A Statistical Approach to Control Porosity in Silica-Doped Alumina Supports

Maryam Khosravi Mardkhe¹, John Lawson², Baiyu Huang¹, Erika D. Handly¹, and Brian F. Woodfield^{1*}

¹ Department of Chemistry and Biochemistry, Brigham Young University, Provo, UT

²Department. of Statistics, Brigham Young University, Provo, UT

*Brian_woodfield@byu.edu

Abstract

A split-plot statistical design was used to identify and systematically study the effects of synthesis variables on the pore properties of silica-doped alumina (SDA) from data obtained for 96 samples. Seven preparation variables (mixing method, time, environment; calcination ramp rate; drying temperature, environment; and alcohol concentration) were found to alter surface area, pore volume, and pore diameter over wide ranges, i.e. factors of 1.8, 1.4, and 3.3, respectively. Large pore diameters (> 40 nm) were obtained by addition of excess alcohol. Large pore volumes (> 2 cm³/g) were obtained by drying before calcination at 100°C for 24 h. High surface area (> 400 m²/g) was obtained when no alcohol was used. The gamma phase of all SDA samples was thermally stable to 1200°C. Using split-plot statistical analysis of the experimental data, models were developed which predict quantitatively the relationship between surface properties (surface area, pore volume and pore diameters) and synthesis parameters. Based on these models, optimal conditions to produce SDA samples with large (40-60 nm) or medium (16-19 nm) pore diameters, high surface area (> 250 m²/g) and large pore volume (> 1 cm³/g) are quantitatively predicted. Model predictions of optimal conditions were accurately

confirmed by follow-up experiments. The chemistry underlying these predictions is also addressed.

Keywords: Control porosity, Split-plot design, Silica-doped alumina, Thermal stability.

1. Introduction

It is known that the performance of a catalyst strongly depends on the combination of textural, chemical and physical properties of the support. Among these properties, pore properties are critical for the successful design and optimization of a catalyst. Pore size is essential since each catalytic system requires a unique pore size for optimal catalyst loading, diffusion and selectivity [1-4]. Examples of this are in (1) Pt, Rh and Pd catalysts for automobile emission control (pore size 3 to 5 nm) [5-8]; (2) Co(Ni)-Mo(W) sulfide catalysts for fuel hydrodesulfurization (pore size > 20 nm) [8]; and (3) Co and Fe catalyst for Fischer-Tropsch synthesis (FTS) (pore size 10 to 20 nm) [4, 9]. In addition, high surface area and large pore volume usually result in higher catalyst loading, which increases the number of catalytic reaction sites and decreases reaction time. Moreover, it is important to produce supports with good thermal stability since pore collapsing due to sintering at high temperatures often results in catalyst deactivation [10-15].

It has been reported previously that the pore properties of alumina catalyst supports are significantly influenced by a number of synthesis parameters, including the choice of aluminum source, synthesis route, structure directing agent, and solvent [16-22]. For example, Du et al. [16] synthesized alumina with pore diameters from 2-20 nm using sodium aluminate. Alumina having pore diameters from 4 to 8 nm have been prepared

using nonionic polyethylene oxide-based surfactants [17], CTAB (Cetyltrimethylammonium bromide), carboxylic acid, and stearic acid surfactants [18-20], but poor thermal stability at high temperatures is reported. Zhang et al. [21] further enlarged the pore size range from 3.5 to 15 nm using TPAOH (tetrapropylammonium hydroxide), CTAB, and NaOH. Recently, Huang et al. [23] reported control of pore properties without using templates or surfactants. In their study, alumina having pore diameters from 4 to 18 nm are obtained by varying the water to aluminum molar ratio in the hydrolysis of aluminum alkoxides [23], and the pore size range is further extended from 4 to 37 nm by changing the alcohol used during the gelation [24]. In addition, it is well known that drying and calcination conditions are critical to the pore properties of alumina, since the former affects the formation of alumina precursors [25-28] and the latter induces the removal of surface hydroxyl groups, crystallization and sintering [26, 29, 30].

Recently, we reported a facile solvent-deficient one-pot method to produce a high surface area and large pore volume γ -Al₂O₃ that is thermally stable up to 1200°C without transformation to α -Al₂O₃ [31, 32]. These synthesized aluminas are not well-organized alumina [22] and do not have aligned channels of pores that discussed in previous papers [33, 34]. However, the synthesized aluminas in this paper belong to less ordered alumina category, and pores are made of interstice between particles and agglomerate [23, 24, 35]. One of the application of the less ordered alumina is in FTS process as a catalyst support [35], and significant enhanced catalytic performances were observed on the catalyst using less ordered silica doped alumina. In this paper, the control of pore sizes, with large (40-60 nm) or medium (16-19 nm) pore diameters of thermally stable γ -Al₂O₃, is achieved by

controlling a number of synthesis factors, including mixing method, time, environment; calcination ramp rate; and alcohol concentration.

Since the pore properties are influenced by a large number of factors, it is important to understand the relationship between pore properties and each synthesis parameter; however, this requires significant time and cost to conduct all possible experiments to elucidate the effect of each variable. In this paper we will show that through the use of a statistical design, the important relationships can be determined at a fraction of the experimental cost and time.

Split-plot factorial statistical designs [36, 37] are useful when a randomized run order is structurally impossible, expensive, or inconvenient. Statistical reasons have been provided by Anbari et al. [38] to prefer a split-plot arrangement over a completely randomized design in these situations. They have shown that a smaller prediction variance can be achieved in some split-plot arrangements of two-level factorial designs than can be achieved with the corresponding completely randomized designs. Therefore, split-plot designs are more efficient when one or more of the factors need larger experimental units than other factors, or it is harder to change the levels of one or more of the factors [36]. In the synthesis of silica doped aluminas, a full factorial split-plot experimental design was useful because factors in the mixing process (mixing method, time, environment; and alcohol concentration) could only be varied between batches of reagents, while factors in the drying and calcination steps could be varied between portions of a single batch.

In this paper we used a split-plot fractional-factorial experimental design to obtain a useful mathematical model for the control of textural properties with a reduced cost and number of experiments [39, 40]. Statistical analysis of the data from the experiments

identified the most significant factors and interactions that affect on the pore diameter, surface area and pore volume of the resulting SDAs. The models obtained were then used to predict the ideal conditions necessary to produce high surface area, large pore volume, and differing pore sizes in the synthesis process.

2. Experimental

2.1. Material

The aluminum isopropoxide ($C_9H_{21}O_3Al$) (granular, 98+%) and the tetraethyl orthosilicate ($SiC_8H_{20}O_4$) (liquid, 99.9%) (TEOS) were purchased from Alfa-Aeser. Distilled water was used throughout the synthesis.

2.2. Synthesis method

Silica-doped aluminas (100 g batches) were prepared by adding aluminum isopropoxide (AIP) and water in a 5:1 water to AIP mole ratio, 5 wt.% silica from tetraethyl orthosilicate (TEOS), and more water in a 2:1 water to TEOS mole ratio. The mixture was then mixed and thermally treated at 700°C in air for 2 h with a 5 h ramp rate. To measure thermal stability, samples were calcined to 1200°C in air for 2 h with a 5 h ramp rate.

The factors that were chosen to be varied in the split-plot factorial design were: (1) a sealed mixing environment (yes or no), (2) mixing method (hand or mechanical mixing), (3) alcohol concentration (yes or no), (4) drying precursor temperature (25°C or 100°C), time (no or 24 h), a sealed drying environment (yes or no), (5) calcination ramp (1°C/min or 10°C/min). Mechanical mixing was carried out using a Bosch Universal mixer (model: MUM6N10UC). The total number of experiments were 96.

2.3. Statistical analysis

The specific design that we used is called a split-plot design with a full 2^4 factorial in the whole plots, and a $\frac{3}{4}$ fraction of a 4×2 factorial design in the subplots. The analysis of the un-replicated split-plot experiment was made in two steps. Following the procedure described by Bisgaard [41], the whole plot means were analyzed in the first step to find which whole-plot factors and interactions were significant. This was done by calculating all effects and interactions in the saturated model for the 2^4 design in the whole plots, and then identifying significant effects using a half-normal plot. After eliminating the insignificant whole plot effects and interactions, the second step was performed by fitting a mixed model to the individual observations [42]. The batch was considered to be a random factor, and the model was fit using the REML method with JMP 10 software. The JMP Fit Model menu was used to test all fixed effects in the model.

2.4. Characterization

The prepared silica-doped alumina samples were analyzed by powder x-ray diffraction (XRD) using a PANalytical X'Pert Pro diffractometer with a Cu K α x-ray source ($\lambda = 1.5418 \text{ \AA}$) operated at 45 kV and 40 mA. Scans were performed between 10° and 90° 2θ with a step size of 0.0167° at a rate of 0.013°s^{-1} .

Nitrogen adsorption measurements were carried out using a Micromeritics Tristar 3020 for the determination of surface properties at -196°C . Surface area was calculated using the Brunauer-Emmett-Teller (BET) model in the P/P_0 range from 0.05 to 0.20. Pore volumes were determined at a single point of P/P_0 equal to 0.990. Pore size distributions were calculated using an improved slit pore geometry (SPG) model for large pore sizes [43]. Samples were degassed at 200°C under N_2 flow overnight before every measurement.

Microscopic image of sample of batch two with no drying condition (Table 1) was obtained with an FEI Philips Tecani F30 transmission electron microscope (TEM) at a voltage of 200 kV. TEM sample was prepared by placing a drop of silica-doped alumina (1% dispersed in ethanol) on a carbon film with a copper mesh grid (Ted-Pella Inc.).

3. Results

3.1. Synthesis

Table 1 shows the list of experiments for the un-replicated split-plot design experiments to produce the silica-doped alumina (SDA) catalyst supports. It shows that all synthesized SDAs are mostly in gamma or theta phases at 1200°C (based on XRD data) suggesting high thermal stability. Figure 1 shows that all isotherms are Type IV, indicating synthesized aluminas pores are mesoporous. [4, 24, 44]

3.2. Statistical model

The statistical prediction equations determined from the data analysis for surface area, pore volume, and pore diameters are shown in Equations 1– 3 below.

$$SA_{ijklm} = \mu + A_i + M_j + w_{(ij)k} + D_l + C_m + AM_{ij} + AD_{il} + AC_{im} + DC_{lm} + AMD_{ijl} + AMC_{jml} + \varepsilon_{ijklm} \quad (\text{eq. 1})$$

where SA_{ijklm} is the surface area in the k th batch, prepared using the i th level of excess alcohol and the j th level of mixture method, the l th level of drying method and the m th level of calcination ramp. A_i is the fixed main effect of the excess alcohol, M_j is the fixed main effect of the mixing method, and $w_{(ij)k}$ is the random effect of the k th batch nested in the

combination of excess alcohol and mixing method. D_l is the fixed main effect of drying method, C_m is the fixed main effect of the calcination ramp, ε_{ijklm} is the random subplot error term, and the other terms in the model are interactions among the main effects.

$$PV_{ijk} = \mu + M_i + w_{(i)j} + D_k + \varepsilon_{ijk} \quad (\text{eq. 2})$$

where PV_{ijk} is the pore volume in the j th batch prepared using the i th level of excess alcohol, and the k th level of drying method. M_i is the fixed main effect of mixing method, D_k is the fixed main effect of drying method, and ε_{ijk} is the random subplot error term.

$$PD_{ijklm} = \mu + A_i + M_j + S_k + T_l + ST_{kl} + MS_{jk} + MT_{jl} + AMST_{ijkl} + w_{ijklm} \quad (\text{eq. 3})$$

where PD_{ijklm} is the large pore diameter in the m th batch prepared using the i th level of excess alcohol, the j th level of mixing method, the k th level of mixing seal, and the l th level of mixing time. A_i is the fixed main effect of excess alcohol, M_j is the fixed main effect of mixing method, S_k is the fixed main effect of mixing seal, T_l is the fixed main effect of mixing time, w_{ijklm} is the random batch effect, and the other terms in the model are interactions among the main effects

3.3 Influences of factors

3.3.1 Surface Area

Figure 2 shows that the excess alcohol usage has the largest effect on the surface area. On average, adding excess alcohol decreases surface area by 72 m²/g. In addition, due to the significant interaction between excess alcohol, drying method, and mixing method, the change in surface area caused by adding excess alcohol depends on both the mixing method and the drying method. Also, due to the interaction between adding excess alcohol and the calcination ramp, the change in surface area caused by adding excess alcohol is slightly different depending on the calcination ramp.

It is shown in Figure 2 that adding alcohol causes a decrease in surface area in most situations. However, when the batch is hand mixed and dried for 24 h at 100°C without sealing the drying environment, adding alcohol increases surface area from 368 m²/g to 407 m²/g. Also, when the batch was mixed by machine and dried for 24 h at 100°C without sealing the drying environment, adding alcohol has very little effect on the surface area. On average the effect of adding alcohol reduces surface area when the batch was mixed by machine rather than by hand.

Figure 3 illustrates the dependency between the effect of excess alcohol and the calcination ramp. When the calcination ramp is 10°C/min., adding excess alcohol decreases surface area by 91 m²/g. However, when the calcination ramp is reduced to 1°C/min. adding excess alcohol only decreases the surface area by 52 m²/g. Figure 2 also shows that the effect of drying method on surface area depends on both the mixing method and whether excess alcohol is added. This is again due to the significant interaction between excess alcohol, drying method and mixing method.

3.3.2 Pore diameter

Figure 4 shows that, on average, adding excess alcohol increases the pore diameter by 18.6 nm. However, due to the significant interactions, the change in pore diameter caused by adding excess alcohol is much greater or less than 18.6 nm depending on the mixing method used and whether a sealed mixing environment was used. In the left panel (Figure 4) where no sealed mixing environment is used and the batch is mixed by hand, adding excess alcohol increases pore diameter by about 25 nm regardless of the mixing time. On the other hand, when a sealed mixing environment is used and the batch is mixed by hand for 30 minutes, adding excess alcohol only increases the large pore diameter by about 5 nm. The change in pore diameter caused by adding excess alcohol for all 8 combinations of sealed mixing environment, mixing method and mixing time is visualized as the vertical differences in the ends of the lines in Figure 4.

3.3.3 Pore volume

As seen in Figure 5, drying method has the most significant effect on pore volume, where drying at 100°C in an unsealed drying environment for 24 h produces the largest pore volume. No drying condition produces the smallest pore volume, and there is little difference in pore volume between the other two drying conditions at 25°C. Switching from hand mixing to machine mixing decreases pore volume on the average by 0.157 cm³/g (see Figure 6).

4. Discussion

4.1. Confirmation of Model Predictions

Equations 1-3 and Figures 2-6 were used to identify seven different optimal synthesis conditions that were predicted to produce SDA with large or medium pore diameters, simultaneously with a large surface area and pore volume. The seven optimal

conditions were combinations of the levels or alternatives for mixing method, environment, and time; alcohol concentration; and the drying method. Table 2 shows these seven optimal conditions along with the predicted surface area, pore volume and large pore diameter at each condition. Confirmation experiments were run where a single batch of SDA was synthesized at each of the conditions listed in Table 2. The surface area, pore volume and large pore diameter for each of these batches was measured and are shown in the last three columns of Table 2. The results of six confirmation experiments agree with the model and graphical predictions except for experiment 3. However, experiment 3 is not reliable since using mechanical mixing in an unsealed environment for 30 minutes dries the mixture and the mixture spills over the bowl. The six experiments in agreement with the model predictions show that the statistical analysis has indeed identified the important synthesis factors that control the surface area, pore volume, and large pore diameter of SDA. In addition it has been demonstrated that batches of SDA can be produced with high surface areas, large pore volumes, and large (40-60 nm) or medium (16-19 nm) pore diameters.

4.2 The effect of excess alcohol

The results from the statistical analysis show that using alcohol in the mixing step has a negative effect on surface area and a positive influence on the pore diameter of SDAs (Figures 2 and 4), which is supported by the chemistry involved in the synthesis. Baker [45] suggested that the formation of an alumina precursor can be viewed as a polymerization of $\text{Al}(\text{H}_2\text{O})_6^{3+}$ octahedrals. When the hydrolysis rate is slow, this polymerization occurs in three dimensions rather than one dimension under fast hydrolysis conditions. This is confirmed by the TEM images of the SDAs. As shown in Figure

7, the primary particles of SDAs are slab like under slow hydrolysis condition, consistent with Baker's and Huang's results [23, 45]. Since there are a significant number of hydroxyl groups on the surfaces of the alumina precursor, excess alcohol is adsorbed on the surface planes of the bohemite crystallite (alumina precursor) via hydrogen bonding. This reduces the surface energy of the alumina precursor and inhibits the polymerization of the primary crystallites [46-48]. In addition, excess alcohol enhances the mobility of the alumina precursor and avoids pile stacking of the alumina plates. When the alcohol evaporates, an open 3D-stacking structure (or "house of cards") consisting of the alumina plates is formed and large pore diameters are observed, consistent with the results of previous studies [18, 24, 49-52]. In addition, when excess alcohol is used in combination with sealing the Bosch mixer and increasing the mixing, the pore diameter increases further, since sealing limits alcohol evaporation and helps maintain an alcohol rich environment and increased mixing enables the completion of the hydrolysis reaction and hydrogen bonding formation. Note that larger pore diameters are often observed with lower surface area [14, 15, 23, 24, 53].

4.2 The effect of excess alcohol and calcination ramp rate

As mentioned in section 4.1, adding excess alcohol decreases the surface area. In the case of a high calcination ramp rate, the surface area decreases by 91 m²/g; however, when the calcination ramp rate is slow, the surface area decreases by 52 m²/g (Figure 3). A slow calcination ramp rate results in slow shrinkage and formation of the isolated small particles [54]. The isolated particles have a lower tendency to bond to adjacent particles enabling them to grow into larger particles. A slow calcination ramp rate also provides sufficient time for both the interlayer hydroxyls and extra solvent to be removed without damaging the structure [24].

4.3 Effect of drying

From the statistical results, it is evident that drying affects the pore volume and surface area of SDAs. Pore volume and surface area increase with drying of the precursor compared to no control of the drying conditions, especially at higher temperature (100°C) (Figures. 2, 5). Drying leads to formation of further M-O-M cross-links in the gel as covalent linkages replace weak interactions between surface hydroxyl and alkoxy groups. This allows neighboring M-OH or M-OR groups to approach each other and undergo a condensation reaction [54] resulting in larger pore volumes. Solvent evaporation in the drying step produces a capillary pressure due to the difference between the solid-vapor and solid-liquid interfacial energies [54]. When the capillary pressure increases, liquid moves to smaller interstices (pores) with the greatest surface to volume ratio. As a result primary particles rearrange themselves during the drying process to form pores with similar sizes [53]. Since the solvent is slowly evaporated when the precursor is dried at low temperature (25°C), there is enough time for this rearrangement process to finish [55] and a smaller pore volume is observed. In contrast, when drying occurs at higher temperatures (100°C), the solvent is removed much faster and the rearrangement is not completed resulting in a larger pore volume. Maintaining drying conditions at 25°C with a sealed environment for 24 h resulted in a higher surface area and larger pore volume than the unsealed drying environment, suggesting more cross linking and reduced pile stacking of plates due to slower alcohol evaporation.

5. Conclusion

The synthesis of thermally stable silica-doped alumina (SDA) catalyst supports has been studied using a split-plot full fractional factorial design. From this study, the following conclusions can be drawn:

1. It was found that mixing method, time, and environment; calcination ramp rate; drying temperature and environment; and alcohol concentration can alter surface area, pore volume, and pore diameter by factors of 1.8, 1.4, and 3.3, respectively. Large pore diameters (> 40 nm), large pore volumes (> 2 cm³/g), and high surface area (> 400 m²/g) were obtained by addition of excess alcohol, drying at 100°C for 24 h, and no alcohol usage, respectively.
2. The proposed quantitative models can predict optimal conditions to produce SDAs with high surface areas (> 250 m²/g), large pore volume (> 1 cm³/g), and large (40-60 nm) or medium (16-19 nm) pore diameters.

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Tables

Table 1. Experiments to make silica-doped aluminas (SDA)

Batch	Surface area (m ² /g) ^a	Pore volume (cm ³ /g) ^a	Pore diameter (nm) ^b	St. dev (nm)	Mixing method H:hand M:Bosch	Mixing seal Y:sealed N: not sealed	Mixing time (min) H:30 L:15	Alcohol Y:yes N:no	Drying: N:no Y:yes (Time(h)/T(°C)/ cap(on or off))	calcination ramp (°C/min)	Phase at (1200°C) ^c
1	262	1.527	35.7	1.6	H	Y	L	Y	N	1	γ
1	233	1.431	37.7	1.6					N	10	γ
1	353	2.124	21.4,58.4	1.9,1.3					24h/25°C /cap on	1	γ +traceα
1	272	1.564	44.0	1.6					24h/25°C /cap on	10	γ
1	269	1.524	44.2	1.6					24h/25°C /cap off	1	γ
1	280	1.647	45.4	1.5					24h/25°C /cap off	10	γ
2	312	1.689	18.8,60.4	2.9,1.4	M	Y	H	N	N	1	γ +traceα
2	342	1.667	18.7,50.1	1.6,1.6					N	10	γ +traceα
2	367	1.948	15.9,49.3	1.5,1.6					24h/100°C /cap off	1	γ +traceα
2	393	2.134	16.1,49.4	1.5,1.6					24h/100°C /cap off	10	γ +traceα
2	330	1.735	16.7,49.4	1.6,1.6					24h/25°C /cap on	1	γ +traceα
2	320	1.542	19,51.3	1.8,1.9					24h/25°C /cap on	10	γ +traceα
3	402	1.937	16.9	1.3	H	Y	L	N	N	1	γ +traceα
3	336	1.799	18.2	1.2					N	10	γ +traceα
3	384	1.63	15.9	1.2					24h/100°C /cap off	1	γ +traceα
3	434	2.128	16.4	1.4					24h/100°C /cap off	10	γ +traceα
3	447	2.194	15.5	1.4					24h/25°C /cap on	1	γ +traceα
3	389	1.969	17.8	1.2					24h/25°C /cap on	10	γ +traceα
4	345	1.768	17.2	1.3	M	N	L	N	N	1	γ +traceα
4	356	1.635	18.3	1.3					N	10	γ +traceα
4	408	1.836	17.0	1.3					24h/25°C /cap on	1	γ +traceα
4	386	1.888	17.5	1.3					24h/25°C /cap on	10	γ +traceα
4	348	1.662	18.7	1.4					24h/25°C /cap off	1	γ +traceα
4	340	1.719	18.7	1.3					24h/25°C /cap off	10	γ +traceα
5	336	1.651	21.5,53.8	2.1,1.6	M	N	L	Y	24h/25°C /cap on	1	γ +traceα
5	285	1.56	22.4,60.2	2.5,1.2					24h/25°C /cap on	10	γ +traceα
5	319	1.493	36.6	1.7					24h/25°C /cap off	1	γ +α
5	289	1.578	21,54.7	2.0,1.6					24h/25°C /cap off	10	γ +α
5	408	2.245	17.8,47.9	1.5,1.7					24h/100°C /cap off	1	γ +traceα
5	382	2.264	18.6,49	1.8,1.6					24h/100°C /cap off	10	γ +traceα
6	316	1.198	20.7,53.5	2.3,1.5	M	Y	L	Y	N	1	γ
6	209	1.167	28.6,61.2	3.2,0.9					N	10	γ
6	430	2.437	18,48.4	1.6,1.7					24h/100°C /cap off	1	γ +traceα
6	320	1.815	22.2,58.8	2.5,1.6					24h/100°C /cap off	10	γ
6	336	1.594	22.0,57.2	2.2,1.5					24h/25°C /cap on	1	γ +traceα
6	310	1.786	21.1,50.5	2.0,1.8					24h/25°C /cap on	10	γ
7	235	1.139	27.7,61.7	3.5,1.0	M	Y	H	Y	N	1	γ
7	294	1.64	22.6,60.6	3.4,0.9					N	10	γ +α
7	388	2.364	20.0,57.5	1.9,1.0					24h/100°C /cap off	1	γ +traceα
7	378	2.284	19.4,48.8	1.6,1.8					24h/100°C /cap off	10	γ +traceα
7	242	1.275	23.5,59.5	2.4,1.4					24h/25°C /cap off	1	γ
7	246	1.319	23.1,60	2.8,1.4					24h/25°C /cap off	10	γ
8	368	1.681	16.6	1.27	H	N	L	N	24h/100°C /cap off	1	γ +traceα
8	393	1.536	17.2	1.24					24h/100°C /cap off	10	γ +α
8	350	1.48	13.7	1.31					24h/25°C /cap on	1	γ
8	367	1.922	17.2	1.23					24h/25°C /cap on	10	γ +traceα
8	424	2.145	19.4	1.37					24h/25°C /cap off	1	γ +traceα

8	414	2.145	17.5	1.26					24h/25°C /cap off	10	$\gamma + \text{trace}\alpha$
9	340	1.721	16.8,48.4	1.5,1.9					N	1	γ
9	356	1.643	15.6,45.4	1.6,1.4					N	10	γ
9	315	1.74	16.9,48	1.5,1.9	H	Y	H	N	24h/100°C /cap off	1	γ
9	356	1.9	17.3,47.9	1.4,1.7					24h/100°C /cap off	10	γ
9	431	2.359	16.6,47.1	1.4,1.6					24h/25°C /cap off	1	γ
9	431	2.196	15.9,44.7	1.4,1.3					24h/25°C /cap off	10	γ
10	421	2.936	20,47.8	1.7,1.5					24h/100°C /cap off	1	$\gamma + \text{trace}\beta$
10	397	2.968	21.2,49.7	1.8,1.4					24h/100°C /cap off	10	$\gamma + \text{trace}\beta$
10	280	1.658	36.4	1.6	H	N	H	Y	24h/25°C /cap on	1	$\gamma + \text{trace}\beta$
10	258	1.762	34.8	1.6					24h/25°C /cap on	10	$\gamma + \text{trace}\beta$
10	247	1.52	34.9	1.6					24h/25°C /cap off	1	$\gamma + \text{trace}\beta$
10	220	1.508	35.9	1.6					24h/25°C /cap off	10	$\gamma + \text{trace}\beta$
11	234	1.476	26.7,59.7	2.1,1.3					N	1	$\gamma + \text{trace}\alpha$
11	189	1.393	38.3	1.6					N	10	$\gamma + \alpha$
11	239	1.519	25.3,56.3	2.0,1.3	H	Y	H	Y	24h/25°C /cap on	1	$\gamma + \text{trace}\alpha$
11	236	1.588	25,58.9	2.2,1.4					24h/25°C /cap on	10	$\gamma + \text{trace}\alpha$
11	397	2.77	21,49.8	1.7,1.4					24h/100°C /cap off	1	$\gamma + \text{trace}\beta$
11	366	2.75	19.3,48.3	1.6,1.6					24h/100°C /cap off	10	$\gamma + \text{trace}\beta$
12	323	1.634	17.0	1.2					24h/25°C /cap on	1	γ
12	366	1.899	17.4	1.2					24h/25°C /cap on	10	γ
12	323	1.533	17.5	1.2	M	N	H	N	24h/25°C /cap off	1	$\gamma + \text{trace}\beta$
12	362	1.657	17.5	1.2					24h/25°C /cap off	10	$\gamma + \text{trace}\beta$
12	368	2.074	17.7	1.2					24h/100°C /cap off	1	γ
12	390	2.042	18.2	1.2					24h/100°C /cap off	10	γ
13	257	1.427	40.4	1.6					N	1	γ
13	213	1.172	44.8	1.5					N	10	γ
13	288	1.385	41.7	1.7	M	N	H	Y	24h/25°C /cap on	1	γ
13	272	1.43	41.1	1.7					24h/25°C /cap on	10	γ
13	252	1.421	41.1	1.6					24h/25°C /cap off	1	$\gamma + \text{trace}\beta$
13	266	1.592	41.5	1.7					24h/25°C /cap off	10	$\gamma + \text{trace}\beta$
14	327	1.737	18.2	1.3					N	1	γ
14	360	1.608	17.3	1.3					N	10	$\gamma + \text{trace}\beta$
14	361	1.639	16.5	1.3	H	N	H	N	24h/25°C /cap off	1	$\gamma + \text{trace}\beta$
14	338	1.725	17.6	1.2					24h/25°C /cap off	10	$\gamma + \text{trace}\beta$
14	345	1.811	17.1	1.2					24h/25°C /cap on	1	$\gamma + \text{trace}\beta$
14	410	1.832	15.6	1.3					24h/25°C /cap on	10	$\gamma + \text{trace}\beta$
15	325	1.682	17,48.5	1.6,1.5					N	1	$\gamma + \text{trace}\beta$
15	356	1.913	16.6,49.7	1.9,1.5					N	10	$\gamma + \text{trace}\beta$
15	417	1.999	14.4,46.9	1.8,1.5	M	Y	L	N	24h/100°C /cap off	1	$\gamma + \text{trace}\beta$
15	358	1.765	13.6,44.7	1.9,1.6					24h/100°C /cap off	10	$\gamma + \text{trace}\beta$
15	350	1.738	15.4,45.2	1.9,1.3					24h/25°C /cap off	1	$\gamma + \text{trace}\beta$
15	368	1.698	15.9,43.2	1.8,1.2					24h/25°C /cap off	10	$\gamma + \text{trace}\beta$
16	232	1.583	39.9	1.7					N	1	$\gamma + \text{trace}\beta$
16	236	1.429	45.1	1.6					N	10	$\gamma + \text{trace}\beta$
16	248	1.496	34.7	1.6	H	N	L	Y	24h/25°C /cap off	1	γ
16	227	1.57	36.4	1.6					24h/25°C /cap off	10	γ
16	424	2.763	18.3,45.9	1.6,1.5					24h/100°C /cap off	1	γ
16	402	2.685	17.9,46.5	1.5,1.6					24h/100°C /cap off	10	γ

- Determined by N₂ adsorption at 77 K
- Determined by improved slit pore geometry (SPG) model for large pore size using desorption branch
- Determined using X-ray diffraction method

Table 2. Trials to confirm the models and predictions

Mix Method	Mix Seal	Mix Time (min.)	Excess Alcohol	Drying (T/°C)	Pred. Surface Area (m ² /g)	Pred. Pore Volume (cm ³ /g)	Pred. Pore Diameter (nm)	Actual Surface Area (m ² /g) ^a	Actual Pore Volume (cm ³ /g) ^a	Actual Pore Diameter (nm) ^b
Hand	No	30	No	100	368	1.87	17.2	282.2	1.5	18.01
Hand	Yes	15	No	100	368	1.87	16.5	414.7	2.1	18.19
Machine	No	30	No	100	388	1.71	17.8	375.4	1.9	46.7
Machine	No	15	No	100	388	1.71	18.0	381.1	1.8	20.99
Hand	Yes	30	No	100	368	1.87	47.3	340	2.5	48.7
Machine	No	30	Yes	100	350	1.71	41.9	272.8	2	45
Machine	Yes	30	Yes	100	350	1.71	58.4	371.7	2.4	47.9

a. Determined by N₂ adsorption at 77 K

b. Determined by improved slit pore geometry (SPG) model for large pore size using desorption branch

Figure Captions:

Figure 1. Representative N₂ adsorption/desorption isotherms and corresponding pore size distributions of SDAs with bi-model pore size distribution.

Figure 2. Interaction of excess alcohol, drying method and mixing method on surface area.

Figure 3. Interaction of excess alcohol and calcination ramp on surface area.

Figure 4. Interaction between excess alcohol, mixing time, mixing seal and mixing method on pore diameter.

Figure 5. Average effect of drying method on pore volume.

Figure 6. Average effect of mixing method on pore volume.

Figure 7. TEM micrograph of SDA synthesized from second batch with no drying condition.

Figures

Figure 1.

Mixing method: H (hand mix), M (machine)
 Excess alcohol: N (No), Y (Yes)
 Drying method: 24h 100°C cap off (24 h drying at 100°C in unsealed mixing environment)
 Drying method: 24h 25°C cap on (24 h drying at 25°C in sealed mixing environment)
 Drying method: N (No)

Figure 2.

Excess alcohol: N (No), Y(Yes)

Calcinations ramp: 10°C /min or 1°C/min

Figure 3.

Mixing time: 15 or 30 minutes
 Excess alcohol: N (No), Y (Yes)
 Mixing seal: N (No), Y (Yes)
 Mixing method: H (hand mix), M (machine)

Figure 4.

Drying method: 24h 100°C cap off (24 h drying at 100°C in unsealed mixing environment)
Drying method: 24h 25°C cap on (24 h drying at 25°C in sealed mixing environment)
Drying method: N (No)

Figure 5.

Mixing method: H(hand mix), M(machine)

Figure 6.

Figure 7.