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EFFECT OF ADDITION OF SOME OLIGOMERS ON THE SURFACE CHARACTERISTICS OF ALUMINA

T.M. EL-AKKAD

Chemistry Department, Faculty of Science, Ain Shams University, Abbassia, Cairo (Egypt)

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ABSTRACT

The surface properties of pure alumina and alumina containing glycol oligomers 400 and 4000 were investigated by nitrogen adsorption at —195°C. Structural and phase changes were studied by X-ray and differential thermal analysis. The addition of a low molecular weight oligomer led to a decrease in the relative intensity of the diffraction pattern characteristic of β-$Al_2O_3 \cdot 3\ H_2O$ (bayerite). On the other hand, the addition of a high molecular weight oligomer completely prevents the appearance of any diffraction lines, giving only broad bands which indicate that the sample becomes amorphous. On thermal treatment at high temperature (550°C) the addition of both oligomers prevents the appearance of γ-Al_2O_3, whereas the pure sample clearly exhibits the diffraction patterns of γ-Al_2O_3 at 550°C.

The addition of a low molecular weight oligomer led to a decrease in surface area, while the reverse was true on addition of a high molecular weight oligomer. On thermal treatment, shrinkage of the oligomers led to the disappearance of the area, with slight widening in the pore radii.

INTRODUCTION

Previous studies were carried out to show the effect of the addition of synthetic polymers and resins during the precipitation of alumina gel, and it was found to bring about significant changes in the porosity of the gel. Basmadjian et al. [1] used a high pressure mercury penetration technique to follow changes in pore volume distribution. The effect of the addition of polyvinylpyrolidone [2] and melamine formaldehyde resin [3] were studied previously. It seems of interest to study the effect of the addition of oligomers of varying molecular weight on the adsorption properties and pore volume of the gel. In this investigation, two types of polyglycol oligomers of different molecular weights, 400 and 4000, were added during the precipitation of the alumina gel in a trial to show the effect of molecular weight of the added oligomer on the surface characteristics of the gel.

EXPERIMENTAL

Preparations

Polyethyleneglycol of two different molecular weights was added to alumina gel by dissolving it in the solution used to prepare the gel [0.2 M solution of $Al_2(SO_4)_3 \cdot 16\ H_2O$]. The precipitation was then carried out by adding 20% aqueous NH_4OH dropwise with constant stirring. The precipitate was allowed to settle, the bulk of the liquid decanted, and the remaining liquid removed by suction. The filter cake was washed, dried at 110°C for 96 h, and calcined at 550°C for 6 h. Both 5 and 10 wt.% of the oligomer 400 and 4000 were used in the preparation.

Apparatus

X-Ray diffraction patterns were obtained by means of a General Electric X-ray diffraction unit Model XRD-6 using Ni filter $K\alpha$ radiation. The d distances were calculated and compared with their relative intensities with data in the JCPDS files [4].

Differential thermal analysis was carried out using α-alumina on an inert standard, a programme temperature controller "ether" transitrol type 996/2 to permit a linear heating of 12°C min^{-1}, and a Cambridge Recorder Model "B" for recording the temperature difference.

Adsorption—desorption isotherms of nitrogen at —195°C were carried out by means of conventional volumetric apparatus. The calcined samples were outgassed at 550°C under a pressure of 10^{-5} torr 6 h prior to any adsorption measurements. The samples dried at 110°C were evacuated after 12 h under a pressure of 10^{-5} torr prior to any measurement.

RESULTS AND DISCUSSION

X-Ray and differential thermal analysis

X-Ray diffraction patterns (XRD) determined for pure alumina and alumina containing glycol oligomers 400 and 4000 either dried at 110°C or thermally treated at 550°C are represented in Figs. 1 and 2. Pure alumina gave β-$Al_2O_3 \cdot 3\ H_2O$ (bayerite) at 110°C. The addition of oligomer 400 during precipitation led to the appearance of the XRD pattern of bayerite but with a very weak relative intensity. On the other hand, the addition of the high molecular weight oligomer, 4000, led to the disappearance of the characteristic diffraction lines of bayerite and the sample possessed a poorly developed framework from which the crystal unit was formed.

On thermal treatment of the pure gel at 550°C, the characteristic lines of γ-Al_2O_3 appeared. On the other hand, the addition of the two kinds of oligomers led to the disappearance of the XRD patterns of γ-Al_2O_3.

The differential thermal analysis of the pure Al_2O_3 and Al_2O_3 containing oligomers 400 and 4000 indicate that the extent of dehydration decreases with increase of molecular weight and the content of the oligomer in the sample.

Surface areas and pore size distribution analysis

Adsorption—desorption isotherms of nitrogen at —195°C on pure alumina and alumina containing glycol oligomers 400 and 4000 heated at 110 and

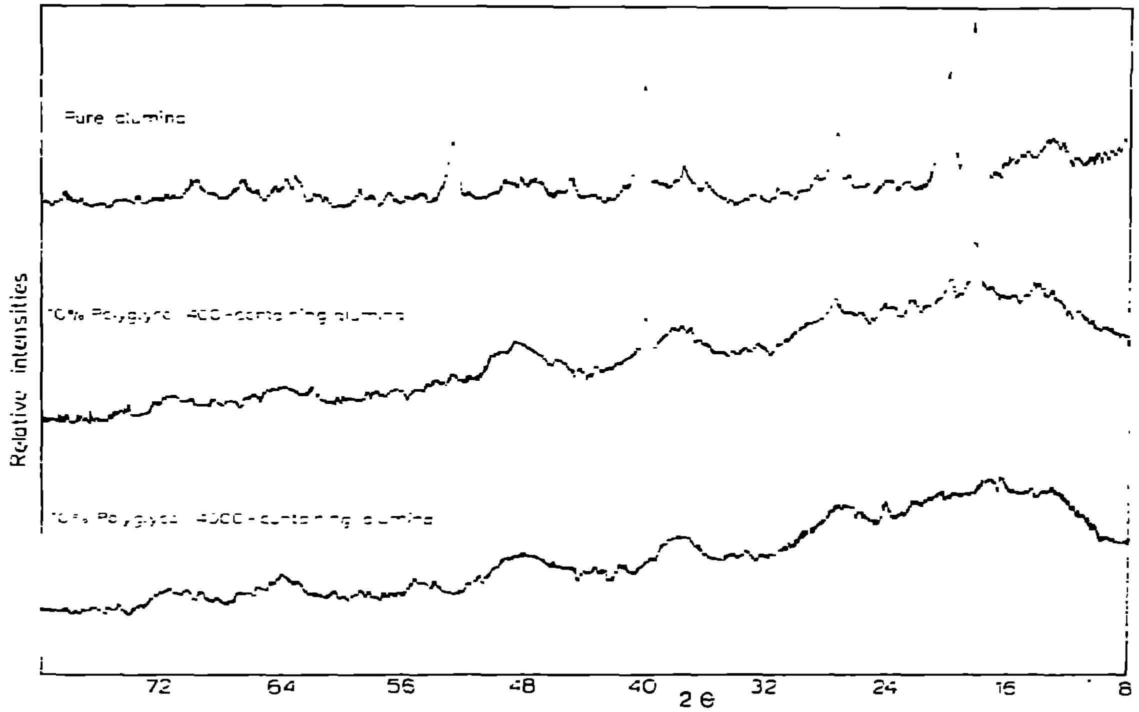

Fig. 1. X-Ray diffraction patterns of pure alumina and alumina containing oligomers heated at 110°C.

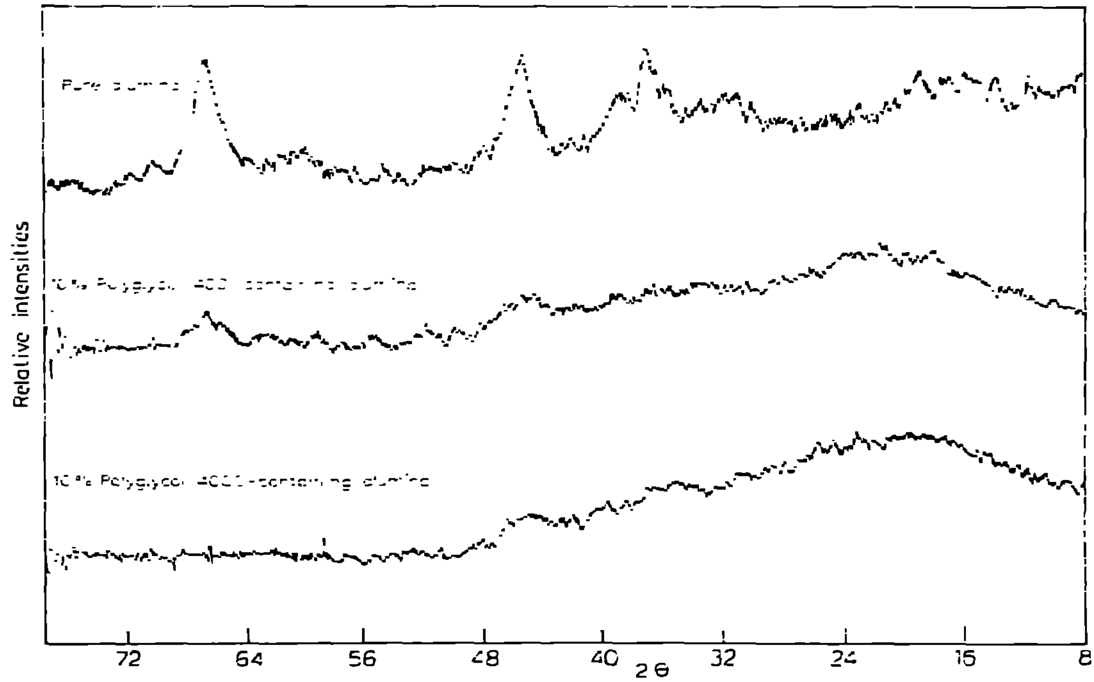

Fig. 2. X-Ray diffraction patterns of pure alumina and alumina containing glycol oligomers heated at 550°C.

550°C are represented in Figs. 3 and 4. Table 1 includes surface areas (m^2 g^{-1}) and pore volume V_p (ml g^{-1}) for these samples which were calculated from nitrogen adsorption isotherms. $S_{BET}^{N_2}$ was calculated using the BET equation and adopting 16.2 $Å^2$ as the molecular area of nitrogen. The pore size analysis was determined from nitrogen adsorption data where a suitable *t*-curve [5] could be employed for the V_l—*t* plots. The samples contain both micro- and mesopores; the latter being analyzed by the "corrected [6] modeless" method using a computer program [7] written in FORTRAN IV language for the IBM 1130 computer. The analysis is based on the desorption

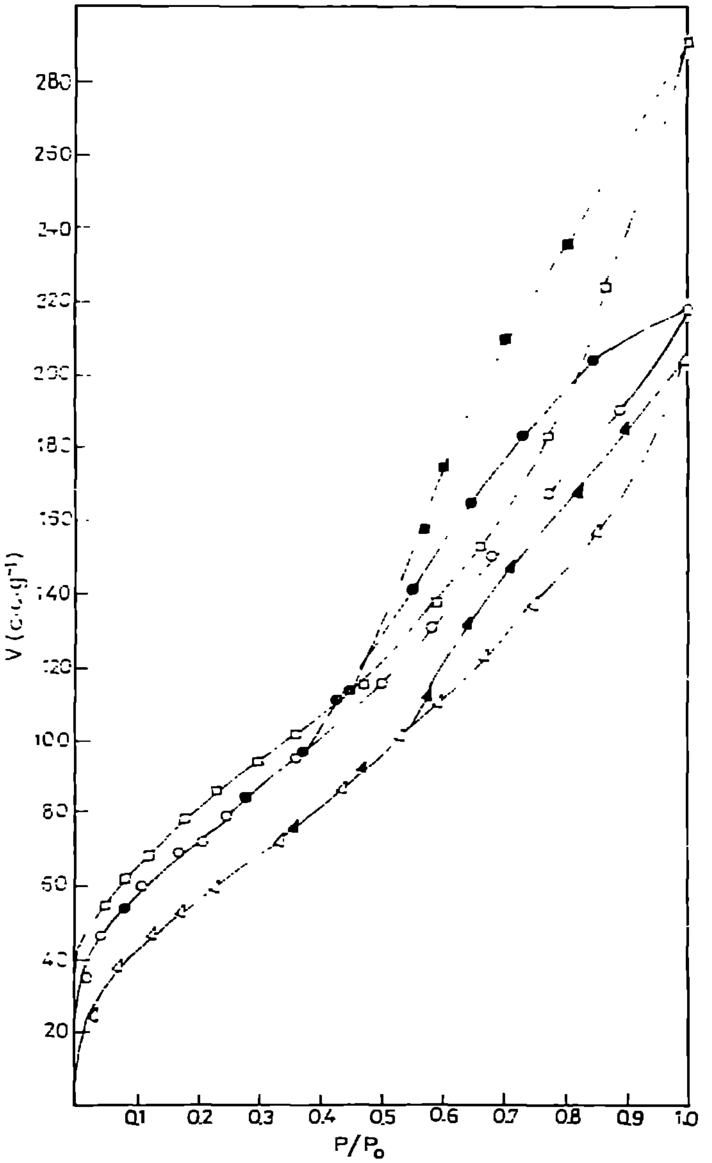

Fig. 3. Adsorption—desorption isotherms of nitrogen on pure alumina and alumina containing polyglycols heated at 110°C. o, Pure alumina; □, 10% polyglycol 4000 containing alumina; △, 10% polyglycol 400 containing alumina; ●, ■ and ▲ represent the desorption isotherms.

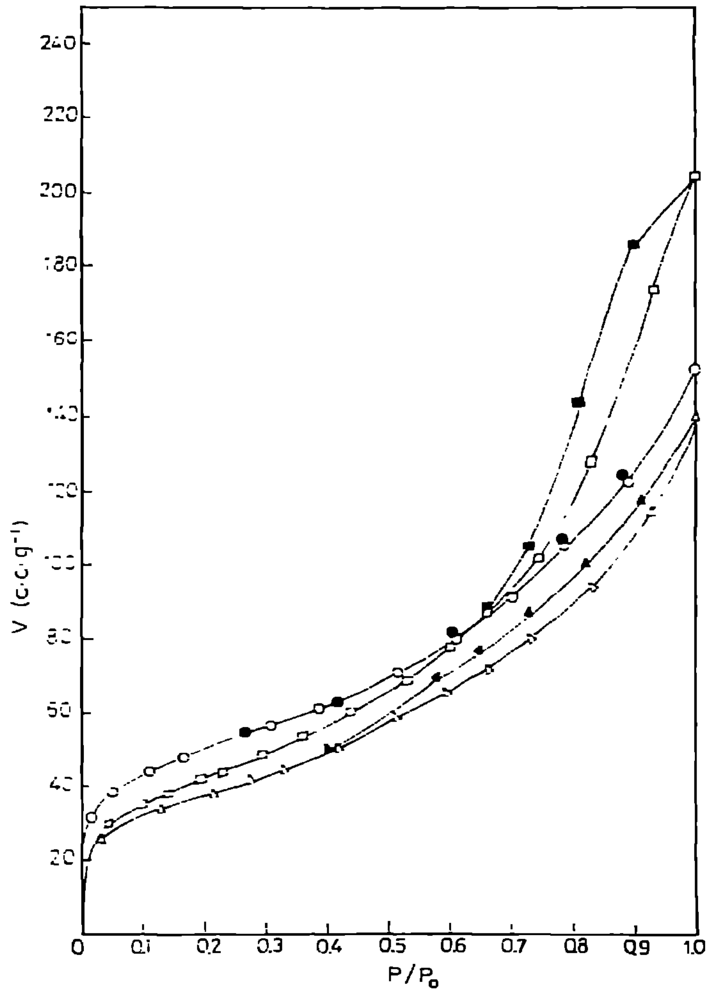

Fig. 4. Adsorption—desorption isotherms of nitrogen on pure alumina and alumina containing polyglycols heated at 550°C. ○, Pure alumina; □, 10% polyglycol 4000 containing alumina; △, 10% polyglycol 400 containing alumina; ●, ■ and ▲ represent the desorption isotherms.

branches of the isotherms and was continued downward to the closure points of the hysteresis loops adopting cylindrical pore shape. On comparing the results of mesopores analysis, in which the cumulative area may represent the area located in wide pores S_w, with the S_{BET} and S_t, it is possible to evaluate the fraction of area located in micropores, S_n. Total pore volume V_p (ml g^{-1}), S_t, S_w and S_n are summarized in Table 1.

Some variations in surface characteristics were obtained after the addition of high and low molecular weight oligomers, and may be summarized as follows.

Samples dried at 110° C.

(i) Addition of polyglycol 400 during the precipitation process led to a decrease in nitrogen area. This decrease is higher the greater the percentage of oligomer added; also the S_n/S_w ratio, and V_p decrease, as shown in Table 1.

TABLE 1

Surface characteristics of pure alumina and alumina containing glycol oligomers 400 and 4000

Sample	S^{N}_{BET} (m^2 g^{-1})	S_t (m^2 g^{-1})	S_n (m^2 g^{-1})	S_w (m^2 g^{-1})	S_n/S_w	V_p (ml g^{-1})	r_h (Å)	$\bar{r}$ (Å)
Al_2O_3	260	260	50	210	0.2380	0.3361	12	26
5% Al_2O_3-400	220	225	35	190	0.1842	0.3159	13	29
10% Al_2O_3-400	200	200	20	180	0.1111	0.3081	13	30
5% Al_2O_3-4000	270	275	65	210	0.3095	0.3880	13	29
10% Al_2O_3-4000	300	300	70	230	0.3043	0.4506	13	30
Al_2O_3	180	180	100	80	1.2500	0.2359	13	26
5% Al_2O_3-400	150	160	70	90	0.7770	0.2048	18	27
10% Al_2O_3-400	135	135	35	100	0.3500	0.2173	18	32
5% Al_2O_3-4000	155	155	60	95	0.6315	0.2949	23	38
10% Al_2O_3-4000	150	150	30	120	0.2500	0.3182	23	42

(ii) On the other hand, an increase in the surface area after the addition of high molecular weight oligmer 4000 is observed. The S_n/S_w and V_p values also increased.

(iii) For both cases, the variations in the surface area are not accompanied by variation in average pore radii ($\bar{r}$) (cf. Table 1) or mean hydraulic (r_h) radii (Fig. 5).

The dehydration process is important in the course of the preparation of the calcined gel with a large internal surface area and pore volume. During drying, the volume of the hydrogel shrinks many fold. This shrinkage is attributed to the high surface tension of the water contained in the gel [8]. Basmadjian et al. [1] introduced another factor modified by the reactive compound. This factor is the strength of the skeletal walls to withstand interfacial forces.

Thermal treatment at 550° C.

The decrease in surface area was observed for both the pure and the oligo-

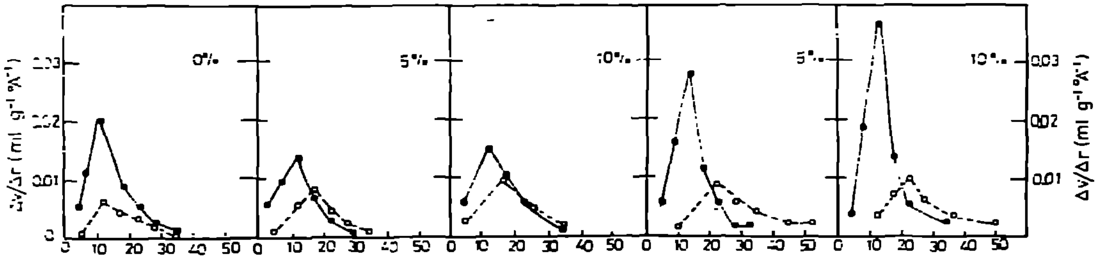

Fig. 5. Pore size distribution curves of pure alumina and alumina containing polyglycols heated at 110 (●) and 550°C (○).

mer containing alumina. For the pure alumina and alumina containing oligomer 400, the decrease amounted to about 30%. For alumina containing oligomer 4000, the decrease was 42 and 50% on addition of 5 or 10%, respectively. The decrease in the area is accompanied by an increase in the pore radii. For the pure sample, the ratio S_n/S_w increases due to the perforation of the gel during the evolution of water of hydration. For alumina containing oligomer, a greater decrease in the perforation of the gel than the pure sample was observed, which indicates that the presence of oligomer inhibits perforation of the gel. The addition of low molecular weight oligomer led to the blocking of the pores in the gel. On the other hand, the addition of the high molecular weight gel produced a large matrix during the precipitation process on which the gel spread giving a higher surface area. On thermal treatment, the decrease in surface area may be attributed to either the presence of the oligomers which inhibit perforation of the gel during the evolution of water of hydration or to the shrinkage of the oligomer by heating, leading to the disappearance of a certain area.

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