Sintering of alumina and effects of rare earth metal addition

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Sintering of alumina and effects of rare-earth metal addition via incipient wetness impregnation

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Abstract

The effect of adding cerium and lanthanum via incipient wetness impregnation post preparation, as a means of lowering sintering rates is investigated. As opposed to adding a stabilizer during the production of the alumina support. The effect of adding the cerium and lanthanum is clearly positive, with 68% of the initial surface area retained at 1,100 °C sintering after 4h, compared to 28% for the non-stabilized material. All the materials transfer from delta to theta-phase during the high temperature treatment, showing that it is a true stabilization and not merely an in crease in phase-transition temperature.

Introduction

One of the most common catalyst support materials used in the world is aluminium oxide or alumina. It is used in all sorts of reactions, including high temperature applications. Alumina is a flexible material, with several crystal structures and different properties depending on these. In the case of high temperature applications, it is of interest to improve the resistance of the material to sintering by adding a stabilizer. This way, catalytic activity can be retained also under harsh operating conditions. The stabilization is normally performed by adding a stabilizer with high melting point during the preparation of the alumina prepared for instance by precipitation [1]. The stabilizer is added in amounts ranging from 1-15% by weight. In here, another approach is described. Here the stabilizing material is added to an already finished catalyst support via incipient wetness addition.

[1] Crucq, A., *Catalysis and Automotive Pollution Control II*. 1991: Elsevier Science

Materials and Methods

The starting point for the experimental work is a commercial delta-phase alumina extrudate provided by Sasol GmbH. The extrudate has a diameter of 3.15 mm and is 3-9 mm long. The surface area as measured by nitrogen adsorption is 120 m^2/g, the pore radius is about 12 nm and the pore volume 0.72 ml/g. The material was dried in a hot air oven for 12 h at 120 °C. There after the material was sintered in air at 1,100 °C for 4 hours in a muzzle furnace. In addition, the virgin material was sintered at 750, 800 and 1,000 °C for comparison. The resulting materials were analyzed using powder x-ray diffraction and the resulting alumina crystal structure verified.

Figure 1. The alumina starting material**.**

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Results and Discussion

The sintering of the non-stabilized sample is quite severe as temperature is increased. However, when increasing the heat treatment temperature further, there is a quite sharp decrease in surface area. When the temperature is increased to 1,100 °C the surface area drops to 33 m^2/g or a mere 28% of the initial value. At the same time, the pore volume of the sample drops from the initial 0.72 ml/g to 0.22 ml/g and the average pore size increased to 28 nm.

However, for the material stabilized by Ce and La added through incipient wetness there is a vast difference for the most part. The average pore size is actually larger than for the non-stabilised sample coming in at 29 nm. Also the values for surface area and pore volume is higher than for the non-stabilized value. The surface area is retained at 68% of the initial value or 81 m^2/g. The pore volume on the other hand is retained at 0.60 ml/g. The reports of the sintering is illustrated in figure 1 with respect to surface area and summarized in table 1. All samples sintered at 1,100 °C show a theta-phase crystal structure.

Table 1. Surface area, pore volume and pore diameter of samples with varying sintering temperature.

Sample	BET surface area (m^2/g)	BJH desorption pore volume (ml/g)	Pore diameter (4V/A BET) nm	Crystal form of alumina
Fresh	119	0.72	24	Delta
750	119	0.73	25	Delta
800	116	0.73	25	Delta
1,100 °C	33	0.22	28	Theta
1,100 °C Ce La	81	0.60	29	Theta

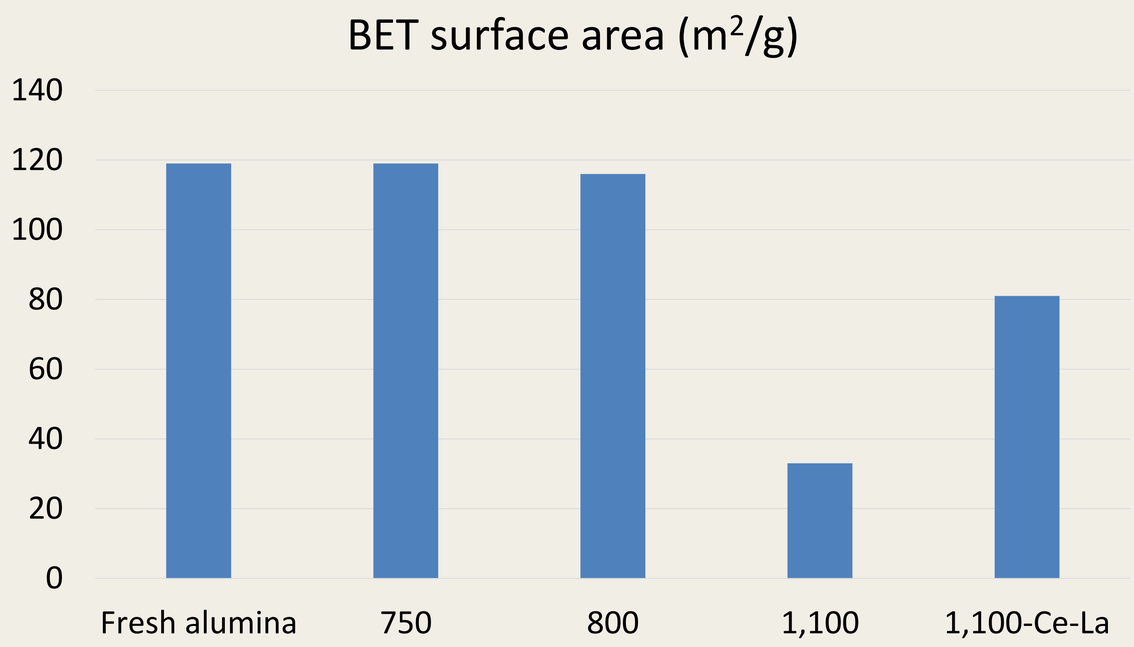

Figure 2. The results of the stabilization of the alumina support material.

Conclusions

The work performed clearly show that a pre-prepared alumina can be stabilized using incipient wetness addition of Ce and La. Adding the stabilizing material in low amounts, 1% of each Ce and La in the resulting catalyst support, makes it much more resilient to sintering. This implies that the post addition of the alkaline earth metals stabilizes the material, despite the transition from one phase to another. It is thus not a stabilization due to increasing the phase-transition temperature but a true stabilization also after the phase transition**.**