THERMAL ANALYSIS OF ALUMINA PRECURSORS PREPARED BY 'PFHS' METHODS

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Thermal analysis of alumina precursors prepared by two different PFHS (precipitation from homogeneous solution) methods and a conventional method is described. All three precursors exhibit distinct thermal behaviour patterns, marked by multiple phase transformations, to yield γ-Al$_2$O$_3$ ultimately. Thermal analysis studies, coupled with XRD, IR and elemental analysis data, indicate that the precursors obtained by the PFHS methods are monophasic in nature, and hence yield relatively small, uniform microspheroidal alumina in comparison with the alumina obtained by the conventional method.

Preparation of alumina with desired structural, textural, physical and chemical characteristics for catalyst supports can be achieved by carefully controlling the preparation procedure. Generally, the preparation involves the precipitation of hydrated alumina as precursors from salts of aluminium under well-defined conditions and the calcination of these to yield various transition aluminas. The properties of the precursors and their calcination procedures largely determine the characteristics of the final alumina samples. Depending on the precipitation conditions, one can attain single phases or a mixture of the following hydrated alumina phases as precursors, with varying degrees of crystallinity, crystallite size and morphology [1]: gibbsite, bayerite, boehmite, diaspore and nordstrandite. PFHS (precipitation from homogeneous solution) methods of preparation are known to give coarse and easily filterable precipitates with uniform and finer crystallites and, since the precipitation conditions are uniform throughout the solution, a monophasic alumina precursor can be obtained [2].

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Table 1 Designations of alumina precursors and alumina samples

Designation	Method of preparation	Preheating temperature, K	Sample
EA–373	Neutralization of sodium	373	Precursor
EA–673	aluminate by ethyl acetate hydrolysis.	673	Alumina
SA–373	Precipitation of alumina	373	Precursor
SA–773	precursor from a solution of aluminium nitrate and succinic acid by urea hydrolysis.	773	Alumina
NA–373	Neutralization of sodium	373	Precursor
NA–723	aluminate with nitric acid	723	Alumina

In our studies [3] on the preparation of alumina and its role as a support for nickel (hydrogenation) and cobalt-molybdenum (hydrodesulphurization) catalysts, we attempted two methods of PFHS, namely a) neutralization of sodium aluminate by ethyl acetate (EA) hydrolysis and b) precipitation of an alumina precursor from aluminium nitrate by urea hydrolysis in the presence of succinic acid (SA), together with a conventional method, i.e. neutralization of sodium aluminate with nitric acid (NA), to obtain the alumina precursors. Since the characteristics of the aluminas derived from these precursors are also dependent on the nature of the thermal treatment during calcination, a detailed analysis of their thermal behaviour has been carried out in conjunction with other analyse, such as XRD, IR, SEM and elemental analysis. The features of the thermal analysis studies are reported in this paper.

Experimental

Detailed methods describing all the conditions of precipitation of the precursors have been presented elsewhere [3]. However, a brief summary of the preparation method, the designation of the samples and the calcinations are given in Table 1. All chemicals used in the preparation were of 'AnalaR' grade or equivalent. The precursors were filtered, thoroughly washed and dried at 373 K for 24 hours before being subjected to thermal analysis in a static atmosphere of air in the range 300–1223 K using Stanton and Redcroft DTA and TGA instruments (Model 673–4). A heating rate of 10 deg/min was used.

Results and discussions

Alumina precursors differ widely in their crystal structure, degree of hydration and crystallinity, and hence in their thermal behaviour [4]. Mutual transformations between the precursor phases can also occur under favourable conditions. Depending on their nature and temperature of pretreatment, the precursors yield a variety of transition aluminas. The thermal curves of the precursors serve as their fingerprints, revealing in detail all information regarding the above features.

The DTA and TG curves for the three precursors, EA–373, SA–373 and NA–373, are shown in Figs 1 and 2. The characteristics of the precursors as determined by the other techniques, such as XRD, IR and elemental analysis, are presented in Table 2. The DTA profile of EA–373 (Fig. 1, curve A) shows the presence of two endothermic peaks, at 393 K and 563 K. The second peak is asymmetric in shape, with an unclear shoulder at 483 K. The presence of a dehydration peak at 563 K indicates that EA–373 is aluminium trihydroxide, i.e. bayerite. The observed peak temperature (563 K) is close to that reported in the dehydration of bayerite [5]; XRD and IR analyses of EA–373 confirm [6] that it is only bayerite. On dehydration, bayerite might yield η-alumina directly, or γ-alumina via boehmite, depending on the conditions of dehydration and its physical nature (i.e. crystallite size). The formation of a boehmite phase requires hydrothermal conditions [7–10] during dehydration, which is possible at high heating rates (10 deg/min) and when the crystallite size is large. Of the two trihydroxides, bayerite and gibbsite, conversion to boehmite during dehydration is
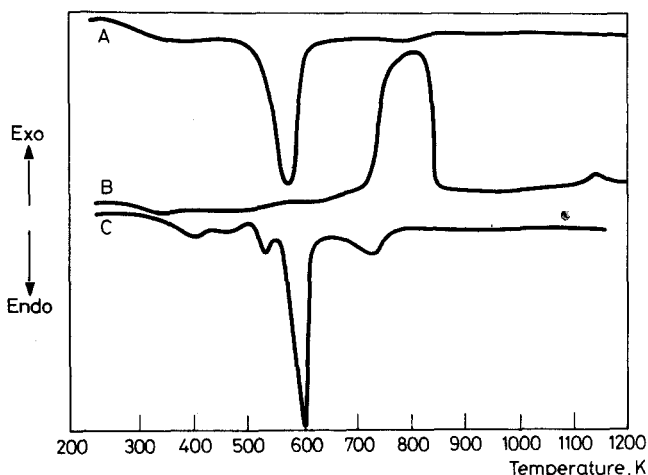

Fig. 1 DTA curves for alumina precursors. A) EA–373, B) SA–373, C) NA–373
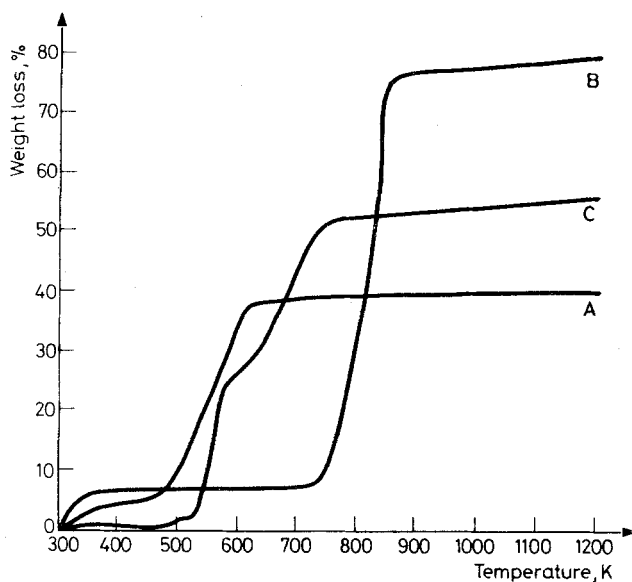
Fig. 2 TG curves for alumina precursors. A) EA–373, B) SA–373, C) NA–373

maximum (25%) with the latter, and is usually less (5%) with the former [10], since bayerite is generally obtained as fine crystallites.

In the present case, the shoulder at 434 K corresponds to the formation of boehmite [11, 12] and a small broad peak centres around 723 K is due to the dehydration of boehmite to γ-Al$_2$O$_3$. It appears that a heating rate of 10 deg/min is high enough for the partial conversion of bayerite to boehmite.

In order to substantiate this point, thermal curves of EA–373 were obtained by heating it at a rate of 1 deg/min up to 463 K, followed by isothermal heating for 1 hour at the same temperature and further programming up to 773 K. The DTA curve reveals the complete prevention of the phase transformation from bayerite to boehmite at the low heating rate of 1 deg/min, and a single peak corresponding to the dehydration of bayerite to η-alumina is observed. In the absence of the transformation to boehmite, the corresponding dehydration peak at 723 K is also absent. The TG curve for EA–373 (Fig. 2, curve A) shows a continuous weight loss of 32.4% between 463 and 610 K, and a further loss of 2.2% from 610 to 1073 K. The observed weight loss is equal to the theoretical weight loss for any pure aluminium trihydroxide conversion to alumina. Thus, DTA and TG analyses clearly show that EA–373 is a pure bayerite phase, and mainly yield η-alumina, with a very small amount of γ-alumina, originating from the boehmite phase formed during the calcination of bayerite. This observation has been confirmed by XRD analysis of EA–373 after calcination at 673 K [6].

Table 2 Characteristics of alumina precursors

No.	Characteristics	Alumina precursors		
		EA–373	SA–373	NA–373
1	Phase composition (by XRD)	100% bayerite	100% basic aluminium succinate	9.5% bayerite[a] 34.0% pseudo-boehmite 44.7% crystalline boehmite
2	Crystallite size, nm (by XLBA)[b]	17.1	6.8	14.1[c]
3	Infrared spectroscopy	bands at 3650, 3533, 3455, 1025 and 975 cm^{-1} corresponding to bayerite	characteristic bands of succinate ion at 1595 and 1400 cm^{-1}	bands at 3280, 3080, 1150 and 1070 cm^{-1} corresponding to boehmite
4	Elemental analysis, wt%			
	Aluminium	34.5	16.9	38.7
	Carbon	—	30.0	38.7
	Hydrogen	3.96	3.13	3.0
	Sodium (ppm)	60	205	85
	Potassium (ppm)	53	147	121

[a] Based on XRD and TG results.
[b] X-ray line broadening analysis.
[c] Average crystallite size (pseudo- and crystalline boehmites).

DTA of SA–373 (Fig. 1, curve B) exhibits an intense and broad exothermic peak around 813 K; the corresponding weight loss (between 730 and 850), as observed by TG, is 68.1% (Fig. 2, curve B). The exothermic nature of the decomposition rules out the presence of aluminium hydroxides in SA–373. Elementary analysis and infrared spectroscopic evidence of the succinate ion indicate the possible presence of free succinic acid. However, the presence of free acid is most unlikely, since neither DTA nor TG provides any evidence for its melting or decomposition. Willard and Tang [13] observed the formation of a dense precipitate of basic aluminium succinate during the preparation of alumina by a PFHS technique using urea hydrolysis. Detailed characterization of SA–373 [6] by XRD, IR, SEM and elemental analysis has shown it to be basic aluminium succinate $Al(OH)(C_4H_4O_4)$. Weight loss measurements (68.1%) are also in accordance with the above formula. Therefore, it can be stated that the exothermic peak at 813 K is due to the decomposition of basic aluminium succinate to alumina. The decomposition is
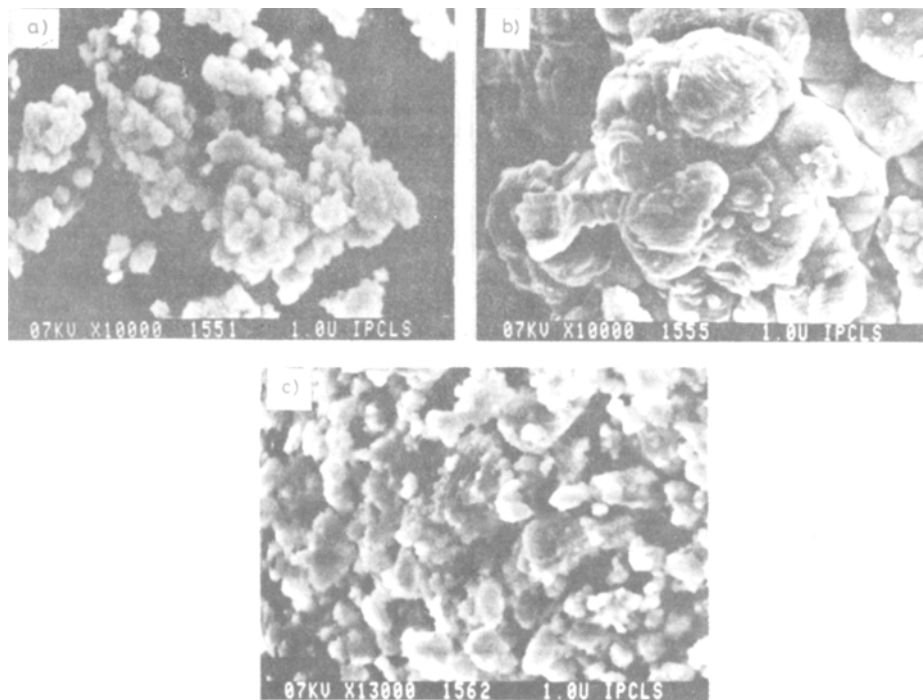
Fig. 3 Scanning electron micro-photographs of A) EA–673, B) SA–773, C) NA–723

basically endothermic, as expected, but one of the products of decomposition (CO) is oxidized in ambient air, this being a largely exothermic reaction, and thus endothermic decomposition peak is masked and a resultant exothermic peak emerges. In general, basic salts of organic acids (formates, acetates) decompose exothermally [14, 15].

The DTA profile of NA–373 (Fig. 1, curve C) exhibits three endothermic maxima, at 507, 570 and 731 K, besides a low-temperature endothermic peak at 410 K, due to the evolution of adsorbed water. From the TG curve, the corresponding weight losses are calculated to be 3.3%, 20.2% and 26.9%, respectively, for the three maxima. This thermal behaviour indicates the presence of at least three different precursor phases. The first peak is due to the dehydration of a trihydroxide, mostly bayerite; from weight loss measurements, the bayerite content in NA–373 is calculated to be 9.5% by weight. The second endothermic peak, at 570 K can be considered to be due to the dehydration of pseudo-boehmite to γ-Al_2O_3. As pseudo-boehmite always contains water in excess of that required by stoichiometry, the calculation of the amount of pseudo- (gelatinous) boehmite from

weight loss measurements could be erroneous. The third endothermic peak, at 731 K, should be due to the dehydration of crystalline boehmite to γ-Al_2O_3. From the weight loss measurements, the amount of crystalline boehmite is calculated to be 44.7%. Hence, by material balance, NA–373 should contain 45.8% gelatinous boehmite and water. The individual weight percentages of pseudo-boehmite and water are then calculated by utilizing the elemental analysis data on the precursor, and the values are 34% (gelatinous boehmite) and 11.8% (water).

The XRD pattern of NA–373 gives lines due only to the boehmite phase. Due to its very low concentration, the presence of bayerite is not revealed. The presence of sharp d lines with a broad base in the diffractogram are indicative of a size distribution and a gelatinous boehmite phase. Thus, NA–373 is a mixture of three different phases of alumina precursors: bayerite, gelatinous boehmite and crystalline boehmite. SEM photographs (Fig. 3) of the precursors after calcination indicate that the aluminas obtained by the PFHS methods are microspheroidal, while the conventional method yields irregularly-shaped particles.

Conclusion

The studies described above have established the distinct advantages of using PFHS methods for the preparation of alumina. Well-defined monophasic pure precursors with a narrow size distribution result from the PFHS methods. While the EA method yield only a bayerite phase, the SA method gives rise to a unique salt, basic aluminium succinate, with a very small average crystallite size. The conventional NA method yield a mixture of phases. Thermal methods of analysis have proven to be extremely valuable in the analysis of such complex phases and mutual phase transformations, and explicitly demonstrate the dependence of the routes of transformations on the experimental conditions.

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Zusammenfassung — Die Thermoanalyse von Aluminiumoxidpräkursoren, hergestellt durch zwei verschiedene PFHS (Precipitation From Homogeneous Solution) und eine herkömmliche Methode, wurde beschrieben. Alle drei Präkursoren zeigen ausgeprägte thermische Verhaltensformen, gekennzeichnet durch Mehrfachphasenübergange zur letztendlichen Bildung von γ-Al$_2$O$_3$. Die Thermoanalysen, verbunden mit Röntgendiffraktions-, Infrarot- und Elementaranalysen zeigen, dass die durch PFHS-Methoden erhaltenen Präkursoren über Einphasen verfügen und verglichen zu herkömmlich hergestelltem Aluminiumoxid relativ kleines, einheitliches Kugelaluminiumoxid liefern.

Резюме — Проведен термический анализ «прекурсоров» окиси алюминия, полученных двумя разными методами осаждения из гомогенного раствора, а также обычным методом. Все три «прекурсора» показывают различное термическое поведение, характеризующиеся многофазным превращением и заканчивающееся в конечном счете образованием γ-Al$_2$O$_3$. Термический анализ, сопряженный с рентгенофазовым анализом, а также ИК спектроскопия и элементный анализ показали, что «прекурсоры», полученные осаждением из гомогенного раствора, являются однофазными по природе и выход при этом однородного микросферического глинозема относительно меньше по сравнению с окисью алюминия, полученного обычным методом.