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Catalysis Today 29 (1996) 427–431

CATALYSIS TODAY

Synthesis of a mechanically strong and thermally stable alumina support for catalysts used in combustion processes

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Abstract

It is shown that simultaneous modification of spherical alumina by bi- and three-valence cations (that are strengthening and thermally stabilizing additives, respectively) by a special method leads to the formation of supports with unique properties. These results are due to the specific interaction between the additives and alumina.

Keywords: Aluminium supports

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1. Introduction

The interest in high-temperature catalyst application, such as jet engines or gas turbines, has evolved in recent years. In this application, goal temperatures will be in the range of 1100–1400°C. It is evident that an important role in developing efficient and stable catalyst systems belongs to the support and its behavior at high temperature.

Previously, the authors proposed a new method of preparation of alumina with high mechanical strength [1]. We have also studied the conditions for the formation of thermally stable alumina support doped with lanthanum [2,3]. The understanding of the mechanism of strengthening upon Mg^{2+}-doping and phase stabilization upon La^{3+}-doping allows to suggest the special procedure of double modification of support with Mg and La cations for the preparation of alumina support with unique properties.

2. Experimental

Spherical alumina hydroxide ($d = 1.4$–2.0 mm) was prepared by method of hydrocarbon–ammonia moulding [4]. The initial reagent for the moulding procedure was aluminum hydroxide of pseudo-boehmite structure prepared according to Ref. [5]. The introduction of magnesium ions into spherical granules of aluminum hydroxide, with subsequent drying at 100°C and thermal treatment (at 550°C for 4 h) was carried out as described in Ref. [1]. The magnesium content in samples, 3.2 wt.-% MgO, was optimal for the preparation of the strongest support [1–3]. The resulting γ-alumina was further used as an initial material for lanthanum introduction.

The subsequent lanthanum introduction was performed by incipient impregnation with a lanthanum nitrate solution. Then the samples were

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SSDI 0920-5861(95)00315-0

dried in air at ambient temperature for 10 h and at 100°C for 4 h. The thermal treatment was carried out in air stream with a space velocity of 1000 h^{-1} at 550°C for 4 h. Sintering tests were carried out at 900–1400°C at different duration of calcination in order to study the stabilizing and strengthening effects of modifying elements on the phase transformation, surface area and mechanical strength.

X-ray analysis of the samples was carried out in a diffractometer HZG-4 with the copper radiation as in [1,7].

The mechanical crushing strength of the granules was determined as in [1].

3. Results and discussion

Table 1 presents the properties of spherical alumina after high temperature calcination, prepared via the special procedure, in comparison with earlier published data [1–3].

The dependence of mechanical strength of doped aluminas on the calcination temperature are shown in Fig. 1. The introduction of magnesium increases the mechanical strength of granules by a factor 1.5–2.0 in comparison with pure alumina. The introduction of the second cation–lanthanum results in the increase of mechanical strength at high temperatures (1200–1300°C). At the same time, introduction of lanthanum preserves thermal stability with additional increase of efficiency at high temperatures. In Fig. 2, surface areas of doped samples are presented relative to that of the undoped alumina as a function of the calcination temperature.

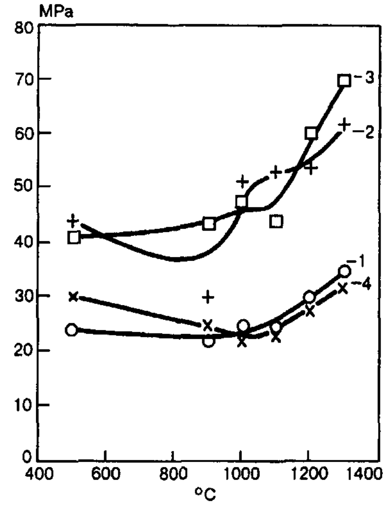

Fig. 1. The dependence of mechanical strength on the calcination temperature. The numbers of samples are same as in Table 1.

X-ray of the system Mg–La–Al_2O_3 has shown that the solid solution of Mg–La–γ-Al_2O_3 is formed with the introduction of Mg and La into alumina. The parameter of the cell

Table 1
The structural and mechanical properties of high temperature alumina supports

No.	Additives (wt.-%)	S_{BET} (m^2/g)	α-Al_2O_3 content (%)	Mechanical strength (average) (MPa)
1200°C				
1	–	8	100	28
2	3% MgO [1,2]	7	100	54
3	5% La_2O_3 [3]	29	15	35
4	12% La_2O_3 [3]	24	trace	34
5	3% MgO + 5% La_2O_3	23	15	65
6	3% MgO + 12% La_2O_3	27	trace	60
1300°C				
1	–	5	100	30
2	3% MgO	6	100	62
3	5% La_2O_3	8	100	44
4	12% La_2O_3	12	100	35
5	3% MgO + 5% La_2O_3	14	100	65
6	3% MgO + 12% La_2O_3	24	trace	70

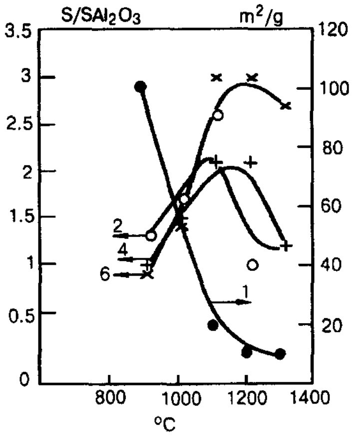

Fig. 2. Specific surface areas of the doped samples relative to that of alumina as a function of the calcination temperature. The numbers of samples are same as in Table 1.

was 7.942; at the same time the coefficient *B*, which is determined as the ratio of the heights of lines 311 and 222 in γ-Al_2O_3 structure and characterizes structural changes in a support, slightly increased to 1.90. This is probably due to the substitution of aluminum ions for lanthanum in the structure of the solid solution Mg–γ-Al_2O_3. This solid solution begins to decompose with the formation of α-Al_2O_3 and 2 $MgO \cdot La_2O_3 \cdot 11\,Al_2O_3$ (ASTM 26-873) under thermal treatment at 1200°C. Mixed solid solutions of magnesia and lanthania in γ-Al_2O_3 containing 10 and 12 wt.-% La_2O_3, respectively, completely decompose at 1400°C.

The observation that the thermal stability of double modified alumina (Mg–La–Al_2O_3) is higher than that of La_2O_3–Al_2O_3 system apparently can be adequately explained on the basis of the 'hydroxide model' of the structure of low-temperature alumina [7] and the analysis of the possible paths of the structural rearrangement of solid solutions upon thermal treatment [8]. According to this model, which was derived on the basis of the full-profile X-ray analysis of diffraction patterns, γ-Al_2O_3 has a protospinel structure, slightly different from the spinel one, and is assigned to compounds of the common formula:

$$C_{(x1)}A_{(x2)}[D_{(y1)}B_{(y2)}]O_{(32-z)}\{OH\}_{(z)}$$

where A and B are spinel tetrahedral and octahedral cation positions; C and D are 'protospinel' cation positions considered in respect to spinel structure as defects. These positions are

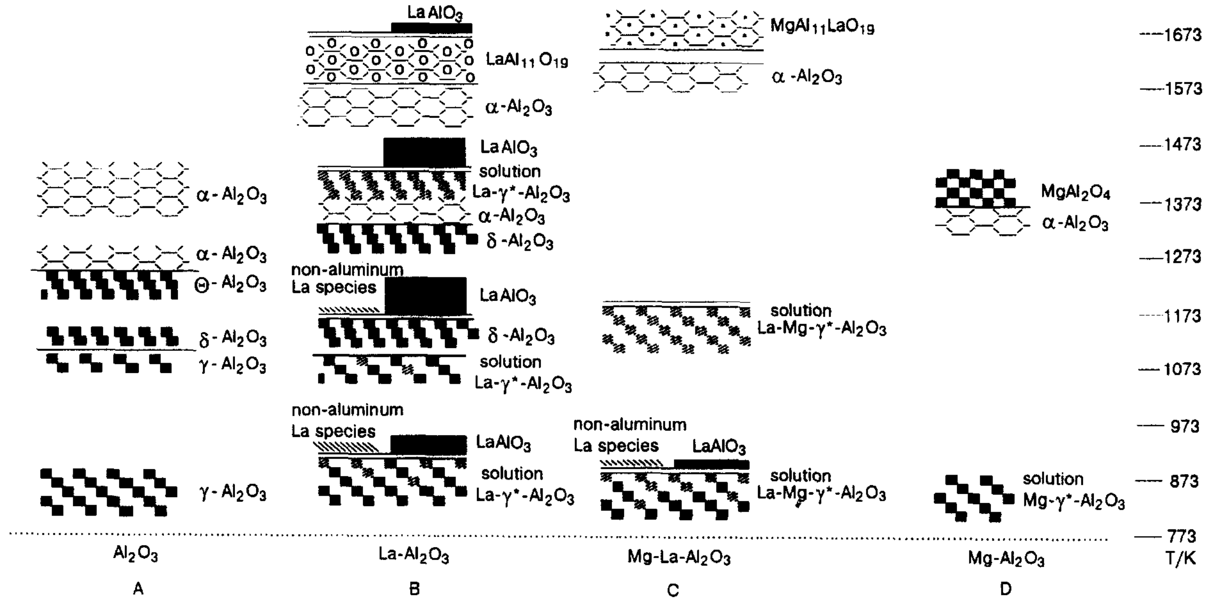

Fig. 3. Scheme of the changes of the structure and phase composition of aluminas doped with magnesium (ca. 3 wt.-%) and lanthanum (ca. 10 wt.-%) upon the increase of temperature.

present as an alternative set of cation positions in spinel structure.

Low-temperature solid solutions formed in γ-Al_2O_3 have principally a similar structure, differing only in the values of x, y, and z coefficients. As the temperature is raised, simultaneously with the resulting removal of OH groups and the perfection of cubic anionic framework, the process of the compact filling of cationic positions takes place. This process can occur in two principally different ways:

(1) Through the preferential filling of octahedral positions by Al at the expense of the packing of the defective (imperfect) positions. The final result of this process is the formation of stoichiometric spinel AB_2O_4. This way of structural rearrangement of Al_2O_3 is typical for alumina solutions of Mg [9], Ni [10], i.e., cations with the preference for tetrahedral cationic positions.

(2) Through the preferential filling of tetrahedral positions by Al. In this case new positions, untypical for spinel and low-temperature alumina, in practically cubic anionic framework are occupied. This mode of structural rearrangement is characteristic for alumina itself and alumina solutions of Cr [10] and possibly La [6], i.e., cations with the preference for octahedral cationic positions. The final result of the structural rearrangement is the transition from practically cubic closely packed anionic framework to the hexagonal one (with the formation of α-Al_2O_3 and solid solutions on its basis).

The changes observed in the structure and phase composition of alumina doped with magnesium (ca. 3 wt.-%) and lanthanum (ca. 10 wt.-%) upon the increase of temperature are illustrated in Fig. 3:

3.1. *Pure alumina (Fig. 3a)*

This scheme is based on earlier data [7,8].

3.2. *The low-temperature solid solution containing lanthanum ions (Fig. 3b)*

Upon lanthanum introduction a low-temperature solid solution is formed, with the structure similar to that of γ-Al_2O_3. In contrast to aluminum ions, lanthanum ions fill only octahedral positions, their presence in transient structures creates additional limitations for structural rearrangement with the formation of δ-, or α-Al_2O_3 [6].

3.3. *The low-temperature solid solution containing magnesium ions (Fig. 3d)*

The low-temperature solid solution containing magnesium ions has a structure similar to that of the low-temperature alumina, with magnesium replacing aluminium in tetrahedral positions (A and C). As the temperature increases, a preferential filling of octahedral positions takes place, while the occupation of defective positions decreases. At temperatures above 1000°C, owing to the diffusion of magnesium ions, the decomposition of the solid solution to α-Al_2O_3 and stoichiometric $MgAl_2O_4$ occurs; the latter has a cubic anionic framework, and its cationic framework has 24 occupied positions (2/3 of which are octahedral ones). The degree of the decomposition increases with the increase of magnesium introduced.

3.4. *The system La_2O_3–MgO–Al_2O_3 (Fig. 3c)*

After thermal treatment at 823 K, lanthanum appears to be present both in the composition of the low-temperature solid solution Mg–La–γ-Al_2O_3, and in the form of finely dispersed particles of lanthanum oxide. Coexistence of Mg and La, different in the preference for filling particular cationic positions in the anionic oxygen framework, in a solid solution based on the structure of γ-Al_2O_3 does not permit the realization of the ways of solid solution structural rearrangement typical for each of the cations. Moreover, the stabilization of a 'loose' structure of the low-temperature solution favors the admittance of lanthanum ions into the support structure. No formation of lanthanum aluminate is observed upon temperature increase, as opposed to the system La_2O_3–Al_2O_3, because in this case the preferential process is apparently the diffusion of lanthanum ions into the structure of the mixed solid solution. At temperatures above 1200°C two compounds with hexagonal packing of oxygen framework (α-Al_2O_3 and $MgAl_{11}LaO_{19}$) coexist in the system.

4. Conclusion

The modification of γ-Al_2O_3 by a composition of two-valence (Mg) and three-valence (La) cations, increases mechanical strength and thermal stability of alumina. Thermal stability of the doped alumina results from the suppression of structural rearrangement of low-temperature solid solutions with a rise of temperature.

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