasing concentration)

In experiments designed to increase the AIP throughput (i.e. to increase the yield of aerogel produced from a given reactor volume), as well as to further study effects of the H_2O/AIP ratio, AIP input was varied in amounts ranging from 8.5 to 102 g per run. In two cases, at 17 and 41 g AIP, sufficient data points (runs) were taken to "bracket" or establish the optimum or near optimum H_2O/AIP ratio for that particular loading. In other cases only one or two runs were made, the latter being sufficient to indicate the optimum H_2O/AIP ratio for the best pore volume.

A formulation problem developed with the runs with 41 g or more AIP (and marginally so, even at 27 g AIP) such that the two-step gelation of alumina became impractical. The mobile, fresh slurry of AIP and methanol gradually thickened within the course of an hour at 60° C, probably arising from trans-esterification. If there was insufficient methanol, as was the case when the AIP/methanol ratio was high, the gelation was so intense the mass could not be stirred. This made it difficult to disperse the water for hydrolysis during the second step. The gelation was reduced if the AIP and a solution of methanol–water were combined in only one step. A run with 102 g of AIP was carried out in a special manner. The liner tube was first packed full with the dry, powdery AIP, and then saturated with a solution of 44 g methanol and 32 g water. (No mixing was possible before pressurizing in the autoclave.) The results of all these experiments at varying H_2O/AIP inputs are presented in Table VII and depicted in Fig. 1 where the optimization of H_2O/AIP for the various loadings is shown.

Results summarized in Table VI and Fig. 1 show that as the loading of AIP is increased, thereby decreasing the MeOH/AIP ratio, the optimum water required with respect to AIP decreases. Furthermore, the best attainable pore volume falls off with AIP loadings above 17 g. One reason for this may be the formation of isopropanol upon hydrolysis of AIP.

It is generally considered (from our past experience) that methanol, or methanol/H_2O, is a superior medium for forming aerogels with high surface properties. Increased dilution with isopropanol might be expected to weaken the positive effects of methanol.

TABLE VI Alumina aerogels from aluminium isopropoxide (AIP)

Sample no.	AIP (g)	MeOH (g)	H_2O (g)	H_2O/AIP (mass/mass)	Pore volume ($cm^3\,g^{-1}$)	Surface area ($m^2\,g^{-1}$)	Notes
7741	17	90	4.6	3.1	3.8	215	Refer to Table I
7742	17	90	4.6	3.1			
7743	17	90	4.6	3.1			
7744	17	90	4.6	3.1	to	to	Refer to Table I
7745	17	90	4.6	3.1			
7746	17	90	4.6	3.1			
7747	17	90	4.6	3.1	4.6	327	Refer to Table I
7748	17	90	3.1	2.1	3.8	273	Less H_2O*
7749	17	90	9.4	6.3	5.6	387	More H_2O*
7750	17	90	14.1	9.4	8.6^{Peak}	438	More H_2O*
7751	8.5	90	7.1	9.4	4.6	300	Less AIP†
7752	17	90	14.1	9.4	8.6^{Peak}	436	*¶
7754	17	90	18.6	12.4	7.4	348	More H_2O
7755	41	65	32.4	9.0	3.8	248	Large charge†
7759	41	65	21.6	6.0	4.3	340	Large charge*
7760	41	65	21.6	6.0	4.2	319	Large charge‡
7761	6	32	5.0	9.4	8.1	483	*¶
7762	22	124	18.3	9.4	8.5^{Peak}	461	*¶
7763	41	65	11.3	3.1	5.1	455	Large charge‡
7765	8.5	90	4.1	18.8	8.1	438	Optimum small AIP†
7766	27	76	22.3	9.4	4.3	310	Medium charge‡
7767	41	65	7.4	2.1	4.7	442	Large charge‡
7768	–	–	–	9.4	8.2	359	§
7769	27	84	11.9	5.0	6.3^{Peak}	410	Medium charge‡
7770	17	90	14.1	9.4	6.8	485	1 step + age‡
7771	102	44	31.5	3.5	3.4	309	Maximum charge‡
7772	17	90	14.1	9.4	5.9	445	'clave at T = 290°C‡
7773	17	90	14.1	9.4	4.3	568	'clave at T = 270°C‡
7774	17	90	14.1	9.4	5.9	425	'clave at T = 325°C‡
7775	17	90	14.1	9.4	8.1	427	Unlined†
7776	17	90	14.1	9.4	2.1	317	217°C flash
7777	61.3	56	16.2	3.0	2.8	543	1 step, large AIP‡
7778	61.3	56	16.2	3.0	3.5	218	2 step large AIP
7779	20.4	45	16.2	9.0	4.1	339	+45 g sec-butanol

*Formulate (AIP + MeOH 30 to 60 min at 60°C) + (H_2O 1 h, 60°C) and overnight age before autoclave treatment.
†As 7741 but omit ageing overnight.
‡One-step AIP + (MeOH + H_2O), 60°C, 1 to 2 h.
§5 × scale up pregel as 7750.
¶Three volume levels in 7752, 7761, 7762.

TABLE VII Effect of H_2O/AIP ratio at different AIP loadings

Sample no.	Amount of AIP (g)	Molar ratio H_2O/AIP	Weight ratio (g methanol/g AIP)	Pore volume ($cm^3\,g^{-1}$)	Surface area ($m^2\,g^{-1}$)
7751	8.5	9.4	10.5	4.6	300
7765	8.5	18.8	10.5	8.1	438
7748	17	2.1	5.3	3.8	273
7742	17	3.1	5.3	4.3	327
7750	17	6.3	5.3	5.6	387
7752	17	9.4	5.3	8.6	437
7754	17	12.4	5.3	7.4	348
7769	27	5.0	3.1	6.3	410
7766	27	9.4	3.1	4.3	310
7767	41	2.1	4.6	4.7	442
7763	41	3.1	4.6	5.1	435
7759	41	6.0	4.6	4.3	240
7755	41	9.0	4.6	3.8	248
7777	61	3.0	0.91	3.8	543
7771	102	3.5	0.43	3.4	309

It is assumed that AIP converts during the pregelation step substantially to a hydrated alumina gel with formation of isopropanol and consumption of water. In fact, in the complete absence of methanol, our standard run yielded a pore volume of 2.1 cm^3 g^{-1}. (Caution: the large excess of isopropanol also produces an unusually high pressure within the autoclave. This increase is probably due to the formation of propylene and water.)

Fig. 1 illustrates most of the values of pore volume as a function of AIP loadings (i.e. AIP/MeOH ratios) and of water/AIP (mass/mass) ratios. The peak pore volume at each of four AIP loadings is indicated. Single-point data for two other AIP loadings are also shown. The input compositions as shown were designed to fall along constant AIP/MeOH tie lines (not shown). Constant water/AIP tie lines are indicated at the base line of the graph. The peak pore volumes seem to fall on or near a constant tie line of 0.16 g water per g MeOH. In other words, the applied water/MeOH ratio was important for best pore volume at any AIP loading. Interestingly, on reviewing the summary (Table VI) of all our data, surface area was less affected by input composition than by pore volume. This suggested that one can alter the input composition in the direction of maximum aerogel pore volume, and not lose surface area. In fact, the surface area appeared to reach a maximum coincident with pore volume.

3.5. Increased AIP throughput (concentration experiments)

It has been shown in this report that loading of the autoclave above about 17 g AIP per run (220 cm^3 liner) results in a lowering of peak pore volume despite adjustments of conditions and inputs. From a practical standpoint it was desired to increase the autoclave throughput in some way. We chose some traditional approaches involving sedimentation, filtration, or evaporation of the gels.

3.5.1. Concentration by simple setting of solids

A standard pregel batch (like that used for sample no. 7795) was allowed to stand at room temperature for 3 weeks; only minor settling occurred, making clear decantation impossible. Although this approach was unsuccessful, the material was run as a test for long term ageing of the pregels. Despite the long standing of the gelated intermediate, the pore volume was a creditable 7.7 cm^3 g^{-1} (sample no. 9705). The surface area was 478 m^2 g^{-1}.

3.5.2. Doubling the concentration by evaporation (sample no. 7795)

A double batch comprising 34 g AIP, 210 cm^3 methanol and 28.2 g water was formulated in standard fashion. Approximately half of the liquid phase was removed by evaporation and the slurry processed in the autoclave by hypercritical solvent removal. The alumina aerogel pore volume was 7.1 cm^3 g^{-1}; the surface area was 431 m^2 g^{-1}. These were considered to be fairly good values.

3.5.3. Tripling the concentration by evaporation (sample no. 9701)

Two double batches (as no. 7795 above) were prepared, combined, and then evaporated to a residual volume low enough to be run in the 220 cm^3 line autoclave. Aerogel pore volume fell to 4.8 cm^3 g^{-1}; the surface area was 373 m^2 g^{-1}. In this case the AIP concentration was much too high to be successful. No more evaporation experiments were conducted.

3.5.4. Concentrating by filtration (sample no. 9704)

A single batch (17 g AIP, 90 g methanol and 14.1 g water) was formulated and slowly vacuum filtered to a residue of about 35 to 40% of the original volume. Filtration required several hours on a coarse "C" frit glass funnel. The filtrate was clear. When the concentrated cake was processed through the autoclave, the resulting alumina aerogel had a pore volume of 7.4 cm^3 g^{-1} and a surface area of 578 m^2 g^{-1}. From this experiment it appeared that filtration was more effective than evaporation to maintain high pore volumes.

3.5.5. Tripling the concentration by filtration (sample no. 9712)

Two double batches were made up as no. 9701 above and combined. One-fourth was set aside (as a reference) and of this 22.5% of the unfiltered, uncut original was run through the autoclave in regular fashion to form the usual alumina aerogel (sample no. 9712: pore volume = 8.6 cm^3 g^{-1} and surface area = 409 m^2 g^{-1}). The remaining 75% of the original was filtered through a "C" frit to about one-third the original volume, or to a volume represented by no. 9701 above. It appeared that the filtration was taken too far, for there was channelling and incipient drying of the filter cake. The cake was washed with several small portions of dry methanol (which should tend to remove water and isopropanol). The filter cake was packed into the liner tube, resaturated with methanol to the solid level, and then processed in the autoclave in normal fashion to form the alumina aerogel residue. The product appeared to differ in density from top to bottom, so different samples were withdrawn for analysis (sample no. 9712 – top: pore volume = 5.5 cm^3 g^{-1} and surface area = 443 m^2 g^{-1}; no. 9712 – bottom: pore volume = 6.4 cm^3 g^{-1} and surface area = 677 m^2 g^{-1}).

In summary, filtration of the premix gave better results than evaporation. Furthermore, the concentration by filtration should be carried no further than to 40% or more of the original mixture. It was desirable to wash the filter "cake" with neat methanol. Insufficient concentration experiments were made in order to provide a complete story, but enough work was done to indicate that concentration by filtration or by evaporation resulted in increased autoclave capacity with a fair retention of peak pore volume. Using one of these techniques, capacity might be doubled, but not tripled, without undue loss of peak pore volume. In principle, evaporation would be less desirable since more water and isopropanol are left behind because of the greater volatility of methanol. This would not be the case with simple filtration.

4. Conclusions

We determined the critical factors for producing high pore volume ($> 5.0\,\mathrm{cm^3\,g^{-1}}$) Al_2O_3 aerogels. The most unexpected result was the need for a high ratio of water to alkoxide and the addition of an extra step in the synthesis of the pregel. In addition, we tripled the yield of alumina aerogels produced per unit of reactor volume while maintaining the aerogel's high pore volume. This could be a crucial step in developing any economical, large-scale process. In addition, we doubled reactor throughput by controlled evaporation of the pregel, or tripled the throughput by prior filtration of the pregel. In general the surface area was the highest where the pore volumes were the greatest. Interestingly, the high pore volumes are retained on calcination to at least 800° C.

Acknowledgements

We wish to acknowledge that A. E. Laverick and Roy Riggitano performed all the analyses of surface area and pore volume on the aerogels described herein. We acknowledge Dr A. J. Fanelli's advice and assistance, particularly at the onset of the investigation. We are also grateful to Pete Petersen for his assistance with the autoclave operations. We thank Allied-Signal Inc. for permission to publish this work.

References

1. E. J. CARLSON and J. N. ARMOR, "Aerogels as Hydrogenation Catalysts", Abstracts of 1983 North American Meeting on Catalysis, Philadelphia, Pennsylvania, USA, May 1983 (paper B-29), and in *Appl. Catal.* **19** (1985) 339.
2. J. N. ARMOR and E. J. CARLSON, US Patent 4469816 (1984).
3. A. J. FANELLI and A. T. WALSH, US Patent 4387085 (1983).
4. A. J. FANELLI and A. K. PRICE, US Patent 4478987 (1984).
5. J. N. ARMOR and E. J. CARLSON, US Patent 4692652 (1986) and 4615737 (1986).
6. S. S. KISTLER, *J. Phys. Chem.* **36** (1932) 52.
7. S. J. TEICHNER, G. A. NICOLAON, M. A. VICARINI and G. E. E. GARDES, *Adv. Colliod Interface Sci.* **5** (1976) 245.
8. M. ASTIER, A. BERTRAND, D. BIANCHI, A. CHENARD, G. E. E. GARDES, G. PAJONK, M. B. TAGHAVI, S. J. TEICHNER and B. L. VILLEMIN, in "Preparation of Catalysts" edited by B. Delman, P. A. Jacobs and G. Poncelet (Elsevier Scientific, Amsterdam, 1976) Vol. 1, p. 315.
9. M. ASTIER and S. J. TEICHNER, *Can. J. Chem. Eng.* **60** (1982) 40.
10. S. J. TEICHNER and G. GARDES, US Patent 3963646.
11. A. SAYARI, A. GHORBEL, G. M. PAJONK and S. J. TEICHNER, *Bull. Soc. Chim. France* (1981) I-220.
12. J. W. ZARZYCKI, M. PRASSAS and J. E. H. PHALIPPOU, US Patent 4432956.
13. S. HENNING and L. SVENSSON, *Physica Scripta* **23** (1981) 697.
14. G. VON DARDEL, S. A. HENNING and L. G. SVENNSON, US Patent 4402927 (1983).
15. L. L. RAYL, US Patent 4268317 (1981).
16. J. A. McWILLIAMS, US Patent 4221672 (1981).
17. T. WOIGNIER, J. PHALIPPOU and J. ZARZYCKI, *J. Non-Cryst. Solids* **63** (1984) 117.
18. M. PRASSAS, J. PHALIPPOU and J. ZARZYCKI, *J. Mater. Sci.* **19** (1984) 1656.

Received 26 August
and accepted 25 November 1986