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Studies of physicochemical and surface properties of alumina modified with rare earth oxides.
II. Porous structure

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Results are presented of investigations of the porous structure of the Al_2O_3–La_2O_3 systems containing up to 10 wt% of the La modifying oxide prepared by the coprecipitation method. Pore size distribution was determined on the basis of low temperature nitrogen adsorption measurements and mercury intrusion porosimetry. The changes in pore size distribution of different forms of Al_2O_3–La_2O_3 are discussed in relation to the concentration of the lanthanum oxide.

Keywords: Al_2O_3–La_2O_3; porous structure

1. Introduction

The porous structure of a catalyst or catalyst support is one of the most important factors governing its catalytic activity. Thus, the pore size distribution determines the availability of active centers and also the transport of the reactant and product molecules to and from the active surface. Any problems resulting from these particular properties can be satisfactorily resolved using a transition alumina or its modified form as a catalyst carrier [1].

The modification of transition aluminas boils down to a formation of new forms of chemically defined structures with different chemical properties on the one hand, and particular porous structures on the other hand. The porous structure of alumina is controlled through the nature of the hydroxide content which is determined through the aging and calcination processes [2,3]. An increase in the calcination temperature, however, usually leads to undesirable changes both in the physico-chemical and textural properties [4].

A cause of the deactivation of exhaust gas catalysts is the clogging of the porous structure by traces of lead, phosphorus and zinc which are contained in the exhaust gases [5]. One way of dealing with this problem is to use double-porosity (known as bimodality) alumina. Micropores of diameter less than 2 Å are the starting point used to develop specific surface area, and macropores of diameter more than 10 Å to assist the mass transport of reagents within the particles.

Attempts to eliminate undesirable properties of transition aluminas by addition of an alien oxide have been made [6–16]. In a previous paper [15] we described the effects of the preparation method, nature and amount of some lanthanide oxides (e.g. La, Ce, Pr, Nd or Sm added to alumina) on the structure and thermal stability of the resultant modified aluminas. It has been found that the addition of a lanthanide oxide to Al_2O_3 retards the transformation (through sintering) of γ-Al_2O_3 to α-Al_2O_3. The presence of a perovskite-type structure of lanthanide aluminate could be responsible for the thermal stabilization of such transition aluminas [15,17,18].

In the case of boehmite-derived alumina, almost independent control of microporosity, surface area, pore distribution, and pore volume can be attained, through the size, morphology, and packing of the oxyhydroxide crystallites [2].

High surface area and close pore size distribution depend on the ability to create and maintain respectively, small and monodispersed crystallites. This may be achieved by controlling the nucleation and crystallization processes, which two processes are readily controlled by the introduced admixture. Another problem in the case of alumina derived supports is their textural stability at higher temperatures. One of the most interesting stabilization methods is achieved through the addition of a small amount of an alien oxide, such as a rare earth metal oxides.

The aim of the current paper was an investigation of the changes in the porous structure of γ-Al_2O_3 induced through the method of preparation, and also through variations in the concentration of the introduced lanthanum oxide. This type of investigation is important in the application of modified aluminas in the transformation of ecologically sensitive compounds such as chlorofluorocarbons. Unpublished results to date show the importance of pore size and the nature of surface OH groups on the conversion activity of this type of catalyst [19].

2. Experimental

2.1. PREPARATION

The method of preparation of the Al_2O_3–La_2O_3 systems was described in detail in a previous paper (part I) [15]. Briefly, the binary composition Al_2O_3–La_2O_3 containing up to 10 wt% of lanthanum oxide was synthesized by coprecipitation methods. The chemical composition and the symbols as well as temperatures of calcination of the samples subjected to the textural analysis are given in table 1. The annealing process was carried out in air for 6 h at a temperature of 800°C. All samples were ground in a mortar before the annealing and sieved to collect the 0.1–0.3 mm fraction.

2.2. DETERMINATION OF THE PORE SIZE DISTRIBUTION

Low temperature (77 K) nitrogen adsorption measurements were carried out using a Sartorius micro-balance (Gravimat type 4133). Samples were outgassed under vacuum (1.33×10^{-4} Pa at 723 K) until a constant weight was reached, after which adsorption measurements were made. Nitrogen adsorption and desorption were carried out in the relative pressure range $p/p_0 = 0$–1. The micropore size distribution in the diameter range from 10 to 300 Å, was calculated using the Creanston-Inkley method [20]. The calculations, based on the desorption branch of the sorption isotherm were carried out on an IBM computer using a specially elaborated routine. Data on cumulative pore volume V_{cum}, cumulative pore surface area S_{cum}, mean pore radius r_{av}, was obtained and plots of pore volume distribution as a function of the pore diameter developed.

Measurements based on the Ritter–Drake method [21] were carried out on a mercury porosimeter AG-65a made by Carlo Erba to determine the pore size distribution in the diameter range 20–37500 Å. The apparatus recorded the mass of mercury forced into the pores as a function of the applied pressure. The reproducibility of the low temperature nitrogen adsorption and mercury porosimetry experiments was checked by repeating measurements for pure and modified alumina (N-La-10-800) at least three times. The standard deviation of V_{cum} was approximately 3–5% of the measured values.

3. Results and discussion

Based on the DTA and XRD [15] measurements, the transition forms of alumina were found to contain $LaAlO_3$ having the perovskite-type structure. Generally,

Table 1
Analysis of nitrogen data: cumulative pore volume (V_{cum}), cumulative pore surface area (S_{cum}), specific surface area (S_{BET}), and mean statistical pore radius (r_{av}) as well as symbols of samples

Sample	Conc. La_2O_3 (wt%)	V_{cum} ($\mathrm{cm^3\,g^{-1}\,10^{-1}}$)	S_{cum} ($\mathrm{m^2\,g^{-1}}$)	S_{BET} ($\mathrm{m^2\,g^{-1}}$)	r_{av} (Å)
N-500	0	4.0	285.5	275.5	28.1
N-800	0	2.1	125.7	133.7	34.0
N-La-1-800	1.0	3.3	137.7	148.1	48.5
N-La-4-800	4.0	3.1	139.3	145.3	44.3
N-La-5-800	5.0	3.7	166.9	160.7	44.0
N-La-10-800	10.0	3.7	202.9	195.8	36.7

the addition of La_2O_3 delays the phase transformation of γ to α alumina and leads to greater resistance of the specific surface area to the thermal treatment. The manner of incorporating lanthanum into the matrix of alumina (coprecipitation or impregnation) was found to affect the surface area of the final sample [15]. It should be added, that in this investigation a better condition for the standardization of samples was developed, leading to a greater reproducibility of the determination of the surface area in comparison to those reported in the preliminary investigations [15].

The present paper comprises a continuation of the studies of the Al_2O_3–La_2O_3 systems obtained via coprecipitation of both components within a wide range of concentration of the introduced lanthanum admixture. The contribution of both components is given in table 1.

Nitrogen adsorption measurements show a change in the porous structure of the γ-Al_2O_3 resulting from the amount of the lanthanum introduced. The extent of the changes observed was significantly affected by the concentration of the second component. The nature of the various adsorption–desorption isotherms obtained is illustrated in figs. 1a and 2a. Pure γ-Al_2O_3 calcinated at temperature of 500°C shows characteristic features of the type IV isotherm (IUPAC nomenclature [22]), which is in agreement with the literature data [23]. Calcination of pure alumina at a temperature of 800°C leads to another type of isotherm shape namely type II, which is characteristic of non-porous or macroporous material. The shapes of isotherms of samples with a lanthanum component, depend on the concentration of the admixture. Small amounts of La_2O_3 (1 wt%) do not change the characteristic

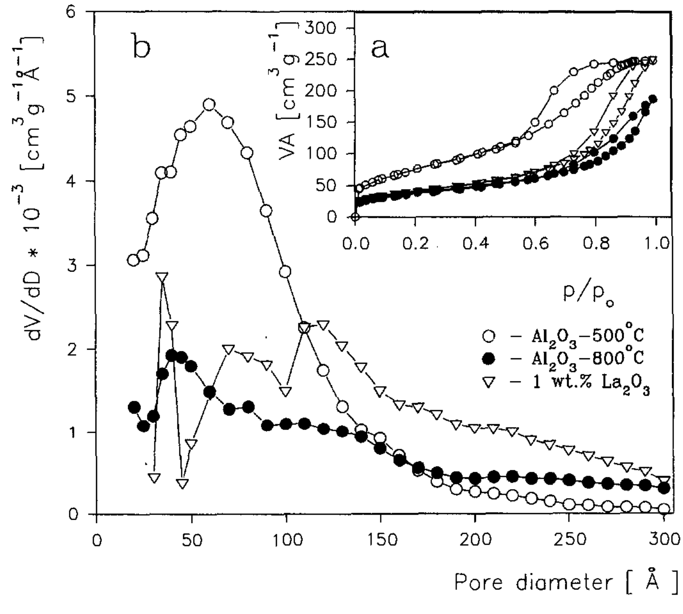

Fig. 1. (a) Nitrogen adsorption–desorption isotherms, (b) pore volume distribution.

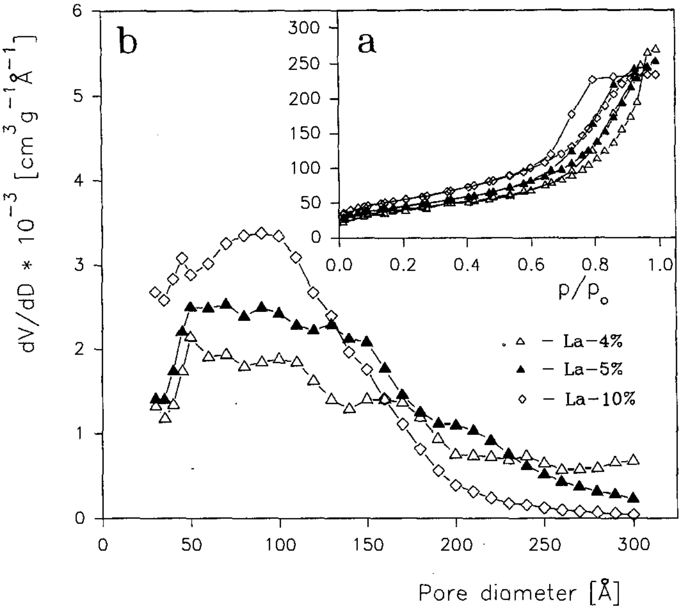

Fig. 2. (a) Nitrogen adsorption–desorption isotherms, (b) pore volume distribution.

features of the type II isotherm, however, in the end section of this isotherm a visible change leading to a type IV isotherm was observed. This indicates that besides unrestricted monolayer adsorption capillary condensation takes place in the mesopores. These changes become more perceptible as the concentration of the lanthanum admixture increases, and in the case of the sample with the maximum concentration of La_2O_3 i.e. 10 wt%, the characteristic of the isotherm is very similar to that of alumina calcined at 800°C (see figs. 1a and 2a).

The total amount of nitrogen adsorbed by a sample of γ-Al_2O_3 calcined at a temperature of 800°C, is almost 50% lower in comparison to that of a sample calcined at a temperature of 500°C. A sample of La_2O_3/Al_2O_3 calcined at 800°C (even at the lowest La_2O_3 concentration, 1 wt%) maintains the amounts of adsorbed nitrogen as that for a sample of pure Al_2O_3 calcined at 500°C.

Comparing the behaviour of isotherms for samples of pure alumina calcined at 500 and 800°C, a shift of the shoulder point towards higher p/p_0 values (from $p/p_0 = 0.42$ to $p/p_0 = 0.67$) is noticeable as the temperature of calcination increases. This indicates the formation of large pores. The position of the shoulder point for the doped samples is remarkably stable at a level around $p/p_0 = 0.65$, regardless of the concentration of the introduced La_2O_3 admixture.

Changes in the quantitative relationship of the Al_2O_3/La_2O_3 system bring about changes in the shape of the hysteresis loop. Two quantitative divisions can be observed:

(1) Al_2O_3/La_2O_3 containing 1–5% La_2O_3 has a hysteresis loop shape H4 similar

to that for a high temperature calcined pure alumina matrix (IUPAC classification [22]). Such a system is associated with narrow slit-like pores.

(2) For Al_2O_3/La_2O_3 where the concentration of La_2O_3 is increased from 5 to 10%, transformation to a fully characterized loop shape H2 is observed, corresponding to that of a low temperature (500°C) calcined alumina. Such a system is described as having pores of "ink bottle" type and is more resistant to thermal sintering. At this stage of the work, we cannot exclude a connection between the presence of an H2 type hysteresis loop, and presence of La_2O_3 in $LaAlO_3$ form or as a separate La_2O_3 phase.

The higher temperature calcinated alumina results in changes to the behaviour of the pore volume distribution curve (fig. 1b). Thus, alumina calcined at a low temperature (500°C), has a monodispese distribution with the major volume of the pores being provided by pores of diameter less than 150 Å. In the case of alumina calcined at 800°C, this monodisperse distribution cannot be clearly distinguished from the broad distribution observed. A similar phenomenon of diminishing the contribution to the total volume from pores of diameter <50 Å, and a corresponding increase to the total volume from pores of greater diameter has been reported by Chookin and Seleznev [2]. They attributed this phenomenon to the appearance of secondary pores ($d>50$ Å) replacing most of the primary (original) pores ($d<50$ Å).

A small amount of lanthanum oxide brings about the appearance of three clearly distinguished maxima on the distribution curve (fig. 1b). Our proposed interpretation is that the first maximum reflects the presence of original pores falling in the diameter range less than 50 Å which occurs in the low temperature form of alumina. These pores remain, even with an increase in the temperature of calcination because of the thermostabilizing effect of the added lanthanide. The introduced admixture must, however, significantly affect the formation of secondary pores as seen by the two maxima (75 and 125 Å) on the pore volume distribution curve.

With increasing concentration of the La admixture introduced into the alumina matrix, a significant shift towards pores of greater diameter occurs, resulting in the two initially clearly distinguishable maxima (sample N-La-1, fig. 1b.), eventually fusing into a single broad band having a shape similar to that of the low temperature calcined alumina (fig. 2b.).

To better illustrate the effect of changes of the porous structure, it is seen in fig. 3 that the contribution of pores of a given diameter range to the total volume (V_{cum}) depends on the temperature of calcination of alumina as well as on the concentration of lanthanum in the admixture.

The effect of the calcination temperature (500–800°C) on pure γ-alumina is to cause a twofold decrease in the contribution to the total pore volume due to pores in the 20–50 and 50–100 Å range. At the same time no change is observed in the contribution to the total pore volume from pores in the 100–300 Å range.

The effect of increasing the lanthanum content in γ-Al_2O_3 calcined at 800°C, (fig. 3), is to increase the contribution of pore diameters in the range 50–100 Å and

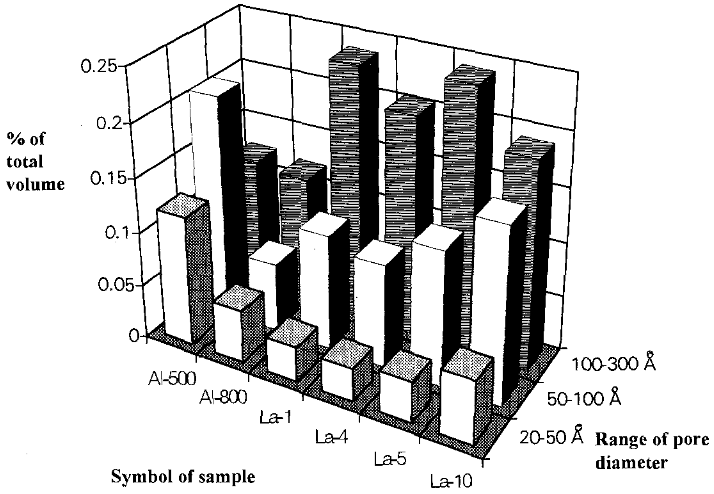

Fig. 3. Contribution of pores in diameter ranges 20–50, 50–100 and 100–300 Å to the total volume.

100–300 Å to the pore volume, while having little effect on the contribution of pore diameters 20–50 Å. This may mean that the introduced admixture does not affect the process of nucleation and crystallization.

The results of determination of the pore structure of samples obtained using the N_2 adsorption method were partially supplemented with the results of the determination of macroporosity (diameter range 20–37500 Å), obtained by means of the mercury porosimetry method. In the case of pure γ-Al_2O_3, using the mercury porosimetry method the presence of mesopores (polydispersive distribution) was confirmed, however, the maximum of the pore volume is shifted in a direction to higher values of the pore diameter in comparison to results obtained by N_2 adsorption. Introduction of a high concentration of lanthanum oxide leads to the disappearance of macropores above 300 Å.

An analysis of the data in table 1 shows that the mean pore diameter of γ-Al_2O_3, increases by 15 Å on the introduction of La_2O_3.

This average diameter then varies very little with increasing La content, despite the fact that the contributions of the various structural regions do change as noted above. The 10 wt% result, however, declines towards a lower average diameter, which is clearly due to the absence of a high concentration of macropores (fig. 2).

The observed variations may well be important from the point of view of using these systems as catalytic carrier supports.

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