

Effect of Alkyl Chain Length of Quaternary Ammonium Salts on Pore Size Distribution and Surface Area of Sol-gel Derived Alumina

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Several quaternary ammonium salts with different alkyl chain lengths were added to aluminium alkoxide sol; its transferring to a firm gel and then to nano-porous alumina were investigated. The BET surface area and pore size distribution measurements showed that pore size and surface area of γ -alumina can be altered by the type of quaternary ammonium salts. These measurements showed in presence of surface activity and micelle formation that there are two maxima for pore size distribution. Further analyses were done by infrared, XRD and thermal analysis.

Key Words: Nano-porous alumina, BET, Surfactant, Quaternary ammonium salt.

INTRODUCTION

Extensive demand of various industries for high purity alumina with defined surface area, porosity and pore morphology requires a novel approach for its preparation. Preparation of alumina by sol-gel method¹ has been shown to be a good technique for controlling the above mentioned parameters through control of hydrolysis and condensation rate by variation of temperature, concentration, type of alkoxide and water-to-alkoxide ratio². Furthermore, ageing, drying and calcination temperature and the type of atmosphere could affect texture of the final material. In recent years for processing of inorganic and hybrid materials templating approach has also been employed in addition to the above mentioned techniques^{3,4}. In preparation of porous silica such as MCM-41 templating approach has successfully been applied and a wide range of silica with different pore size and morphology has been prepared⁵. Preparations of high porosity vanadium oxide⁶, mesoporous yttria-zirconia⁷, hybrid inorganic-organic mesoporous silicates⁸, hollow spherical silica⁹ and super-microporous silicate¹⁰ have been described in literature. Surfactants have remarkable effect on the texture of materials. In preparation of hexagonal MCM-41 materials, it has been shown that pore size can be controlled by change of the organic chain length of the surfactant⁵. Similar approach has successfully been used for preparation of 3.6 micron spherical silica in presence of anionic surfactants by the sol-gel

method¹¹. Interestingly, morphological studies showed that spherical silica is hollow, which indicates that hydrolysis and condensation take place on micelles. Optionally, surfactant approach has been used to tailor powders with specific properties. Interestingly, careful adjustment of surfactant structure is required for design of a specific product. Templating is not limited to powders; it has also been used in preparation of mesoporous TiO₂ thin films¹².

In this study, we report the effect of various quaternary ammonium salts with different chain lengths on surface area, pore size distribution and properties of sol-gel derived alumina along with combination of calcination temperatures.

EXPERIMENTAL

Synthesis of alumina

All chemicals were purchased from Aldrich Chemical Co. and used without further purification. Five quaternary ammonium salts, tetraethyl ammonium bromide (TEAB), tetrabutyl ammonium bromide (TBAB), tetrahexyl ammonium bromide (THAB), tetraoctyl ammonium bromide (TOAB) and tetradecyl ammonium bromide (TDAB) were used as additives in sol-gel processing of alumina. In a typical experiment 10 g of aluminum isopropoxide was dissolved in 200 mL of isopropanol and, while vigorously stirring, a solution containing 20 mL isopropanol, 4 mL water and 2.45 mmol of pre-selected quaternary ammonium salt were added. The resulting mixture was refluxed for 5 h and aged at 50°C in a desiccator; after that a film of transparent gel resulted. Aging was continued for 90 h under the same condition, when the gel converted to a fine powder. The resulting raw alumina was divided into two portions; one portion was suspended in 50 mL hot isopropanol (denoted by W in Table-1) in order to remove the quaternary ammonium salt and then filtered. Washed (W) and unwashed samples were dried at 50°C for 15 h and then at 140°C for 5 h. Each washed and unwashed sample was again divided into two portions. One portion was calcined at 650°C and another portion at 800°C for 6 h to examine the effect of calcination temperature.

A total of 24 samples were prepared for surface area and pore analysis measurements. The procedure that was used for the preparation of alumina in the presence of cationic (cetyltrimethyl ammonium bromide, CTAB), anionic (sodium dioctyl sulfosuccinate, SDSS) and non-ionic (ethoxylated sorbitan monooleate, Tween 60) surfactants was similar.

Characterization

Nitrogen gas adsorption, using ultra high purity nitrogen gas (99.99%), adsorbed volumetrically on samples at -196°C, led to their specific surface area evaluation. A stainless-steel automatic volumetric adsorption apparatus was used to make these measurements. Experimental details for the volumetric adsorption setup are given elsewhere¹³. Prior to adsorption calculations, the sample weight is corrected for any weight loss due to degassing or drying. Pore distributions for diameters in the range of 10–500 Å were calculated using Barrett-Joyner-Halenda (BJH) method. Thermal analysis was performed on a Rheometric Scientific STA-1500 at a heating rate of 10°C/min in air. X-ray diffraction (XRD) patterns were recorded on a Phillips PW-1800 diffractometer with CuK_α radiation.

RESULTS AND DISCUSSION

The physical appearance of sols and the gelation times in the preparation of alumina in presence of quaternary ammonium salt were different to some extent. The samples with quaternary ammonium salt showed monolithic phase whereas in the one without quaternary ammonium salt, separation of liquid and solid phases was visible. By increasing the hydrocarbon chain length of quaternary ammonium salt the viscosity of the gel increased and the monolithic appearance of gel became clearer. A thick gel was obtained for the one prepared with TOAB and its higher homologue. Interestingly, the drying time increased by introducing quaternary ammonium salt. Furthermore, different drying time was observed by increasing hydrocarbon chain length of the quaternary ammonium salt. Apparently, the gel which is processed with long alkyl chain quaternary ammonium salt traps more water and consequently a longer time is required for drying. It appears that in addition to the surfactant templating effects, for a specific alkyl chain length of quaternary ammonium salt, there is a cationic-anionic interaction. This interaction is between quaternary ammonium salt with the most metal oxide surfaces at a pH above their isoelectric points¹⁴. This interaction has effect in gel consistency and their drying behaviour.

Nitrogen adsorption data for washed and unwashed samples after calcination at 650 and 800°C are listed in Table-1. Notably, higher calcination temperature leads to lower specific surface area as a result of further condensation of surface functional groups and collapse of some of the porous structures. Furthermore, all washed samples showed lower surface area in comparison to unwashed samples (Figs. 1 and 2). This can be explained by quaternary ammonium salt templating

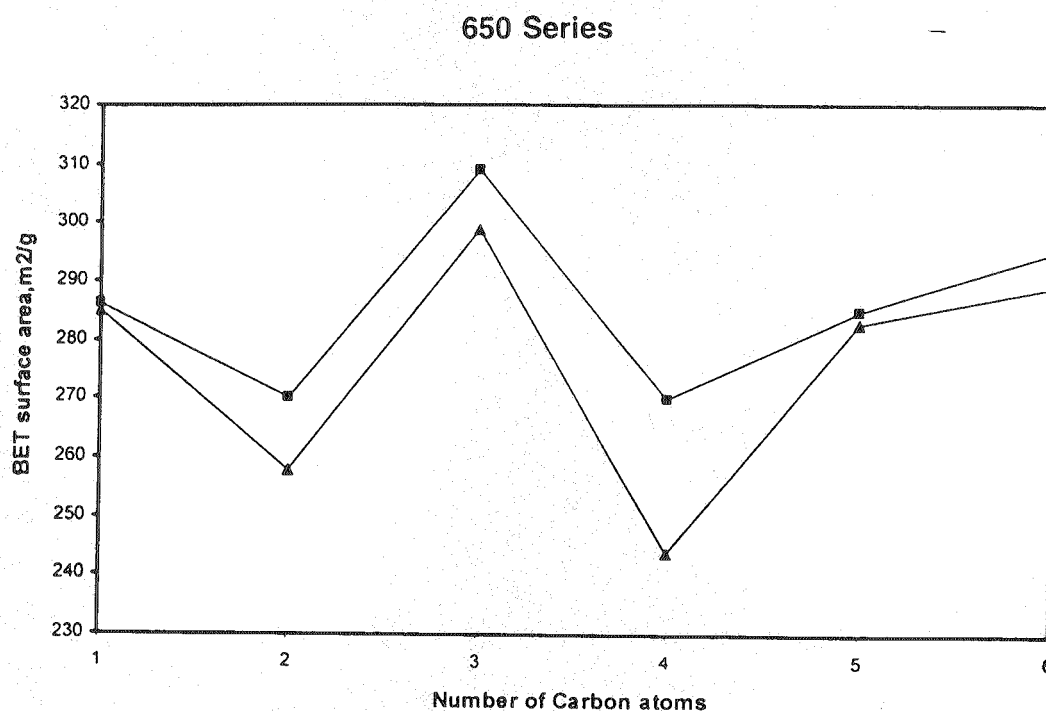


Fig. 1. BET surface area as a function of number of carbon chain for 650°C series, unwashed (■), washed (▲).

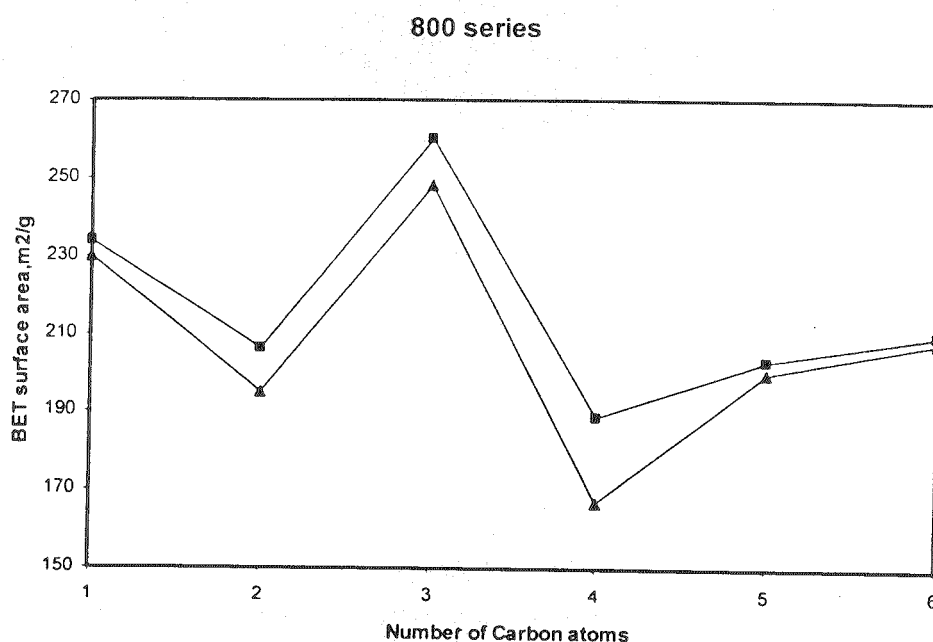


Fig. 2. BET surface area as a function of number of carbon chain for 800°C series unwashed (■), washed (▲)

effect which interacts with alumina precursor in sol stage and remains in the solid phase, and in the calcination stage these agents burn out and produce more porosity. The alumina which was processed in the presence of TBAB showed maximum surface area after calcination at either temperature.

The pore size of the sample which is processed in presence of TBAB is quite different from other samples. All samples which were calcined at 650°C showed larger pore size, except for the one processed in presence of TBAB, regardless of being washed or not. It seems that TBAB is not completely removed in the washing stage and some of it is trapped in pores of alumina precursor due to the critical size of butyl group. Consequently, 650°C calcined sample having the smallest pores (TBAB) show larger surface area (Fig. 1) in comparison to the 800°C calcined sample in presence of TBAB, which show larger pore size with smaller total surface area. Our interpretation is consistent with the large pores that form at 800°C for the samples processed in presence of TBAB. As mentioned above, tetrabutyl ammonium bromide is trapped effectively in pores of alumina precursor and is not removed completely up to 650°C which by calcination at 800°C the quaternary ammonium salt completely burns out and large pores are formed and the mean size of the pores is increased. This was confirmed by thermogravimetric analysis and the slightly yellowish colour of the samples processed in presence of TBAB.

Fig. 3 shows pore size distribution for the sample that was processed in presence of TOAB. As can be seen the pore size distribution curve with two maxima demonstrates a bimodal system. It is well known that the quaternary ammonium salt, similar to other amphiphilic molecules, has polar and non-polar parts and for the surface activity an exact balance should be attained between

these two parts of the molecule. Probably for these types of quaternary ammonium salts, surface activity is introduced with at least eight carbon alkyl chains and micelles are formed above the critical micelle concentration and then hydrolysis condensation occur inside or outside of micelles. Therefore, bimodal pore size distribution should be the result of hydrolysis inside and outside the micelles.

The structures of micelles with these cationic surfactants are cylindrical^{15, 16} with pore sizes in the range of 3–4 nm. The observed pore sizes for alumina prepared in presence of TOAB and TDAB are consistent with these data. It is interesting to note that in presence of these surfactants, under the experimental conditions of the present study, mesoporous γ -alumina having size of 3 nm could be prepared (Table-1). The presence of γ -alumina phase was confirmed by XRD and infrared spectroscopy.

TABLE-I
PORE SIZE AND SURFACE AREA OF ALUMINA PREPARED IN PRESENCE OF
VARIOUS SURFACTANTS

Sample	BET (m ² /g)	C _(BET)	ΔH_{ads} (kJ/mol)	Max. pore size distribution (Å)	
Al ₂ O ₃ -650	286.4	76.0	8.35	443	
Al ₂ O ₃ -650W	285.1	75.8	8.36	438	
Al ₂ O ₃ -TEAB-650	269.6	93.3	8.13	322	
Al ₂ O ₃ -TEAB-650W	258.3	72.1	8.37	418	
Al ₂ O ₃ -TBAB-650	308.7	47.0	8.05	156	
Al ₂ O ₃ -TBAB-650W	298.6	62.1	8.11	113	
Al ₂ O ₃ -THAB-650	270.4	80.5	8.39	252	
Al ₂ O ₃ -THAB-650W	243.8	101.1	8.65	217	
Al ₂ O ₃ -TOAB-650	284.5	38.2	7.91	173	473
Al ₂ O ₃ -TOAB-650W	282.7	51.3	8.05	158	344
Al ₂ O ₃ -TDAB-650	295.2	36.3	7.88	103	363
Al ₂ O ₃ -TDAB-650W	289.5	55.4	7.98	36	195
Al ₂ O ₃ -800	234.0	62.0	8.22	288	
Al ₂ O ₃ -800W	230.2	83.1	8.11	276	
Al ₂ O ₃ -TEAB-800	206.3	105.5	8.56	253	
Al ₂ O ₃ -TEAB-800W	194.8	89.3	8.51	301	
Al ₂ O ₃ -TBAB-800	260.3	103.5	8.55	540	
Al ₂ O ₃ -TBAB-800W	248.2	91.3	8.34	422	
Al ₂ O ₃ -THAB-800	189.5	59.7	8.08	222	
Al ₂ O ₃ -THAB-800W	167.3	53.2	8.38	195	
Al ₂ O ₃ -TOAB-800	203.4	42.8	7.98	232	521
Al ₂ O ₃ -TOAB-800W	200.6	32.1	7.80	54	280
Al ₂ O ₃ -TDAB-800	210.3	48.3	7.83	136	392
Al ₂ O ₃ -TDAB-800W	207.8	62.5	8.12	29	178

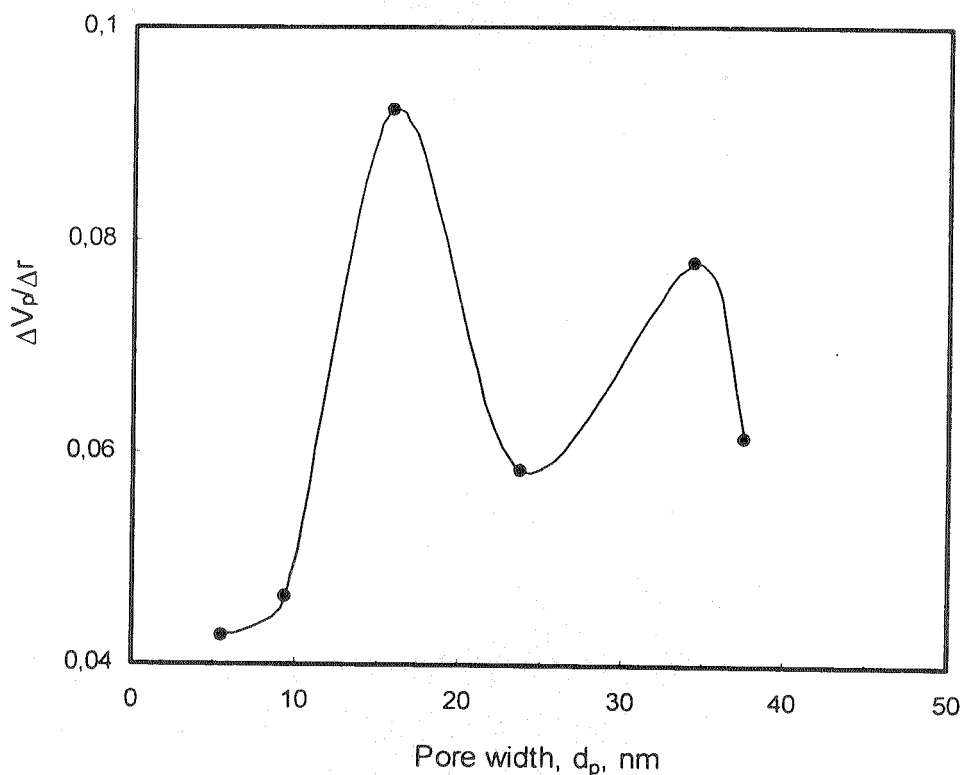


Fig. 3. Pore size distribution of Al_2O_3 -TOAB-650W

To examine the effect of surfactant on pore size distribution, exactly the same procedure was used for the preparation of alumina with three commercial surfactants having different charges. Pore size distribution for samples prepared in presence of CTAB, SDSS and Tween 60 showed a bimodal distribution, which confirms our suggestion that the hydrolysis and condensation of alumina precursor occurs inside and outside the micelles. With these surfactants we have not been able to prepare particles smaller than 10 nm. The reason for this behaviour is not clear at this stage. However, it appears that for the preparation of particles under 10 nm, critical micelle concentration, solubility, micelle type and their size are important parameters.

Conclusion

This work showed that the surface area and pore structure of sol-gel derived γ -alumina can be altered to some extent by using different quaternary ammonium salts. The pore size distribution model in sol-gel processing of alumina is alterable. The bimodal pore size distribution can be achieved due to simultaneous hydrolysis-condensation processes inside and outside the micelles.

ACKNOWLEDGEMENT

Financial support by the Research Council of the University of Tehran (Grant number 514-4-644) is gratefully acknowledged.

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(Received: 7 November 2005; Accepted: 3 March 2006)

AJC-4709

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