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Short Communication

Support moulding —Important variable in solid state reactions between active phase and the support

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ABSTRACT

This work presents results of studies on solid state reaction in CeO_2–Al_2O_3, Yb_2O_3–Al_2O_3 and CeO_2 + Yb_2O_3–Al_2O_3 systems depending on moulding of Al_2O_3 support. Nonporous nano-powder and microporous spheres of γ-Al_2O_3 with differing in moulding were used as the supports. Morphology and structure of lanthanide aluminate phases formed during treatment in hydrogen were studied. Crystallization of large particles of $CeAlO_3$ is strongly hindered on the microporous support (micro-spheres) and, on the other hand, promoted on support containing large pores (nano-powder). We postulate that the effect of spatial confinement present in microporous Al_2O_3 is responsible for observed differences in Ln-aluminates formation at high temperatures in reducing atmosphere.

1. Introduction

High surface area gamma-Al_2O_3 is a very common catalytic support, but in literature several types of alumina in various systems are presented [1–3]. Described in literature, Al_2O_3 supports exhibit visible differences in BET surface area and/or unobtrusive in crystal structure. Given the fact that, used supports differ in physio-chemical properties, it can cause problems with correct interpretation in basic solid state reactions between the dispersed phase and support. One of the most popular gamma-alumina supports, used for catalytic applications, is "Puralox", which is moulded into porous spheres [4]. Many papers described the nano-Me-Al_2O_3 systems, where Me-noble metal or alloy and Al_2O_3-Puralox, as catalysts in oxidation [5], combustion [6] and hydrogenation [7] processes. Another Al_2O_3 support, which can be easily find in literature is "Alu-C" nanopowder [8]. Alu-C is often used as a polymer filler [9] and sometimes as a support for nanocrystalline metals, active catalysts of hydrogenation reactions [2]. In particular, the aluminas presented in this work were used as a catalytic supports for Au/Pd–AluC [2] and Au/Pd-Puralox [7] and tested in hydrogenation reactions. Results of solid state reactions between highly dispersed lanthanide oxides with gamma-Al_2O_3 are described in many papers [1,10–12].

Highly dispersed Ln oxides on alumina are frequently used in catalysis. They stabilize a high surface alumina support against sintering [3], but also improve the catalytic performance of metallic phase [2,5–7]. At elevated temperatures solid state reaction between highly dispersed lanthanide oxides and gamma-Al_2O_3 may occur with the formation of aluminates [2,13–18]. Phase diagrams for Ln_2O_3–Al_2O_3 systems show a possibility of formation of several compounds: $Ln_4Al_2O_9$ (Ln = Nd–Lu), $LnAlO_3$ (Ln = La–Lu), $Ln_3Al_5O_{12}$ (Ln = Eu–Lu) and $LnAl_{11}O_{18}$ (Ln = La–Nd) [14]. Cerium oxide is an exception because it reacts with alumina only in reducing or neutral atmosphere and forms two compounds: $CeAlO_3$ and $CeAl_{11}O_{18}$ [3,14,19]. The course of the reaction depends on many factors, such as temperature [20,21], a contact area between the reactants (method of synthesis) [18] and composition (the concentration of Ln-ions) [14]. An effect of a support moulding on the course of solid state reaction in Ln_2O_3–Al_2O_3 systems has not been studied yet. Data about relationship between support moulding and run of solid state reaction in Ln_2O_3–Al_2O_3 systems are missed in literature.

In this work, results of studies on solid state reaction in CeO_2–Al_2O_3, Yb_2O_3–Al_2O_3 and mixed CeO_2 + Yb_2O_3–Al_2O_3 systems depending on moulding of Al_2O_3 support were presented. Moulding of oxide support was used as a basic variable first time. Samples were studied by XRD, TEM, HRTEM, SAED, SEM and BET techniques.

The choice of CeO_2–Yb_2O_3 mixed oxide as a probe of the interaction with the alumina support was dictated by two reasons. Despite high potential applicability of $Ce_{1-x}Ln_xO_{2-y}$ oxides little is known on their high temperature stability in contact with the support (alumina or silica). Secondly, nanocrystalline $Ce_{1-x}Yb_xO_{2-y}$ mixed oxides are good candidate for such studies because as an unsupported material it shows high structural and chemical stability at elevated temperatures [22]. Hydrogen atmosphere was applied to provide reducing conditions causing partial deoxygenation of the mixed oxide, an important step in oxidation reactions catalysed by such materials. Moreover, the reducing atmosphere strongly enhances reactivity of ceria towards alumina support.

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2. Experimental

CeO_2–Al_2O_3, Yb_2O_3–Al_2O_3 (Ln/Al = 1/10) and (CeO_2 + Yb_2O_3)–Al_2O_3 (Ce/Yb = 1/1, (Ce + Yb)/Al = 1/10) samples were prepared by impregnation of a high surface Al_2O_3 with an aqueous solution of cerium, ytterbium or mixed nitrates. Two different Al_2O_3 supports (Alu-C by Evonik-Degussa – nominal surface area 100 m^2/g and Puralox by Sasol – nominal surface area 90–210 m^2/g) were used to prepared two series of samples. After drying at 200 °C, the samples were preheated at 550 °C for 3 h in static air to clean out organic residues. Such standardized samples were heated at temperatures from 900 to 1100 °C in a hydrogen flow. The methods used to characterize the samples were described in supplementary materials.

3. Results

"Areoxide Alu-C" offered by Evonik-Degussa company was used in this work as a representative of powder like supports. It consists of nanoparticles of pure Al_2O_3 with a hydrophilic character. "Puralox SCCa 150/200" from Sasol company is a nanocrystalline aluminium oxide formed into the porous balls. Texture characteristics of both Al_2O_3 supports are shown in Fig. 1 (pore size distributions) and are summarized in Table S1 (Supplementary materials). SEM images presented in Fig. 2 show clearly difference in the morphology of the supports. Alu-C is in form of lose powder containing aggregates of Al_2O_3 nanocrystallites (10–30 nm), while Puralox contains smaller Al_2O_3 nanocrystallites (5–20 nm) formed into spherical moulds 50–200 μm.

XRD of the "standardized" Ce–Al, Yb–Al and Ce–Yb–Al samples revealed the presence of crystalline CeO_2, Yb_2O_3 and $Ce_{1-x}Yb_xO_{2-(x/2)}$ nanoparticles (~5 nm) supported on Al_2O_3 surface, respectively (Table 1). Fig. S1A depicts a representative TEM image of Yb–Al(AC) 550 sample. It shows a cluster of Yb_2O_3 nanocrystals of various shapes from nanorods to lamella. Similar images were observed for other "standardized" samples.

Heating of the samples in reducing atmosphere at higher temperatures led to solid state reaction between lanthanide oxides and alumina, which proceeds in a different way on Puralox and AluC supports. Fig. 3 shows XRD patterns recorded for the samples heated at 900 °C for 3 h in hydrogen flow. It is clearly visible, that phase composition of the samples depends on the support moulding. In the samples supported on Alu-C extensive solid state reactions between CeO_2, Yb_2O_3 and Al_2O_3 occurred with the formation of crystalline aluminates. On the contrary, crystallization of aluminates is strongly hindered on the Puralox support. It concerns in particular $CeAlO_3$ phase, which according to XRD and TEM crystallizes as the large crystals over 15 nm on Alu-C, but is hardly present on Puralox (Table 1). A possible reason could be different texture characteristics of both supports (Fig. 1, Table S1). Puralox contains pores with a narrow size distribution with a mean size of 8 nm and a maximum size around 11 nm. For Alu-C the size distribution is wider with a mean size of 9.8 and important contribution of large pores between 12 and 18 nm. We postulate that crystalline $CeAlO_3$ phase needs a certain free space to nucleate. For Ce–Al(P) samples, where small pores dominate, this phase may form only on external surface of alumina balls, or within rare large pores. It explains the small amount of this phase observed in XRD pattern (Fig. 3B) and TEM images of Ce-Al(P) sample after thermal treatment at 900 °C. In Fig. S2A and S2B bright field and dark field TEM images of the same area of the Ce-Al(P) 900 sample are shown. The DF image was obtained using the 0.37 nm reflection (0 0 1) of $CeAlO_3$ in the corresponding electron diffraction pattern in Fig. S2C. The bright area in the upper part of the DF image shows therefore irregular, thin crystallite of $CeAlO_3$ phase. HRTEM image (Fig S2D) of the crystal confirmed the presence of 0.37 nm fringes characteristic for $CeAlO_3$ (corresponding to hkl = 0 0 1).

In contrast to growth of $CeAlO_3$, formation of small $Yb_4Al_2O_9$ crystallites occurred in similar manner on both Al_2O_3 supports (Table 1,

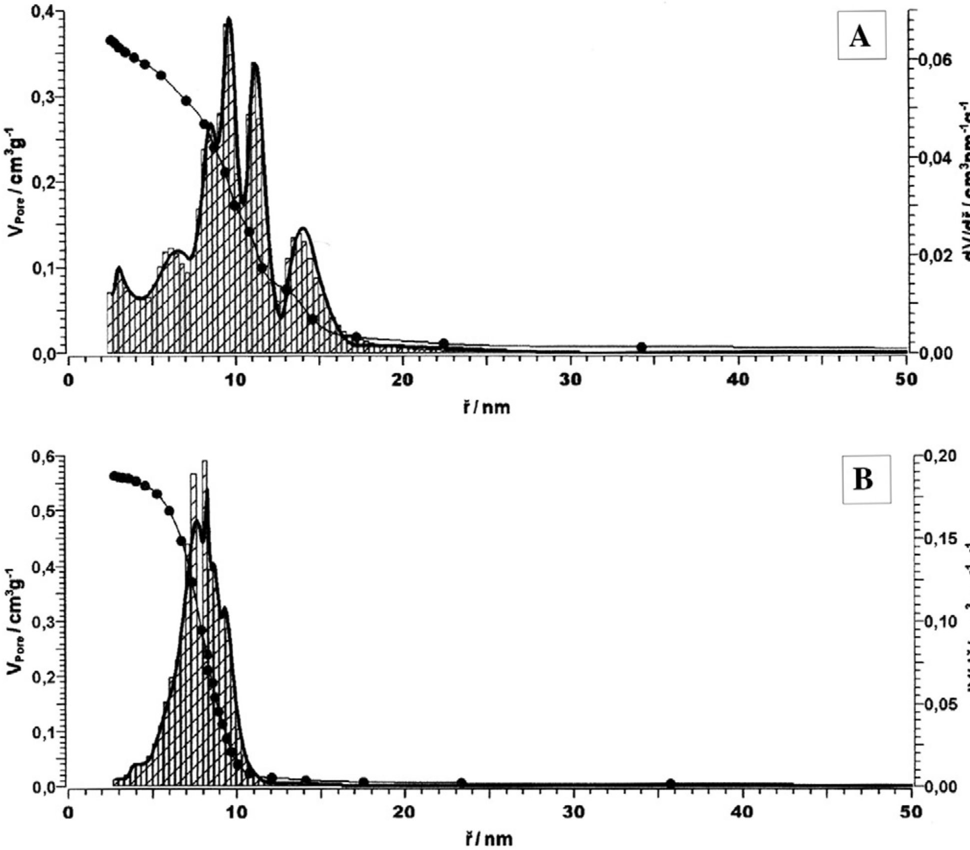

Fig. 1. Pore size distributions for (A) Al_2O_3–AluC and (B) Al_2O_3–Puralox.