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Synthesis of mechanically strong and thermally stable spherical alumina catalyst supports for the process of methane dimerization in a fluidized bed

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1. Introduction

It is known that methane dimerization occurs at 650–850°C, and catalysts which operate under fluidized bed conditions should have the high mechanical strength and thermal stability to comply with severe conditions of this process. It is evident that these properties of catalysts depend mainly on the support properties. One of the most widely used methods to increase the strength and the stability of supports and catalysts is chemical modification with various compounds.

This work is devoted to the development of the method of chemical modification for the preparation of thermally stable spherical alumina with high mechanical strength.

2. Results

Formation of the spherical granules was carried out by the hydrocarbon–ammonia moulding method [1]. The following compounds were used to prepare modified alumina: lanthanum, cerium and magnesium nitrates, and sol SiO_2.

Alumina supports were impregnated with aqueous solution of the salts. In some experiments a special impregnation method was used: the spherical granules of hydroxide were impregnated with aqueous solution of salts [2]. Sol SiO_2 was added to aluminium hydroxides before the hydrocarbon–ammonia moulding.

The amount of modificator added was varied between 1 and 13 wt.-%. Sintering tests were carried out at 900–1300°C at different heating time in order to study the stabilizing and strengthening effects of a modifying element on the phase transformation, surface area and mechanical strength.

The results obtained show that modified spherical alumina properties depend on the method of the introduction of chemical compounds. This is connected with the different nature of the interaction between aluminium compounds and modifying additives.

Magnesium introduction to aluminium hydroxide granules allows to increase sharply the strength of granules (1.5–2 times) in comparison with pure alumina after calcination at 550°C. Introduction of magnesium does not cause support texture to change. It was shown that the increase in durability of modified low-temperature support is due to component interaction and formation of cation–anion type solid solution based on the γ-alumina structure. The samples of spherical granules (diameter 1–3 mm) obtained by the new method have mechanical strength ca. 50 MPa and

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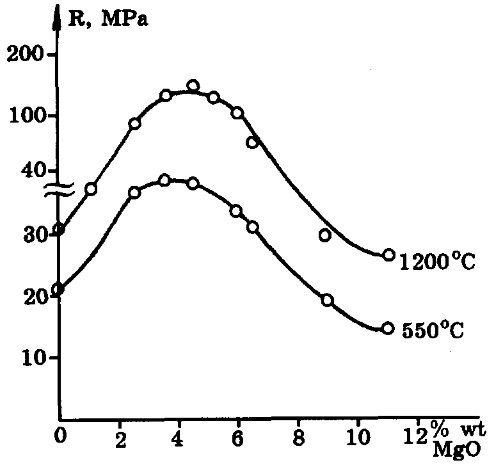

Fig. 1. Mechanical strength of alumina granules (R) versus MgO concentration and temperature.

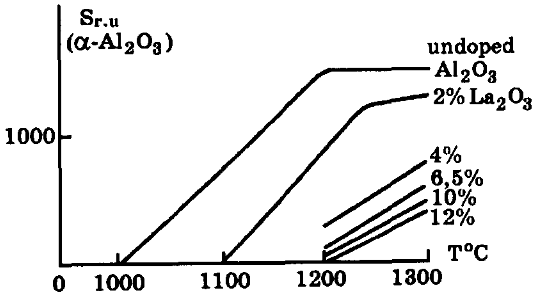

Fig. 2. Dependence of α-Al_2O_3 content in the θ-Al_2O_3/α-Al_2O_3 system on CeO_2 concentration.

contain 2–3 wt.-%. MgO. Fig. 1 illustrates the dependence of the mechanical strength of spherical alumina on the MgO content at different temperatures.

The method of lanthanum introduction influences the support thermal stability. Thus, the incipient wetness impregnation of oxide granules is more efficient as compared with the introduction of the lanthanum salt into aluminium hydroxide granules. The stabilizing effect of lanthanum was assumed to result from the formation of intermediate X-ray amorphous compounds with the transient Al_2O_3 forms. The phase $La_2O_3 \cdot 11Al_2O_3$ is observed only at 1100°C and γ-alumina is detected at this temperature also. The dependence of the α-Al_2O_3 line intensity on La_2O_3 concentration at different temperatures is shown in Fig. 2. It is seen that the higher is the temperature the more La_2O_3 additive should be introduced to decrease α-Al_2O_3 content. When the formation of $La_2O_3 \cdot 11Al_2O_3$ is completed (at 1300°C) the stabilizing effect seems to end, and alumina not involved in the interaction exists as α-Al_2O_3 only. It is shown that the phase lanthanum aluminate which forms preferably when the salt is added to aluminium hydroxide granules does not provide the stabilizing effect.

Unlike La_2O_3–Al_2O_3 system, the method of cerium introduction has no influence on the thermal stability of Al_2O_3. The thermal stability of alumina was shown to increase only at low content of CeO_2 (ca. 5 wt.-%) and only a part of cerium introduced was found to interact with alumina.

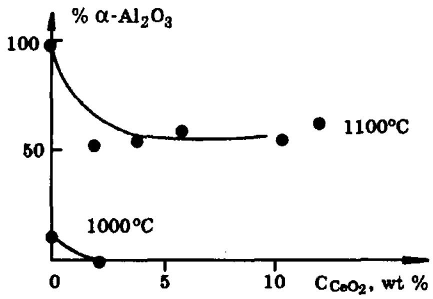

Fig. 3. Integral intensity of lines (d/n = 2.085) for α-Al_2O_3 versus temperature and concentration of lanthanum.

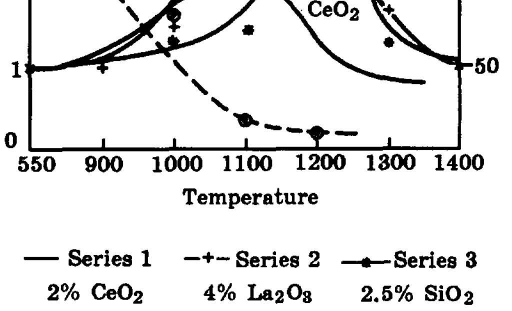

Fig. 4. The efficiency of various additives at different temperatures.

Fig. 3 shows the influence of CeO_2 content on the amount of α-Al_2O_3 formed at different temperature.

Thus, the results obtained allow to conclude that alumina promotion with cerium provides a less profound effect on the thermal stability of the support than that with lanthanum. That is connected with the limited interaction of cerium with the support.

The role of lanthanum and cerium in the increase of thermal stability is discussed in [3,4], where the X-ray study of these systems was carried out to establish dependencies on the method of introduction, type of alumina and amount of additives.

The introduction of silica-sol into plastic mass before hydrocarbon–ammonia moulding also allows the increase of the thermal stability of alumina. For instance, at SiO_2 content 2–3 wt.-% the specific surface area of alumina (S_{BET}) after sintering at 1200°C increases 3–4 times in comparison with pure alumina.

Comparison of the efficiency of La_2O_3, CeO_2, and SiO_2 (characterized by change in S_{BET}) shows that up to 1100°C the best additive is La_2O_3, and SiO_2 promotor is the most effective at 1200°C. The data are represented in Fig. 4.

Thus, the optimal conditions were chosen to prepare strong and thermally stable alumina support, which can be used for the preparation of fluid bed methane dimerization catalysts.

3. References

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