
EFFECT OF PRECIPITATION AND AGING ON POROUS STRUCTURE OF ALUMINIUM HYDROXIDE. II. CHANGES IN PORE SIZE DISTRIBUTIONS

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Differences in porous structure of the dried aluminium hydroxide (containing sulphate ions) caused by changes in temperature and pH of precipitation, the time of aging and by additions of surfactants are documented and discussed. The aluminium hydroxide precipitated at low temperatures (30–50°C) and pH values (7–8) has bi-disperse porous structure with maxima in the region of large and medium pores. The increase of temperature and pH of precipitation limits or completely suppresses medium pores and increases large and small pores. Characteristic trend was the disappearance of medium pores which led to monodispersity in the region of large and small pores. The addition of surfactants suppressed the effect of short-time aging on pore size distributions. At moderate temperatures the effect of surfactants manifested itself in the broad pore size distributions and in the increase of the volume of large and medium pores. Qualitative and quantitative differences in porous structure caused by the action of surfactants were suppressed on increasing temperature and pH of precipitation.

Aluminium oxide is frequently used as the catalyst support. The final stage of its preparation is dehydration of aluminium hydroxide at the temperatures 500–600°C. In this temperature interval, transformation to γ -aluminium oxide does take place, but its pore size distribution is determined by the porous structure of dried aluminium hydroxide. Observable deviations (increase of pore volume) exist essentially in the case of small pores with radii of about 2 nm only. The shape of pore size distributions is one of the factors which affect the distribution of active components in particles of the catalyst prepared by support impregnation¹. Furthermore, pore size distribution affects also the size of active particles located on the catalyst surface after calcination² and reduction³, the selectivity of catalysts as well as their lifetime.

The aim of the present work was to ascertain how changes of precipitation conditions and of aging time in statistically significant cases⁴ manifest themselves in the shape of pore size distribution curves of the dried aluminium hydroxide (containing sulphate ions). Chemicals used, experimental conditions and arrangement of the experiments are described in detail in our previous communication⁴.

RESULTS AND DISCUSSION

*Effect of Temperature, pH of Precipitation and Time of Aging
on Porous Structure of Aluminium Hydroxide*

Changes in porous structure of the samples due to the effect of temperature and pH of precipitation are shown in Fig. 1. On increasing precipitation temperature, the total pore volume increases as a result of large pores development, the volume of medium pores being only slightly decreased. At 30°C and pH 7, the non-aged sample showed bi-disperse pore size distribution with maxima of large pores radii around 420 nm and of medium pore radii around 65 nm. At the same temperature but at the higher pH of precipitation (pH 9), the portion of large pores decreases, which is accompanied by the marked increase of the volume of small pores. A similar trend in the formation of porous structure was found also for the precipitation temperature 50°C. However, at 70°C, the samples with developed structure of large and small pores were obtained. At pH 9, formation of medium pores has not been detected.

The precipitate of aluminium hydroxide when allowed to stand in the mother liquor undergoes changes which lead to the shift of the particle size of the precipitate to the higher values. The precipitate particles coalesce or grow on the expense of the smaller ones. Changes in the size of particles manifest themselves in the porous structure of the dried aluminium hydroxide. During long-time aging, the volume of large pores and total pore volume increase, while the volume of medium pores somewhat decreases. The aging of the sample precipitated at pH 7 and 30°C affected

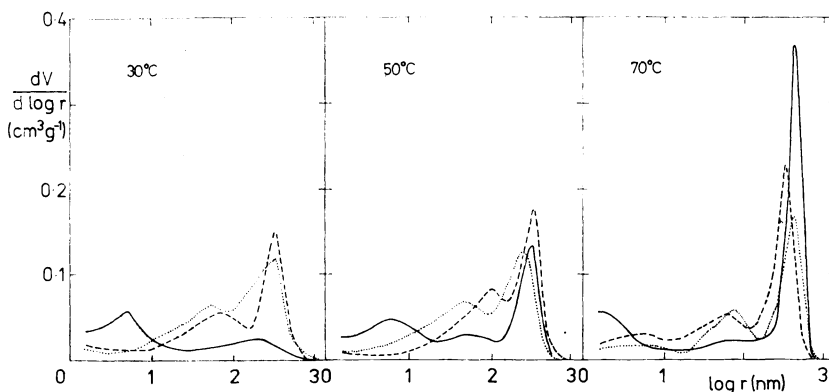


FIG. 1

Pore size distribution curves of the non-aged dried aluminium hydroxide precipitated at 30, 50, 70°C and at different pH values of the precipitation: pH 7 (---), pH 8 (···), pH 9 (—)

mainly the region of medium pores (Fig. 2). The samples precipitated at pH 9 and 70°C showed only large and small pores with the minimum content of medium pores. The aging was thus fast during and after precipitation and further significant changes in pore size distributions have not occurred.

Precipitation of Aluminium Hydroxide in the Presence of Cationic Surfactants

Precipitation at pH 7. At 30°C, the broad polydisperse structure with one distinct maximum in the region of large pores, and of medium pores (see curves 2 and 3 in Fig. 3) is formed. The volume of large pores and medium pores increased significantly, the volume of small pores being unchanged. Both cationic surfactants used acted analogously, differing only in the intensity of their action. The samples prepared in the presence of the more concentrated solutions of cationic surfactants showed the pore size distribution similar to that of the samples precipitated at pH 7 and 30°C. Polydisperse structure of these samples was preserved also during aging. Precipitation at 70°C in the presence of surfactants led to the greater development of the volume of large pores and partially also of small pores (Fig. 4), compared to the standard sample. The exception seems to be the precipitation at the higher concentration of CeMe_3NBr which supported partial development of medium pores.

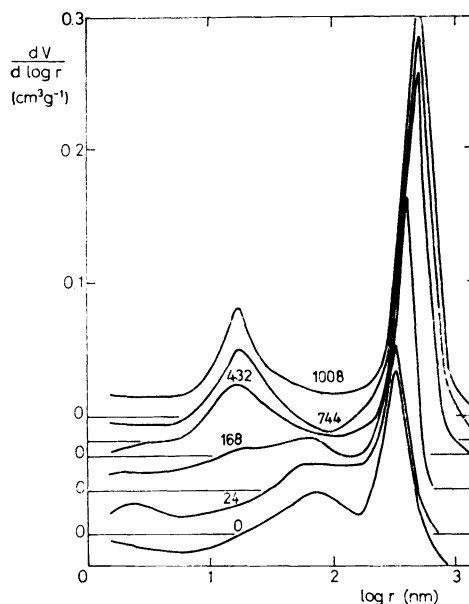


FIG. 2

Changes in distribution of pore radii of the dried aluminium hydroxide precipitated at pH 7 and 30°C in dependence on the aging time t_a . Numbers denote aging time in h

The short aging did not change the volume of medium pores, while with the unmodified samples this volume was somewhat decreasing.

Precipitation at pH 8. At 30°C and in the presence of surfactants, the polydisperse structure of pores (Fig. 3) is formed. In comparison with the unmodified samples, the volumes of large and medium pores increased, with simultaneous decrease of the most frequent radius of large pores by 70 to 170 nm. During 48 h-aging, the volume of medium pores decreased to c. 50% of the initial value. When compared

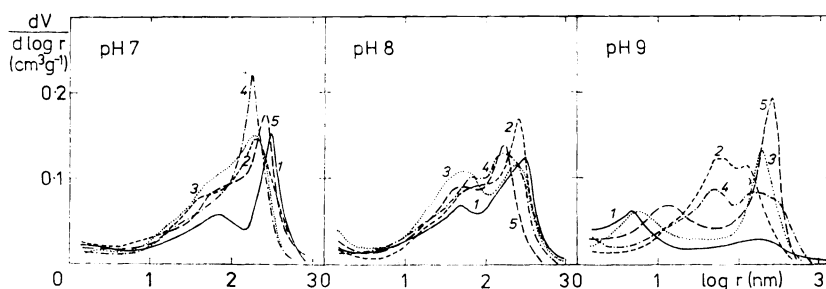


FIG. 3

Distribution of pore radii of the non-aged dried aluminium hydroxide precipitated and washed without and with cationic surfactants at 30°C and different pH values. 1 Without surfactants; 2 Ajatin 0.013 wt. %; 3 Ajatin 0.0013 wt. %; 4 CeMe₃NBr 0.013 wt. %; 5 CeMe₃NBr 0.0013 wt. %.

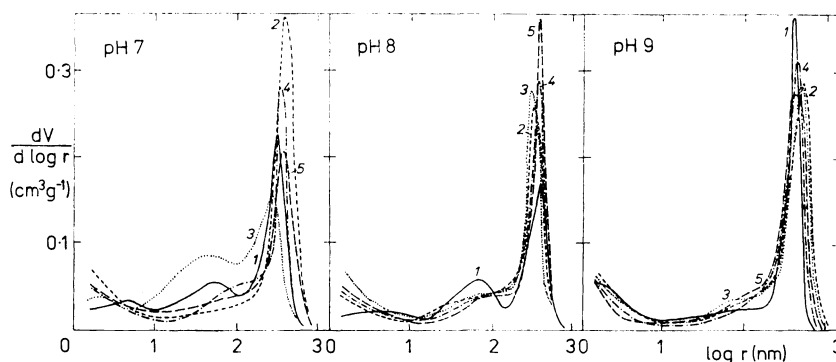


FIG. 4

Distribution of pore radii of the non-aged dried aluminium hydroxide precipitated and washed without and with cationic surfactants at 70°C and different pH values. 1 Without surfactants; 2 Ajatin 0.013 wt. %; 3 Ajatin 0.0013 wt. %; 4 CeMe₃NBr 0.013 wt. %; 5 CeMe₃NBr 0.0013 wt. %.

to the standard, the dried aluminium hydroxide precipitated at 70°C showed the decreased volume of medium pores and the increased volume of large and small pores. During aging, no further changes have been detected.

Precipitation at pH 9. At 30°C, the prevailing pores in the standard sample are small pores. On the other hand, in the presence of surfactants, the volume of the most pores increased markedly, except for small pores (Fig. 3). At the lower surfactant concentration, the polydisperse structure formed showed maximal pore radii around 50–150 nm. The addition of surfactants in higher concentrations caused formation of the typical bi-disperse structure with maxima of pore radii around 5–10 nm and 200–250 nm.

The dried aluminium hydroxide prepared by precipitation in the presence of cationic surfactants contained increased amount of bromide ions. When calculated with respect to the aluminium oxide, Br⁻ concentration (for the more concentrated solution of surfactants) was around 0.35 wt. %.

Precipitation of Aluminium Hydroxide in the Presence of Nonionic Surfactants

Similarly to the sample of the aluminium hydroxide prepared in the presence of cationic surfactants, also here the action of nonionic surfactants leads to the greatest

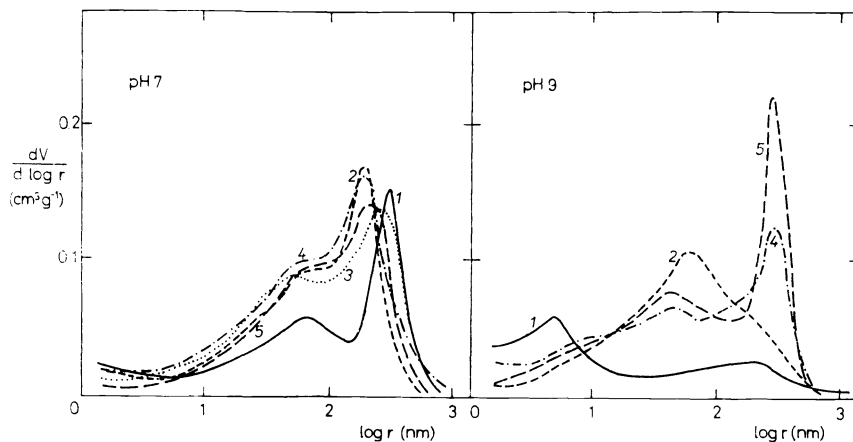


FIG. 5

Distribution of pore radii of the non-aged dried aluminium hydroxide precipitated and washed without and with nonionic surfactants at different pH values. Precipitation temperature 30°C. 1 Without surfactants; 2 Tween 20 0.0013 wt. %; 3 Tween 20 0.013 wt. %; 4 Sloviol R 0.0013 wt. %; 5 Sloviol R 0.013 wt. %

changes in the porous structure of the precipitate obtained at low temperatures and low pH values.

Precipitation at 30°C. At pH 7, the effect of nonionic surfactants resulted in formation of polydisperse structure with maxima around 200–250 nm (Fig. 5) which had the same character as the porous structure of the samples precipitated in the presence of cationic surfactants. On aging, any significant changes in the pore size distributions have not been encountered. In contradistinction to the standard, the increase of pH to 9 led to the increase of the volume of medium and large pores.

Precipitation at 70°C. At all three pH values investigated, the samples with very similar porous structure were formed, They did not differ essentially from the standard samples (Fig. 6). Typical feature was the sharp maximum of large pores that changed from 300 to 500 nm in dependence on the type and concentration of the surfactant used. The dried aluminium hydroxide prepared by precipitation in the presence of nonionic surfactants contained less than 0.2 wt. % of carbon.

As follows from experimental data, the aluminium hydroxide (containing sulphate ions) precipitated from sodium aluminate with nitric acid at low temperatures and pH 7 to 8 shows bi-disperse pore size distribution with the most frequent pore radii

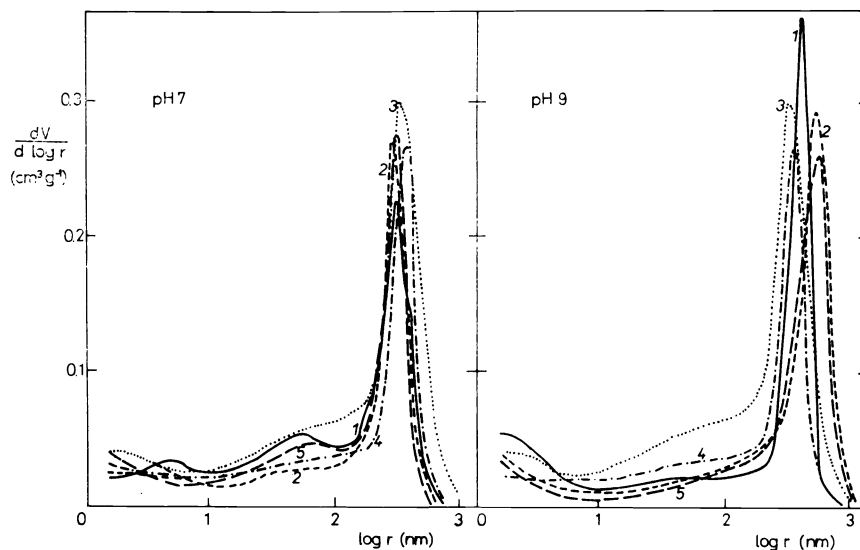


FIG. 6

Pore size distribution curves of the non-aged dried aluminium hydroxide precipitated and washed without and with nonionic surfactants at 70°C and different pH values. 1 Without surfactants; 2 Tween 20 0.0013 wt. %; 3 Tween 20 0.013 wt. %; 4 Sloviol R 0.0013 wt. %; 5 Sloviol R 0.013 wt. %

around 300 and 60 nm. At pH 9, contribution of large pores to the total volume is minimal whereas that of small pores increases markedly. Increase of precipitation temperature to 70°C led to the suppression of medium pores and to the more pronounced formation of large and small pores. Prolongation of the aging time induced the growth of the most frequent radius of large pores and the shift of the most frequent radius of medium pores to the lower values.

Comparison of the pore size distributions for the samples prepared with and without surfactants confirmed the conclusions derived from the statistical analysis⁴. The greatest changes in the pore size distributions were recorded in both cases when precipitation temperature was being changed. In the presence of surfactants and at low precipitation temperature, a broad polydisperse structure is formed, especially at pH 7 and 8. On increasing the temperature of precipitation, the effect of surfactants on the shape of distribution becomes less significant. The time of aging does not change pore size distribution of the modified samples significantly. Obviously, the addition of surfactants slows down or even completely suppresses the aging process. There is no substantial difference between the action of cationic and non-ionic surfactants. It seems likely that for each surfactant, there exists a certain concentration at which its effect on the porous structure of aluminium hydroxide is maximal. One can state that cationic and nonionic surfactants are powerful tools for regulation of porous structure of aluminium hydroxide.

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