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Synthesis and characterization of Al_2O_3 catalyst carriers by sol–gel

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The sol–gel method has been used to synthesize alumina powder with high surface area from boehmite. The characteristics of the final powder product have been systematically studied in light of the preparation method and starting materials by fractional factorial design. The results show that the type of precursor and pH of the precursor sol are the most important parameters for the textural properties of the calcined alumina powder. When the calcination temperature is increased the type of precursor loses its significance, while the pH still has decisive importance after calcination at 1000 °C, on pore volume and surface area. There is also a significant combined effect of several parameters on the surface area and the pore volume. The electrophoretic mobility, agglomerate size and size distribution have been determined as a function of the pH for one type of boehmite sol. The relation between characteristics of the precursor and powder properties is clearly emphasized.

Introduction

Alumina, mainly in its γ-form, is widely used in catalysis as an inert carrier of metal catalysts and as part of bifunctional catalysts. Useful properties are high surface area and good thermal stability. Especially, the stability of γ-alumina is much better compared to other catalyst carriers, e.g. silica, titania and magnesia, in atmospheres containing water vapour [1].

The sol–gel method is convenient in catalyst carrier synthesis because of the possibility of controlling pore size and surface area. Yoldas [2] synthesized alumina powder with uniform pore morphology and size distribution from alkoxide. He concluded that while the pore volume did not change very much during heat treatment at 500 °C for 24 h, the pore size increased and the surface area decreased. Lopez *et al.* [3] synthesized γ-alumina from aluminium-sec-butylate. They observed a great variation in surface area with the pH in the sol. The highest surface area of 252.5 $m^2 g^{-1}$ was obtained at pH 6 after calcination at 600 °C for 72 h. At pH 3 the surface area decreased to 121.1 $m^2 g^{-1}$ due to ramification in the gel at low pH. Moreover, when using NaOH to give pH equal to 12, Na-aluminate with low surface area was formed instead of γ-alumina. Maeda *et al.* [4] have shown that the type of solvent mixed with aluminium isopropoxide is very important for the final pore size distribution of calcined alumina. They suggested that the nature of complexation of the alkoxide determines the gel structure and therefore the final pore structure.

Clearly, the pore texture of the alumina powder depends on the preparation method. However, a systematic study of the variables that control the pore texture is a considerable task. A large number of parameters must be considered, in addition to possible combined effects of them. In this paper, a limited number of preparation parameters that may control the final pore texture are studied. The sol–gel method, with two different starting materials, is considered: commercial boehmite powder or aluminium-sec-butylate which is hydrolysed in the authors' laboratory. The powders resulting from different sols, and treated at various drying and calcination conditions, are characterized with respect to surface area, pore size, pore size distribution and pore volume. The effect of each parameter on the final pore structure has been systematically analysed using an experimental design. In order to reduce the experimental work and still obtain statistically valid results, a so-called fractional factorial design has been used. This gives one the main effects, i.e. the effect of the various parameters on the pore structure. The properties of sols, i.e. electrophoretic mobility and agglomerate size, made from commercial boehmite have been analyzed and related to the properties of the calcined powder.

2. Experimental procedure

2.1. Materials

All the chemicals used were A.R. grade, and the water was twice distilled. Either a commercial boehmite hydrated-alumina powder from Condea Chemie or aluminium-sec-butylate (ASB) from Fluka were used to make aqueous sols. The preparation of sols from ASB was performed according to Leenaars *et al.* [5]. The method comprises the following steps.

ASB was first hydrolysed in water at 85–90 °C, and after 1 h the precipitate was peptized with HNO_3,

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mole ratio $HNO_3 : AlOOH = 0.07$. The sol was kept for 2 h at 90–95 °C in open air and then refluxed for 16 h at 90–100 °C. After cooling to room temperature, a polyvinyl alcohol (PVA) solution was added to the sol and finally aqueous solutions of HNO_3 or NH_3 were added to give the appropriate boehmite concentrations and pH (it is assumed that the hydrolysis is complete and only boehmite is formed). The PVA concentration was 2 wt% of the sol.

The commercial powder was added to distilled water while stirring. The sol was then sonicated with an ultrasonic probe (Cole Parmer, 600 W, 2 min) and PVA was added. Finally, the pH and the boehmite concentration were adjusted with HNO_3 and NH_3 solutions.

Wet gels were formed by leaving the sol at room temperature for more than 24 h. The gels were subsequently dried at room temperature for 48 h and calcined either at 550 or 1000 °C for 2 h in air.

The textural properties of the calcined powders were characterized by the Brunauer–Emmett–Teller method (Sorbtomatic 500, Carlo Erba). The pore radius was calculated as a mean value from the measured pore volume and surface area using the cylindrical pore model. The pore size distribution was calculated as a standard deviation of the mean pore size based on the half-breadth of the pore size distribution peak.

The agglomerate size in sols made from powder was measured by a combined sedimentation and optical transmission method. (Horiba CAPA-700). The electrophoretic mobility was measured by a particle electrophoresis apparatus (Rank Brothers Mk II). In order to minimize changes in agglomeration state, the solutions used to dilute the sols for the particle size and the electrophoretic mobility measurements were adjusted to the same pH as the sol.

2.2. Fractional factorial design

The influence of the various parameters on the powder characteristics was calculated with the help of a method based on fractional factorial design [6]. In this type of analysis, the main effect of each parameter is calculated on the basis of the results of the two extremes, i.e. the lowest and the highest value of a specific parameter. The effects calculated are therefore based on linearity.

However, the analysis of the interaction effects between the different parameters, makes the number of experiments increase rapidly. In order to decrease the number of experiments, a so called combined factorial design has been chosen. This is a technique which, by using as few experiments as possible, systematically isolates effects of potential interest. After conducting the experiments according to the design, the results are analysed and the significance of the different effects tested by use of a F(isher)-test. The F-test is a standard statistical test, and the experiments are designed to meet the requirements of the test. The main principle when testing the significance of a parameter is to compare the effect due to the mean variation in this parameter, (MS), to the mean of the random error (MS_{error}). The random error is calculated by repeating some of the experiments, and then calculating the deviation in the results. This deviation may be due to measurement errors, difficulties in reproducing similar experimental conditions, etc. The ratio MS/MS_{error} (the F-factor) should be larger than a certain value to ensure that the parameter has a significant effect on the powder properties and that the variation is not just due to random variation (error). Since one has a designed experiment, this ratio can be compared to an F-distribution which can be found in statistical tables, and which gives the number that the ratio has to exceed for the effect to be significant. The authors tested the significance of a parameter at a 95% significance level. This means that an effect, due to a change in a parameter, is significant if the F-factor is larger than 7.7, i.e. if one concludes that an effect is significant when the F-factor is larger than 7.7; there is only a probability of 0.05 that this conclusion is wrong.

In the experimental design, eight different experiments were run at two different temperatures (550 and 1000 °C). A low and a high value was tested for each of the four different parameters. These parameters are

1. type of alumina precursor (A),
2. amount of precursor in the sol (B),
3. pH of the precursor sol (C), and
4. drying temperature for the gel (D).

The resulting effects studied by varying the parameters A–D are: specific surface area (SA), pore radius (PR), pore size distribution (PD) and total pore volume (PV).

The value of $MS_{X,Y}$ ($X = A, B, C$ or D, and $Y =$ SA, PR, PD or PV) is calculated according to

$$MS_{X,Y} = \left[\left(\sum_{i=1}^{8} Z_{iX} \times Y_i \right)^2 \Big/ 8 \right] \Big/ \text{(number of degrees of freedom)} \quad (1)$$

The number of degrees of freedom in this experiment is 1 and $Z_{iX} = 1$ or -1, as given by i, the row number in Table I. Y_i is the value of SA_i, PR_i, PD_i or PV_i in row i in Tables II (550 °C) or III (1000 °C).

The value of $MS_{error,Y}$ is calculated from parallel experiments according to

$$MS_{error,Y} = \left\{ \sum_{j=1}^{M} \left[Y_j - \left(\sum_{k=1}^{N_i} Y_{j,k} \right) \Big/ N_i \right]^2 \Big/ \sum_{j=1}^{M} (N_{i,j} - 1) \right\} \quad (2)$$

where N_i equals the number of parallels of experiments i. M equals the number of experiments where parallels were run. The value of the denominator is the number of degrees of freedom.

Test statistics estimating the effect of $X (= A, B, C$ or $D)$ on the response Y (= SA, PR, PD or PV) are then given by

$$F = \frac{MS_{X,Y}}{MS_{error,Y}} \quad (3)$$

F is then compared to the 0.05 value point of the F-distribution with the appropriate degrees of freedom. This represents a 95% confidence level.

TABLE I Experimental design matrix, where + 1 corresponds to a high value and − 1 to a low value for eight experiments and four parameters

No i	Type of alumina precursor parameter A	Amount of alumina precursor (wt%) parameter B	Sol pH parameter C	Drying temperature (°C) parameter D
1	− 1	− 1	− 1	− 1
2	− 1	1	1	− 1
3	− 1	− 1	1	1
4	1	1	− 1	− 1
5	1	1	1	1
6	1	− 1	− 1	1
7	1	− 1	1	− 1
8	− 1	1	− 1	1

TABLE II Experimental factors and parameters used for various alumina powders made by sol–gel. The surface area, pore radius and distribution and the pore volume are determined. The powders are calcined at 550 °C

Sample no.	Parameter				Effect			
	Type of precursor	Amount of precursor (wt%)	pH	Drying temperature (°C)	Specific surface area ($m^2 g^{-1}$)	Pore diameter (nm)	Size distribution (nm)	Pore volume ($cm^3 g^{-1}$)
1	Commercial	5	1	60	246.8	4.4	0.86	0.451
2	Commercial	17	8	60	257.2	4.9	1.66	0.638
3	Commercial	5	8	100	274.1	4.6	1.70	0.633
4	Synthetic	17	1	60	279.5	4.0	0.74	0.493
5	Synthetic	17	8	100	329.4	4.4	1.20	0.659
6	Synthetic	5	1	100	279.1	4.0	1.22	0.523
7	Synthetic	5	8	60	335.9	4.5	1.34	0.701
8	Commercial	17	1	100	251.5	4.6	1.28	0.526

The combined effect of two parameters, say $X1$ and $X2$, $MS_{X1,X2,Y}$ on the effect Y can be found by combining the $Z_{i,X1}$ and $Z_{i,X2}$ values by

$$MS_{X1,X2,Y} = \left[\left(\sum_{i=1}^{8} Z_{i,X1} \times Z_{i,X2} \times Y_i\right)^2 \Big/ 8\right] \Big/ \text{(number of degrees of freedom)} \quad (4)$$

The number of degrees of freedom in this experiment is 1.

The test statistics of the combined effect may then be written

$$F = \frac{MS_{X1,X2}}{MS_{\text{error},Y}} \quad (5)$$

Since one will have the same value for $Z_{i,X1} \times Z_{i,X2}$ when combining AB and CD, or AC and BD, or AD and BC, these pairs of effects will be confounded, i.e. it will not be possible to separate these pairs of effects from each other. It should also be mentioned that even if two parameters each have a significant effect, their interaction may not be significant. This analysis therefore gives information of possible synergy effects between different parameters, but with these few experiments it will not be possible to estimate the separate effect of the interactions between different parameters.

3. Results and discussion

Tables II and III show the results of the systematic experimental work, and Tables IV and V show the various test statistics calculated for the parameters that have been varied in the experiments. The test statistics were calculated by using the MS_{error} values listed in Table VI, which were obtained by running parallels of some of the experiments. X-ray diffraction analysis of the samples show that samples calcined for 2 h at 550 °C only give broad lines from γ-alumina. The samples calcined for 2 h at 1000 °C also show broad peaks, mainly from γ- and δ-alumina in addition to minor amounts to θ-alumina.

Before discussing the results further, a few remarks should be made about the assumption of cylindrical shaped pores in the calcined powder. Boehmite consists of thin needle-like or plate shaped primary crystals [5, 7]. When dehydrated and heated, thicker and more rodlike γ-alumina crystals are formed. Based on the shape and packing mode of the primary particles, a slit-shaped model for the pore symmetry appears to be reasonable for boehmite gels. However, by comparing cumulative surface areas and pore volumes with the total surface area and pore volume obtained by BET measurements, Bautista *et al.* [8] found a good correlation for the cylindrical pore model for γ-alumina calcined at 650 °C. Depending on the extent of heat treatment, various alumina (sub)phases may form and modify the texture of the precursor gel. Furthermore, since textural changes have also been related back to the preparation method of the precursor [4, 9], this may suggest that the best choice of pore shape model also is a variable parameter. All in all, in light of these uncertainties one has at this stage chosen to use the cylindrical pore model on powder calcined both at 550 and 1000 °C, and both prepared from ASB and commercial boehmite.

TABLE III Experimental factors and parameters used for various alumina powders made by sol–gel. The surface area, pore radius and distribution and the pore volume are determined. The powders are calcined at 1000 °C

Sample no.	Parameter				Effect			
	Type of precursor	Amount of precursor (wt%)	pH	Drying temperature (°C)	Specific surface area ($m^2 g^{-1}$)	Pore diameter (nm)	Size distribution (nm)	Pore volume ($cm^3 g^{-1}$)
1	Commercial	5	1	60	94.2	7.7	2.9	0.373
2	Commercial	17	8	60	114.7	7.6	2.9	0.519
3	Commercial	5	8	100	106.6	7.0	3.0	0.533
4	Synthetic	17	1	60	84.1	7.5	2.9	0.427
5	Synthetic	17	8	100	132.7	7.6	2.5	0.474
6	Synthetic	5	1	100	88.1	7.4	2.7	0.441
7	Synthetic	5	8	60	133.0	7.3	2.8	0.594
8	Commercial	17	1	100	88.5	8.1	2.5	0.412

TABLE IV Test statistics of different factors on powder parameters at 550 °C

Parameter	Specific surface area	Pore diameter	Size distribution	Pore volume
Type of precursor	44	8	2	9
Amount of precursor	0	0	0	0
pH	23	6	7	212
Drying temperature	0	0	1	2

TABLE V Test statistics of different factors on powder parameters at 1000 °C

Parameter	Specific surface area	Pore diameter	Size distribution	Pore volume
Type of powder	7	0	0	4
Powder content	0	2	0	5
pH	109	1	0	87
Drying temperature	1	0	0	1

The overall result shows that after calcination at 550 °C, the most important sol parameter for the final pore texture is the type of alumina precursor (synthesized or commercial powder), and pH in the sol. The amount of precursor and drying temperature show practically no importance. After calcination at 1000 °C, the pH in the precursor sol still appears to be important, while the powder content of the sol and type of precursor only have weak responses, close to the 0.95 significance level on the surface area and pore volume.

It is clear that at pH = 8, the powders made from alkoxide have a higher surface area than powders made from commercial boehmite. This could be related to the presence of hard agglomerates in the commercial powder which are not broken down when the sol is prepared. It is known that hard agglomerates can be formed during evaporation of the solvent during powder production [10]. The alumina precursor prepared directly from ASB is not dried during the preparation process, thereby minimizing the possibility of hard agglomerate formation.

In order to elucidate these features closer, dispersion experiments were carried out on the commercial powder. The pH effect on agglomerate size has been investigated. Fig. 1 shows the agglomerate size and size distribution as a function of pH. These dispersions were first treated with ultrasound for 2 min. At low pH, the agglomerate size is small, and the size distribution narrow. At higher pH the agglomerate size increases, and the size distribution is broad. A maximum in both parameters is reached around pH 8.0. Above pH 8.0, the agglomerate size and distribution decrease and reach minima around pH 10 before again increasing to higher values.

The variations in agglomerate size with pH (Fig. 1) can be explained by electrostatic interactions between the boehmite particles. The surface of boehmite, like other oxides, is fully covered by hydroxyl groups when it is dispersed in water. The surface hydroxyl groups have an amphoteric character, and the surface may become positively or negatively charged depending on the pH

$$\equiv \mathrm{Al} - \mathrm{OH} + \mathrm{H}^+ \rightleftharpoons \equiv \mathrm{Al} - \mathrm{OH}_2^+ \qquad (6)$$

$$\equiv \mathrm{Al} - \mathrm{OH} + \mathrm{OH}^- \rightleftharpoons \equiv \mathrm{Al} - \mathrm{O}^- + \mathrm{H}_2\mathrm{O} \qquad (7)$$

The variations in surface charge are confirmed by electrophoretic mobility measurements. The electrophoretic mobility of powder dispersions at different pH values is shown in Fig. 2. The mobility is equal to zero at pH = 7.8. This value is called the isoelectric point (i.e.p.) and is a characteristic of the powder used. The i.e.p. value determined is in accordance with other results reported in literature [7]. The electrophoretic mobility increases in positive values with decreasing pH, and reaches a maximum around pH = 6.0. The same tendency is observed above pH = 7.8, but the mobility increases in negative values. The variation in the electrophoretic mobility reflects changes of charge density in the so-called diffuse layer [11]. The reduction in agglomerate size and size distribution when decreasing the pH may therefore be explained by

TABLE VI Effect of the mean random error (MS_{error}) calculated for two parallels of two experiments

Temperature (°C)	MS_{error}			
	Specific surface area ($m^4 g^{-2}$)	Pore diameter $(nm)^2$	Size distribution $(nm)^2$	Pore volume $(cm)^6 g^{-2} \times 10^4$
550	106.6	0.28	0.14	2.40
1000	20.0	1.16	3.90	3.14

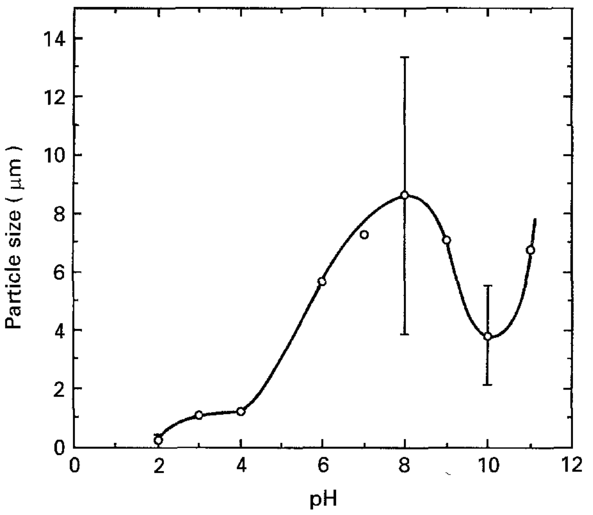

Figure 1 Variation of particle size as a function of pH for boehmite powder suspensions at 25 °C. The bars exemplify the distribution size at pH = 2, 8 and 10.

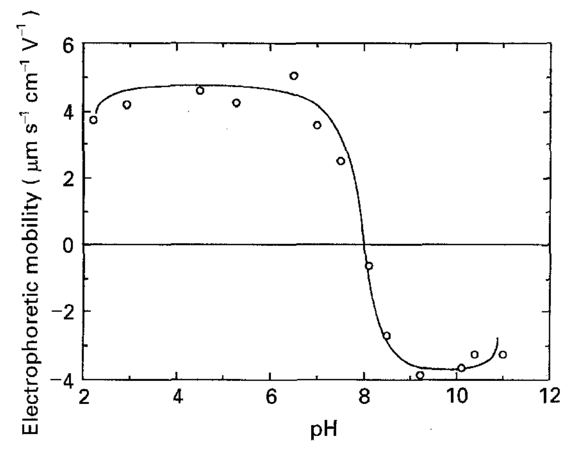

Figure 2 Electrophoretic mobility as a function of pH for boehmite powder suspensions at 25 °C.

an increased electrostatic repulsion between the particles. At pH values close to eight, where the surface charge is low, there is practically no hindrance to contact between the particles, and the agglomerate size and size distribution will show a maximum. Above pH 10, the electrolyte concentration becomes so high, and therefore the thickness of the counter ion layer surrounding the agglomerates so thin, that agglomerates may come into contact and grow. This explains the increase in agglomerate size and size distribution above pH 10. At low pH the same phenomenon is usually encountered. In the case of boehmite, however, dissolution of alumina occurs at pH < 4. This leads to complex adsorption–desorption processes which were not studied in further detail.

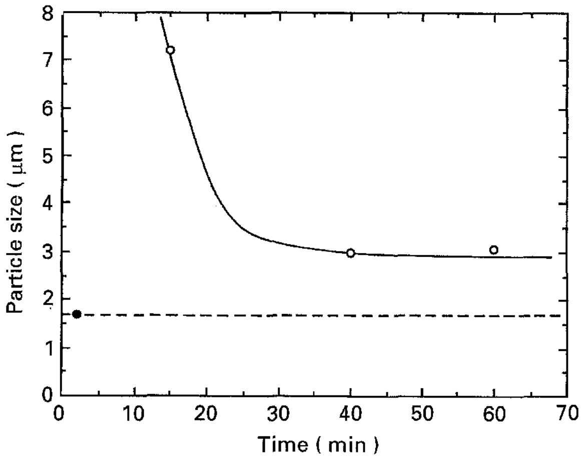

Figure 3 Effect of (●) ultrasound and (○) magnetic stirring for a boehmite powder suspension at pH 4 at 25 °C.

Ultrasonic treatment of the dispersion was very effective in breaking down agglomerates in acidic solutions, but gave no significant effect in near-neutral solutions. Fig. 3 shows the agglomerate size after mechanical stirring and ultrasonic treatment at pH = 4.

The pH dependence of ultrasonic treatment may be explained as follows. The reactions described by Equations 6–7 are fast, and equilibrium between the new particle surfaces of broken agglomerates and H^+/OH^- species is rapidly established. At pH values close to eight, i.e. when the overall charge of the water–oxide interface is close to zero, large agglomerates can be regenerated due to Brownian motion after the ultrasonic treatment. These agglomerates are built by weak interparticle contact, and a broad size distribution may therefore be formed. In acid solutions, however, the new surfaces formed after sonication become positively charged (Equation 6), and re-agglomeration is hindered giving a permanent reduction in size.

In order to summarize the study of properties of the commercial powder, one concludes that the agglomerates are relatively easy to break down to a level below 0.01 μm by a combination of pH control and ultrasound. This size level is within the expected range of primary boehmite particles.

The interpretation of the significance of the type of alumina precursor on the surface area is complicated by the combined effect of pH. A great advantage of the experimental design is the possibility to analyse combined effects between different parameters on the final result. In this study, with only a small number of parameters, the information from a combined effect analysis may, of course, be limited. Tables VII and VIII show the test statistics of the combined parameters. From the general results in Tables IV and V, it appears reasonable to assume that the combined effect is low for parameters B and D and high for A and C.

When the calcination temperature is increased from 550 to 1000 °C, the type of alumina precursor becomes less significant, while the pH of the sol still is very important for the value of the surface area and porosity. This observation shows the importance of the preparation method on the final pore texture in powder calcined at high temperature. More detailed analyses are reported [12], that conclude that the shape of the particles and the mode of clustering these into a three-dimensional matrix are important for particle sintering and evolution of different alumina subphases. Even if these features were not studied in detail in this work, it can be assumed from empirical knowledge that the morphology of the aqua and xerogel formed during the sol–gel transition and subsequent drying, respectively, depends very much on the type of precursor and the pH of the sol.

Even if the pH and type of precursor have a significant effect on the surface area, the effect on the pore size is only weak at 550 °C and insignificant at 1000 °C. Regarding the pore size, the ASB precursor gives a somewhat smaller pore size than the commercial boehmite which suggests that the primary particle size is smaller in powder made from this precursor. A pH dependence on the pore size and pore size distribution in powder calcination at 550 °C is not surprising. At pH = 1 the sol particles have high surface charge, and during the transition to gel the particles are forced into a packed three-dimensional structure. However, at pH = 8, large porous agglomerate structures form a coagulated sol. This sol gives a gel which has different structure from the three-dimensional gel made from the sol at low pH. The results show that the pore size, pore size distribution and pore volume are larger in powders made from coagulated unstable sols. Thus, even after calcination at 550 °C the more porous and random packing of the gel structure made from the latter sol is reflected in the powder pore texture. After calcination at 1000 °C, however, the pH effect on the pore size and size distribution has become insignificant.

TABLE VII Combined effects of various parameters on powder parameters at 550 °C. A, B, C and D represent the type of precursor, the amount of precursor, the sol pH and the drying temperature, respectively

Parameter combination	Specific surface area	Pore diameter	Size distribution	Pore volume
AB + CD	0	1	2	9
AC + BD	6	1	1	1
AD + BC	1	0	0	2

TABLE VIII Combined effects of various parameters on powder parameters at 1000 °C. A, B, C and D represent the type of precursor, the amount of precursor, the sol pH and the drying temperature, respectively

Parameter combination	Specific surface area	Pore diameter	Size distribution	Pore volume
AB + CD	0	0	0	10
AC + BD	19	2	0	2
AD + BC	2	0	0	10

Regarding the pore volume, the importance of the sol rheology is more pronounced. Even after calcination at 1000 °C, the type of packing of agglomerates has a decisive importance on the pore volume. As seen from Tables VII and VIII, there are also combined effects of several parameters on the pore volume. However, without more information these results are difficult to interpret further. From the results, it is seen that the type of precursor loses its significance to the pore volume when the calcination temperature is increased, i.e. the same tendency as observed for the surface area. Tijburg *et al.* [7] concluded that it is the type of contact between the particles that determines the thermal evolution of the material. The present results show that the nature of particle contact established already in the sol, and determined by surface interactions (or pH), has a decisive importance for the powder pore texture, even after calcination at 1000 °C.

4. Conclusions

The effects of the type of precursor, amount of precursor, pH in the precursor sol and drying temperature of the precursor gel on calcined alumina powder have been studied using an experimental design. The results show that the type of precursor and the pH are the most important parameters for the textural properties of the calcined powder. When the calcination temperature is increased, the type of precursor loses its significance, while the pH has decisive importance even at 1000 °C on the pore volume and surface area of the powder. There is also a significant combined effect on the surface area and the pore volume by several of the parameters studied.

The commercial boehmite used in this study consists of weakly bonded agglomerates. The following features were observed regarding this material.

1. Ultrasound is very effective at low pH in preparation of powder dispersion and sols.
2. The agglomerate size and size distribution is pH dependent. Agglomerates of 7 μm are found in sols at pH = 8.0. Particles smaller than 0.01 μm are formed at pH < 2.
3. The isoelectric point of the pseudoboehmite powder is 7.8.

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