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PREPARATION OF CATALYTICALLY ACTIVE γ-Al_2O_3 FROM A BASIC ALUMINIUM SUCCINATE PRECURSOR PRECIPITATED FROM HOMOGENEOUS SOLUTION

Ch. SIVARAJ, B. Prabhakara REDDY, B. Rama RAO and P. Kanta RAO*
Catalysis Section, Regional Research Laboratory, Hyderabad-500 007, India.
*To whom enquiries should be addressed.

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ABSTRACT

A rapid method for making γ-alumina is described. Basic aluminium succinate and bayerite, precursors of γ-alumina, were prepared by precipitation from homogeneous solutions of aluminium chloride with and without succinic acid by urea hydrolysis at 90-95°C. The identification of basic aluminium succinate was confirmed by its infrared (IR) and nuclear magnetic resonance (NMR) spectra. The effect of the calcination temperature on the crystallographic phase, crystallite size, surface area, pore volume, mean pore radius and the acid strength distribution of these aluminas was investigated. Well crystallized γ-alumina could be obtained by calcining basic aluminium succinate at 870°C for 5 h, whereas bayerite under similar conditions yielded θ-alumina. Active aluminas prepared from basic aluminium succinate have comparatively higher surface areas than those made from bayerite. Scanning electron microscope (SEM) studies of γ-alumina made from basic aluminium succinate show that the particles are microspheroidal in shape. The activity of these aluminas for dehydration of ethanol was comparable to that of commercial alumina.

INTRODUCTION

Active aluminas are extensively used as catalysts, co-catalysts, catalyst supports and adsorbents. The preparative techniques for the precursors and the temperature at which they are calcined have a great influence on the surface area and pore structure which control the activity and selectivity of aluminas [1-7]. Much of their special surface chemistry is attributed to defect acidic sites which apparently occur during dehydration of the aqueous gels from which they are usually formed and dehydroxylation of the oxyhydroxides which are their precursors. The composition of precipitates formed from aqueous solutions of aluminium salts depends mainly on the amount of alkali added [8]; only amorphous aluminium hydroxide is formed at pH < 6; pseudoboehmite is precipitated in the pH 7-10 range. These precipitates are generally gelatinous, difficult to filter and wash and crystallization requires aging for long periods.

Precipitation from homogeneous solution (PFHS) has emerged as a good method to produce easily filterable precipitates using hydrolysis of urea [9-11]. The advantage of PFHS is that better control can be exercised over the precipitate with respect to crystallite size, surface area, pore structure and composition.

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The preparation of gelatinous aluminium hydroxide from aqueous solutions containing chloride, nitrate or sulphate and urea by heating at 95°C was reported to yield amorphous aluminium hydroxide or pseudoboehmite [12]. Aluminium hydroxide precipitated by the PFHS method in the presence of organic acids like succinic acid was found to be dense [9]. The precipitate so obtained could be a good precursor for the preparation of active aluminas, but no systematic study has been made on the preparation of the precursor and the effect of the calcination temperature on the characteristics of the aluminas thus obtained.

In this paper, the composition and structure of basic aluminium succinate prepared by urea hydrolysis in the presence of succinic acid are presented. Active aluminas obtained by calcination of basic aluminium succinate and aluminium hydroxide prepared by this method were characterized by their surface area, pore volume, mean pore radius, crystallite size and surface acidity. The dehydration of ethanol was studied as a model reaction to test the catalytic activity of these aluminas.

REAGENTS AND APPARATUS

Aluminium chloride ($AlCl_3$, $6H_2O$, Sarabhai), succinic acid (LCl), urea (Ranbaxy), benzene, n-butylamine, p-dimethylaminoazobenzene (butter yellow), neutral red, bromothymol blue, ethanol (all from Fluka) and hydrochloric acid (BDH) were all of analytical reagent grade.

A conventional high-vacuum glass system was used to measure the BET surface areas by nitrogen (0.162 nm^2) adsorption at -196°C. The same system was employed to determine the pore volume and mean pore radius by the BJH method [13]. X-ray diffractograms were recorded on a Philips PW 1051 diffractometer using nickel-filtered CuKα radiation. The average crystallite size of the aluminas was determined by the application of Debye Scherrer equation [14]. The most intense line of Al_2O_3, corresponding to the (400) plane, was taken for line-broadening measurements. Correction for instrumental and α_1 α_2 separation was done using quartz reflection in the same angular range. The IR spectra were recorded at room temperature on a Perkin Elmer 283 B series spectrometer. The samples were pelleted with small amounts of KBr. NMR (proton) spectra were obtained using a JEOL FX 90 Q FT NMR spectrometer. Scanning electron micrographs were taken with a Cambridge Instruments Stereoscan 150. Gas chromatography was performed on a CIC gas chromatograph. The sodium content of the aluminas was determined using a Perkin Elmer 5000 Atomic Absorption Spectrometer.

EXPERIMENTAL

Preparation

An aqueous solution containing aluminium chloride (0.05 M), succinic acid (0.3 M) and urea (0.8 M) was placed in a 3 L round-bottom glass reactor and heated to 90-95°C with stirring. After the precipitation was complete (pH = 6.6), it was

filtered and washed free from chloride ions with distilled water and dried at 110°C for 24 h. The preparation of aluminium hydroxide by the PFHS method without succinic acid was carried out similarly (final pH = 7.4). The samples were calcined in air at the required temperature for 5 h. The weight per cent of sodium in all the catalysts was found to be 0.015.

Acidity

The acidity was determined by titration of solid acids with n-butylamine in non-aqueous media using Hammett indicators as described by Johnson [15]. Total acidity was measured by back titrating the excess of n-butylamine with standard hydrochloric acid using bromothymol blue as indicator, similar to the procedure adopted by Shibata et al. [16].

Activity measurements

A differential flow microreactor, operating under normal atmospheric pressure and interfaced to a gas chromatograph by a six-way gas sampling valve, was used to measure the activities of the catalysts. About 0.1 g of a catalyst was secured between two glass-wool plugs inside a borosilicate glass reactor of 10 mm i.d. fitted with a thermowell and an electrically heated vertical tubular furnace. The average particle size (0.5 mm) was chosen so as to eliminate mass-transfer effects. Ethanol was passed (0.43 $mol.h^{-1}$) over the catalyst bed using a Lewa metering pump and a preheater. All the conversion rates were measured under steady-state conditions with the help of the equation

$$X = r(W/F)$$

where r is the rate in mol h^{-1} g^{-1} catalyst, W is the weight of the catalyst in g and F is the flow-rate of the reactant in mol h^{-1}. The extent of conversion, X, was maintained below 10% and a straight line was obtained by plotting X against (W/F) for each catalyst. The rates were calculated from the slopes of these lines.

Analysis

The reaction products, ethylene, diethyl ether, water and unreacted ethanol, were analysed by gas chromatography using a 3 mm x 2 m stainless-steel column packed with 10% carbowax 20 M maintained at 90°C. A thermal conductivity detector and hydrogen as carrier gas at a flow-rate of 40 cm^3 min^{-1} were used.

RESULTS AND DISCUSSION

Precipitation from homogeneous solution

The influence of the succinic acid concentration (0.01 M - 0.4 M) on the crystallinity of the precipitate was studied. The nature of the precipitate changed from gelatinous to crystalline as the concentration of succinic acid increased

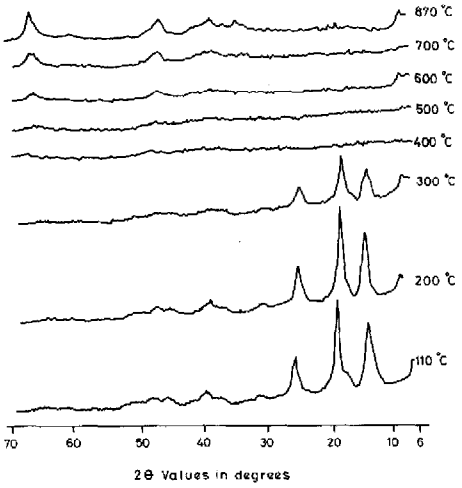
from 0.01 M to 0.3 M. Aluminium hydroxide precipitated by the PFHS method in the presence of succinic acid was crystalline, but gelatinous when precipitated in the absence of succinic acid. Succinic acid may be present in aluminium hydroxide as basic aluminium succinate or adsorbed on the surface of the precipitate. In the case of aluminium hydroxide precipitated in the presence of sulphate ion, there are divergent views on the nature of the association of sulphate ion with the precipitate. Several researchers [17-21] have suggested that basic aluminium sulphate coexists in the precipitates from aqueous aluminium solution containing sulphate ions. However, Sato et al. [12] have concluded that the sulphate ions are strongly adsorbed on the surface of the precipitate from solutions containing aluminium sulphate and urea, influencing its properties. In the present investigation, it has been established that basic aluminium succinate is precipitated from aqueous solutions containing aluminium ion, urea and succinic acid at 95°C. When the dried precipitate was extracted with diethyl ether, no succinic acid was found in the extract. However, dissolution of the precipitate in hydrochloric acid followed by extraction with diethyl ether yielded pure succinic acid, confirmed by the melting point (187.5°C), and proton NMR spectrum which is identical to that of authentic succinic acid (δ = 2.56 ppm for $-CH_2$ protons with CD_3OD as solvent and TMS as reference), showing that succinic acid is chemically bound.

That basic aluminium succinate coexists in the precipitate was also confirmed by IR spectra. The samples show absorption bands characteristic of carboxylate ion (1600 cm^{-1} and 1450 cm^{-1}) and ethylene groups (2920 cm^{-1}) which disappeared for samples calcined at ≧ 400°C for 5 h. A calcination temperature of ≧ 400°C is, therefore, necessary to convert basic aluminium succinate into active alumina. This is in good agreement with DTA data which show that decomposition starts at 360°C followed by combustion of the organic ligand.

The elemental analysis of basic aluminium succinate (Al = 16.7, C = 28.0, H = 2.7, O = 52.5 all in wt% and N = traces) indicated the chemical formulas as $(CH_2COO)_2Al\,OH$.

Characterisation of aluminas

XRD. The XRD data obtained on samples calcined for 5 h at temperatures ranging from 110 to 870°C are presented in Figures 1 and 2. Basic aluminium succinate calcined at 870°C gave 100% γ-alumina conforming to the ASTM standards (ASTM, X-ray data file No. 10-425). The crystallinity of the γ-alumina phase increased as the calcination temperature was raised from 400 to 870°C. It is significant that 100% γ-alumina phase exists at a temperature as high as 870°C. Aluminium hydroxide prepared by the PFHS method in the absence of succinic acid and dried at 110°C for about 24 h exhibited a bayerite phase. Calcination at 300°C for 5 h yielded γ-alumina with very good crystallization which was further improved at 500°C. Increasing the calcination temperature to 870°C yielded θ-alumina containing



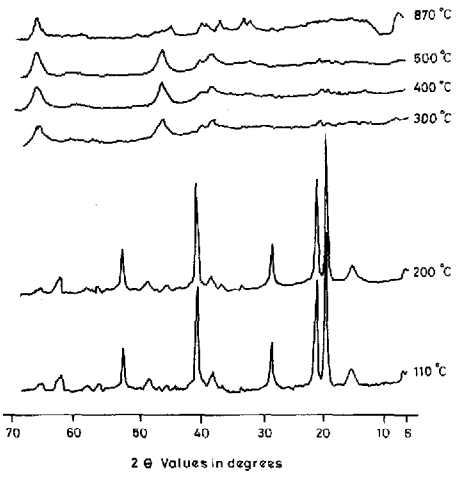


FIGURE 1 XRD patterns of aluminas prepared by the PFHS method in the presence of succinic acid and calcined at the temperatures indicated.

FIGURE 2 XRD patterns of aluminas prepared by the PFHS method in the absence of succinic acid and calcined at the temperatures indicated.

γ-alumina. From these results, γ-alumina prepared from basic aluminium succinate appears to be thermally more stable compared to that prepared from bayerite.

SEM. Micrographs of the aluminas are shown in Figure 3. γ-Alumina obtained from basic aluminium succinate is microspheroidal and evenly grained. However, γ-alumina obtained from bayerite is irregularly shaped, in agreement with the results reported by Inui et al. [22].

Surface area, pore volume, mean pore radius and crystallite sizes

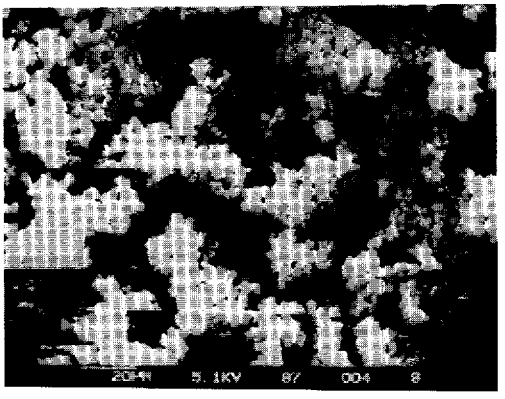
The effect of the calcination temperature on BET surface area, pore volume, mean pore radius and crystallite size is summarized in Table 1. The results obtained with Harshaw alumina (Al-111-61E) are included for comparison (C). Aluminas prepared from basic aluminium succinate (B) show higher surface areas compared to those from bayerite (A). While the pore volumes of aluminas B and C are similar (about 0.66 cc g^{-1}), those of alumina A are very low (about 0.26 cc g^{-1}). This shows that the pore volume of aluminas is profoundly affected by the method of preparation of the precursor. The mean pore radius of all the samples increased with increasing calcination temperature. The crystallite size of aluminas prepared from basic aluminium succinate is somewhat lower than those for the other two aluminas.

TABLE 1

Surface area, pore volume, mean pore radius, crystallite size, acidity and acid strength distribution of aluminas.

S. No.	Catalyst	Calcination temperature /°C	Surface area (BET) /m^2 g^{-1}	Total pore volume /cc g^{-1}	Mean pore radius /Å	Crystallite size /Å	Acidity mmoles/g		
							w.r.t neutral red	w.r.t. butter yellow	Total
1	A	300	274	0.27	18	-	0.199	-	0.370
2	A	400	257	0.28	22	-	0.270	0.060	0.450
3	A	500	171	0.28	33	-	0.370	0.094	0.539
4	A	600	137	0.25	36	-	0.390	0.156	0.557
5	A	700	115	0.26	45	98	0.380	0.126	0.528
6	A	800	106	0.27	50	103	0.300	0.104	0.450
7	A	870	77	0.32	83	-	0.246	0.071	0.397
8	B	300	135	0.19	27	-	-	-	-
9	B	400	348	0.31	28	-	-	-	-
10	B	500	254	0.40	31	-	-	-	-
11	B	600	244	0.60	49	-	0.407	0.116	0.529
12	B	700	205	0.60	59	78	0.378	0.108	0.500
13	B	800	151	0.66	86	79	0.298	0.076	0.405
14	B	870	109	0.75	138	89	0.232	0.057	0.382
15	C	300	224	0.52	46	-	0.089	-	0.329
16	C	400	205	0.56	55	-	0.259	0.049	0.400
17	C	500	200	0.57	56	-	0.397	0.100	0.460
18	C	600	176	0.61	69	-	0.438	0.150	0.500
19	C	700	158	0.62	78	99	0.450	0.159	0.520
20	C	800	138	0.62	90	114	0.350	0.115	0.449
21	C	870	119	0.62	104	114	0.269	0.076	0.385

(i)



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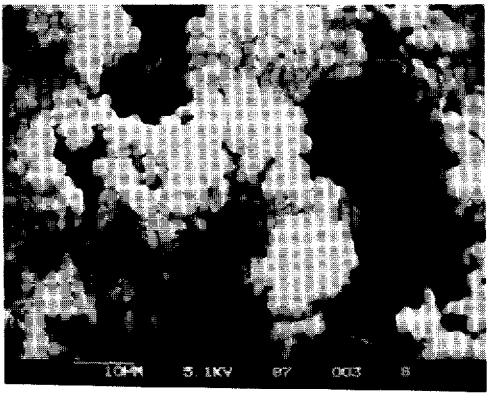

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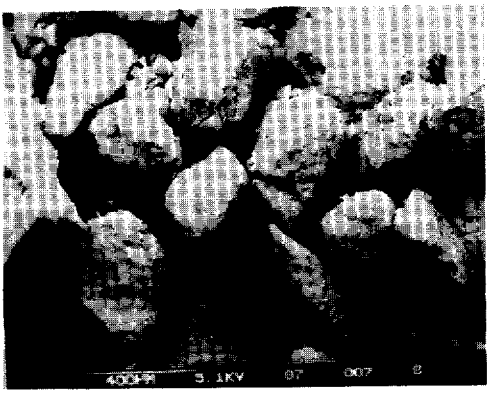

FIGURE 3 Scanning electron micrographs of aluminas obtained by the PFHS method: (i) γ-alumina prepared by calcination of basic aluminium succinate at 870°C. (ii) γ-alumina prepared by calcination of basic aluminium succinate at 700°C, (iii) γ-alumina prepared by calcination of bayerite at 700°C.

Acidity

The acidities of the aluminas are also presented in Table 1. There was no response to indicators having pka values less than + 3.3, showing that strongly acidic sites are not present on the surface of these aluminas. The acidity of aluminas of series B calcined at ≤ 500°C could not be determined as these aluminas were light brown in colour (at the calcination conditions employed) believed to be due to traces of carbonaceous matter arising from basic aluminium succinate. The total acidity and acid strength distribution of the three aluminas are comparable. Being weak acids, these aluminas should be capable of dehydrating alcohols, since alcohols are stronger bases than olefins and therefore are more easily protonated. Pines and Haag [23] have shown that aluminas having many weak acidic sites are excellent dehydration catalysts for 1-butanol.

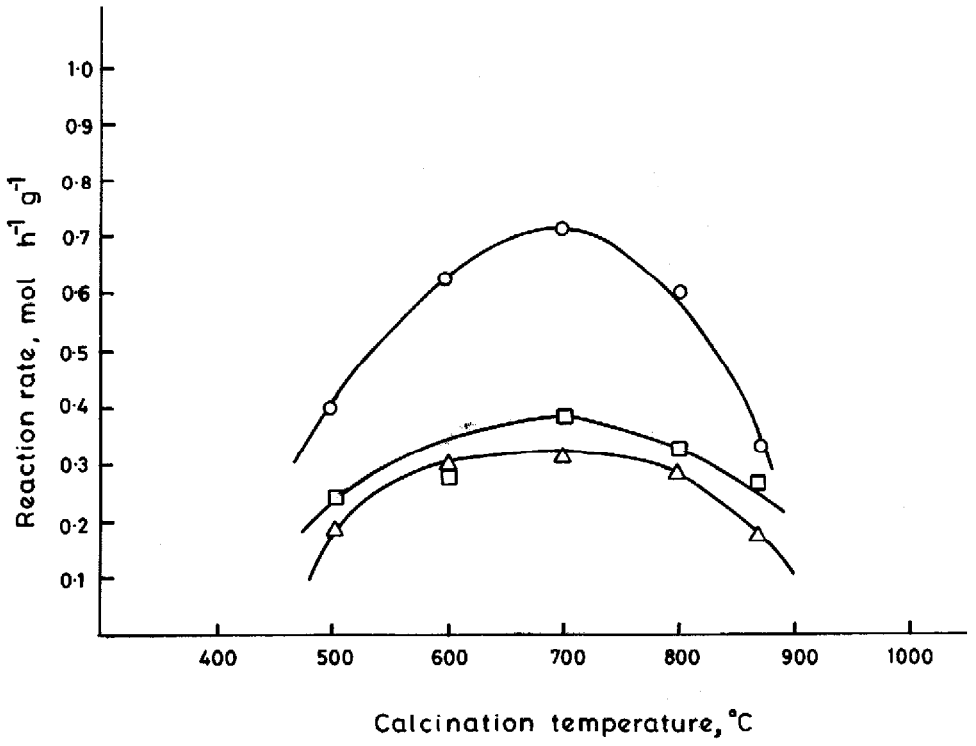

FIGURE 4 Effect of calcination temperature on the dehydration of ethanol. Reaction temperature = 300°C. ○ - Alumina prepared from basic aluminium succinate, △ - Alumina prepared from bayerite, □ - Harshaw alumina (Al-111-61E), respectively.

Dehydration activity

The effect of calcination temperature on the activity of the aluminas expressed in terms of the initial rates is shown in Figure 4. For all the aluminas, the rate

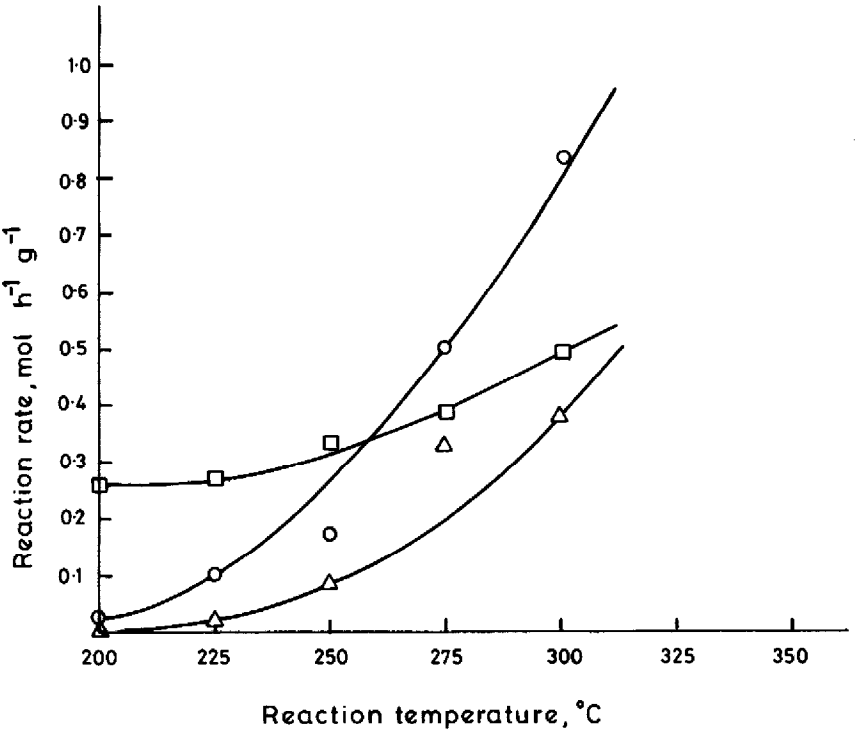

FIGURE 5 Effect of reaction temperature on the dehydration of ethanol. Activation temperature of aluminas = 700°C. ○ - Alumina prepared from basic aluminium succinate, △ - Alumina prepared from bayerite, □ - Harshaw alumina (Al-111-61E), respectively.

of dehydration of ethanol increases with increasing calcination temperature, reaches a maximum of 700°C and then decreases with further increase in calcination temperature to 870°C. However, the alumina prepared from basic aluminium succinate shows a higher activity compared to the other two series of catalysts. The rate of dehydration as a function of reaction temperature is shown in Figure 5 for the three catalysts calcined at 700°C. These aluminas showed increased activity with increasing reaction temperature and the increase is more pronounced with catalyst B and least pronounced with catalyst C; catalyst B exhibited greater activity at reaction temperatures above 275°C compared to the other two catalysts. The selectivity for diethyl ether and ethylene as a function of reaction temperature is represented in Figure 6. As the reaction temperature increases from 200 to 300°C, the selectivity for diethyl ether decreases and that for ethylene increases with all the three catalysts studied, while small differences in selectivity exist. However, when the reactor was operated under integral conditions taking sufficient (2 g) catalyst it was observed that the extent of conversion of ethanol was over 90% at a reaction temperature of 350°C with aluminas B and C. Under these

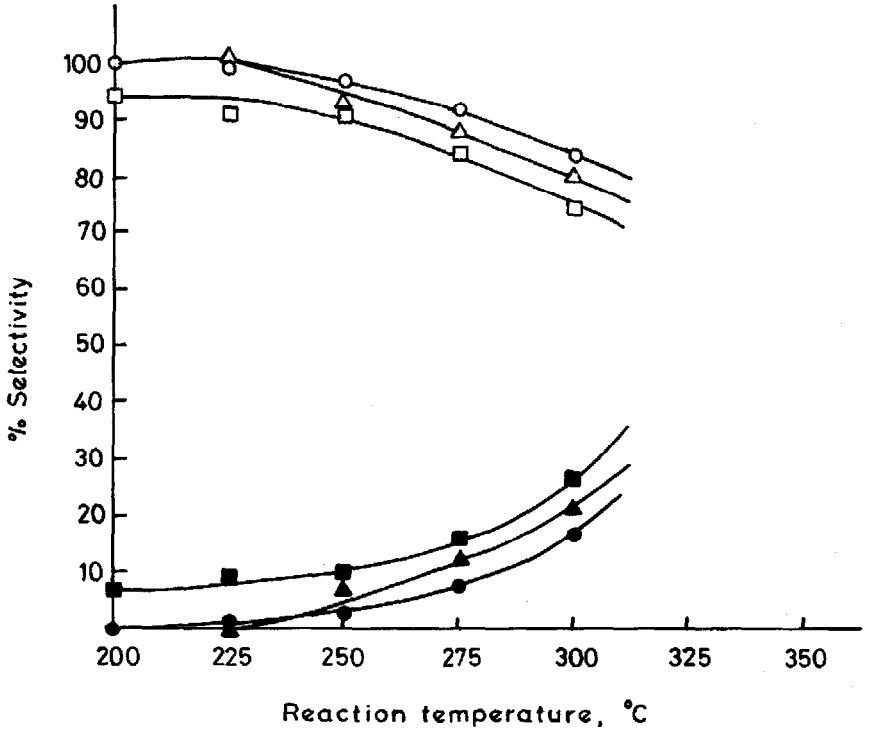

FIGURE 6 Effect of reaction temperature on product distribution. Activation temperature of aluminas = 700°C. ○ ● - Alumina prepared from basic aluminium succinate, △ ▲ - Alumina prepared from bayerite, □ ■ - Harshaw alumina (Al-111-61E), respectively. Empty and filled symbols represent diethyl ether and ethylene respectively.

conditions the products were essentially ethylene with very small amounts of diethyl ether.

It appears that there is a definite dependence of the activity of aluminas on the calcination temperature, maximum activity being shown at 700°C, and a similar relationship was reported by Cremer [24] who also found a maximum in the activity at 700°C. The acidities of the catalysts also show maximum values at calcination temperatures of 600-700°C. It can be concluded that active aluminas prepared by the PFHS method are good dehydration catalysts, comparable with Harshaw commercial alumina catalyst.

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