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Catalysis Today 110 (2005) 53–57

www.elsevier.com/locate/cattod

The synthesis by deposition–precipitation of porous γ-alumina catalyst supports on glass substrates compatible with microreactor geometries

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Abstract

A coating technique based on the deposition–precipitation of aluminium hydroxide from supersaturated aluminate solutions was applied to the preparation of catalyst supports for application in a glass microreactor. The porous alumina layer obtained after calcination of the deposited hydroxide was characterised by BET, SEM and XRD techniques. Pt/Al_2O_3 catalysts were prepared using the deposited porous alumina as support. The microreactor coating obtained demonstrated the adhesion to the glass substrate compatible with liquid/liquid liquid/gas application and good compatibility with the complex microreactor shape. The phase composition and specific surface area of the coating are very similar to a more conventional powdered γ-alumina catalyst support.

Keywords: Deposition–precipitation; Porous alumina coating; Glass microreactor

1. Introduction

Porous catalytic coatings supported on solid substrate are applied in a variety of different catalytic systems such as well-structured honeycomb structures [1,2] and a variety of different catalytic microreactors [3,4]. Several approaches have been used to produce porous catalytic coatings on a substrate. For example, one method of preparation is based on the transformation of a surface layer of substrate material into a porous coating, for example the anodic oxidation of an aluminium substrate to give a porous layer of amorphous alumina [5]. The disadvantages of this method include restrictions on the substrate materials that can be used and the rather low specific surface areas (about 10 $m^2 g^{-1}$) of the alumina obtained. Other approaches include the use of a variety of different techniques for deposition of powder catalysts or supports on a solid substrate, for example by plasma sputtering [6] or flame deposition [7] or by employing different binders to give adherence of a preformed powder to the substrate [8]. Most of these techniques give satisfactory results on flat surfaces but their application on surfaces with complex shape is less satisfactory. In the case of the application of binders, the purity of the final porous layer may also be affected.

Another group of techniques used for the production of porous catalytic coating is based on the use of deposition–precipitation from a liquid. For alumina-based porous coatings, two methods of deposition–precipitation have been used. The first of these uses the hydrolysis of urea in solutions containing an aluminium salt; the urea hydrolysis gives an increase in pH, this resulting in the precipitation of aluminium hydroxide [9]. If the substrate surface can provide nucleation centres for aluminium hydroxide precipitation, the growth of crystals of aluminium hydroxide starts on the substrate surface and this results in the formation of an adherent uniform layer of $Al(OH)_3$; the $Al(OH)_3$ obtained can then be converted to alumina by calcination. This technique can be applied to a substrate with complex shape but there is restriction to the substrate materials that can be used as they must provide nucleation sites for the process described above. A disadvantage of this technique is that the hydrolysis of urea occurs at an adequate rate only at temperatures above 100 °C and

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doi:10.1016/j.cattod.2005.09.003

so the use of an autoclave is necessary for the deposition–precipitation process.

Another technique that can be applied for the deposition–precipitation of aluminium hydroxide as precursor to alumina is precipitation from supersaturated metastable sodium aluminate solutions. Some efforts have been made to apply this technique to coat honeycomb mullite-based ceramic substrates [10] but the use with other substrates appears not to have been examined. This study therefore describes an investigation of the application of this deposition–precipitation technique to the formation of porous alumina layers on milled glass surfaces.

The essence of the aluminium hydroxide deposition–precipitation technique is the precipitation of $Al(OH)_3$ from solution containing aluminate ions ($Al(OH)_4^-$) at concentration higher than the equilibrium amounts, i.e. from supersaturated solutions. The precipitation process may be expressed by Eq. (1):

$$Al(OH)_4^- \leftrightarrow Al(OH)_3\,(\mathrm{solid}) + OH^- \tag{1}$$

This is one of the steps in the commercial production of alumina by the Bayer process. Due to commercial importance of this process, there have been a large number of studies of different aspects of the precipitation step; see, for example, Ref. [11]. The main conclusion relevant to our application is that a supersaturated aluminate solution can be obtained by rapid cooling of a hot fully saturated solution (i.e. at equilibrium), or of a solution with concentration slightly below equilibrium, and that the precipitation process is initiated by suitable nucleation centres. In the Bayer process, these are provided by the addition of seed crystals of alumina; in our application, they could be supplied by the solid substrate.

2. Experimental

2.1. Substrates used

Initial experiments were carried out using 0.6 mm thick tiles of α-alumina as substrate to determine suitable deposition–precipitation conditions, particularly the duration of the process. Subsequent experiments were carried out with microreactor inserts machined from Borofloat 33 glass to test for compatibility of such substrates with the methodology developed. An important feature of these microreactor inserts is the presence of a surface that had been generated by milling without subsequent thermal treatment. This surface has a significant roughness, having multiple chips and, as has been demonstrated in this work, it can provide the nucleation centres necessary for $Al(OH)_3$ precipitation.

2.2. Preparation of supersaturated aluminate solutions

The solutions used in this work were prepared by dissolution of 1.825 g of an aluminium foil (Merck, Aluminium tape, 0.3 mm thick) in 25 cm^3 of a solution containing 3.7 mol dm^{-3} of NaOH and 0.76 mol dm^{-3} of Na_2CO_3 (both from Aldrich, analysis quality). The dissolution was carried out at a temperature close to the boiling point of the solution, ca. 100 °C. (The sodium carbonate was added to the solution in order to reduce any fluctuations that might occur in the sodium carbonate concentrations in the various preparations which might be brought about by absorption of carbon dioxide from the surrounding atmosphere.) After the dissolution step, distilled water was added to bring the volume back to 25 cm^3, thus compensating for any losses of water due to evaporation. Before use, the solution was then cooled quickly to room temperature in a water bath.

The dissolution process can be represented by following Eq. (2):

$$2Al_{\mathrm{metal}} + 2NaOH + 6H_2O \rightarrow 2Na^+ + 2Al(OH)_4^- + 3H_2\uparrow \tag{2}$$

The final composition of the solution obtained was 2.7 mol dm^{-3} $NaAl(OH)_4$, 1.0 mol dm^{-3} NaOH and 0.76 mol dm^{-3} Na_2CO_3. Using Rosenberg and Healy's supersaturation model [12], derived from work carried out by the Bayer industry, the boiling solution prepared was marginally supersaturated, at a value of ~1.3 (i.e. the concentration is 1.3 times the saturation concentration at this temperature) but the rate of precipitation under these conditions is very low and precipitation only occurs with seeding. By decreasing the temperature rapidly to 25 °C, the supersaturation value was increased to ~8.3. Under these conditions, precipitation is favoured but the process is still slow and occurs over a period of some hours; this is discussed in more detail below.

2.3. Deposition–precipitation chamber

In order to reduce the volume of the supersaturated solution required for the precipitation–deposition step, a sandwich type deposition chamber was developed and employed. A schematic cross-section of this deposition chamber is shown in Fig. 1.

The two substrate plates were of the form used in the microreactor, having milled holes and channels for the introduction and transport of the liquid and gas feeds of the reactor. In the deposition chamber, the plates were held at a distance of ca. 3 mm apart by the PTFE spacer and the supersaturated liquid, prepared as described above, was added at room temperature through one of the holes, all of which were then sealed. Deposition, as described below, then occurred on the inner surfaces of both substrates.

2.4. Deposition–precipitation and subsequent treatment of the $Al(OH)_3$ layers formed

The deposition precipitation process was carried out by placing the sealed chamber containing the supersaturated liquid

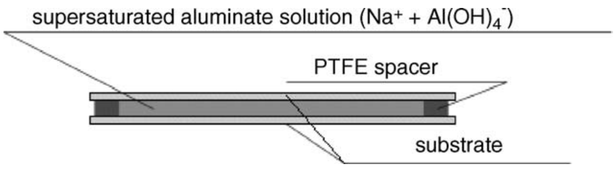

Fig. 1. A cross-section of the deposition–precipitation chamber.

in a thermostat at 25 °C for 40 h. The chamber was then disassembled and the substrate was washed with distilled water to remove all traces of Na^+ ions until the pH of the washing water did not change during several washing steps. The coated substrates were then left to dry in the laboratory atmosphere for 3 h and this was followed by further drying at 120 °C for 2 h before carrying out the calcination step. The temperature program of calcination furnace had five steps: a temperature increase from 25 to 180 °C at a rate of 2 °C min^{-1}; 180 min at a constant temperature of 180 °C; a temperature increase to 450 °C at a rate of 2 °C min^{-1}; constant temperature of 450 °C for 500 min; and finally, slow cooling to room temperature. After calcinations, the substrate was washed again in distilled water to remove any residual sodium impurity released during the calcinations steps. The final loading density of the porous alumina deposited was in the range 60–70 g m^{-2}.

For the catalytic performance tests, a number of samples of Pt/γ-Al_2O_3 catalyst layers were prepared by impregnation of the coated substrates with solutions of chloroplatinic acid hexahydrate (platinum concentration 10 g dm^{-3}). After impregnation for 2 h, the substrate was dried at 120 °C and then calcined at 400 °C for 6 h. The final concentrations of Pt calculated from amount of the Pt containing solution and general alumina weight were in range 4–10 wt.%.

2.5. Characterisation of the substrate and $Al(OH)_3$ and Al_2O_3 coatings

The initial substrate and the coated samples prepared were characterised by BET analysis (Micromeretics Gemini BET instrument) using the N_2 adsorption technique, scanning electron microscope imaging (SEM, JEOL JSM-840) and XRD (Philips X'Pert system).

3. Result and discussion

3.1. Preliminary results on deposition–precipitation on an α-alumina plate

The main goal of the research described here was to develop an alumina coating method compatible with the microreactor insert material and shape in which good adhesion occurred between the inserts and the coating; the coatings were required to have a uniform thickness and porosity. The initial deposition–precipitation experiments were carried out on α-alumina plates which should be able to provide nucleation centres for $Al(OH)_3$ precipitation. These experiments showed that under the conditions described above, the optimal deposition–precipitation time at room temperature was about 40 h. The thickness of $Al(OH)_3$ layer obtained after such deposition–precipitation was found to be around 50 μm. An increased deposition–precipitation time caused the layer thickness to increase but the resulting thicker layer exhibited poor adhesion to the substrate after calcination. If, on the other hand, the deposition–precipitation time was decreased, the $Al(OH)_3$ layer was found to be discontinuous. This could indicate that the surface density of the nucleation cites is quite low or that some nucleation cites need time for activation in alkali solution.

3.2. Deposition–precipitation on glass microreactor inserts

The same conditions of deposition–precipitation were then tested for use with glass microreactor inserts. Two types of glass inserts were tested: glass inserts which had been fired after machining (giving a shiny appearance to the glass surface) and glass inserts which had not been fired after machining (giving a dull appearance). It was found that the fired surfaces did not provide nucleation centres for $Al(OH)_3$ precipitation and the $Al(OH)_3$ formed only in the bulk of the supersaturated solution without any adhesion of precipitate to the glass surface. However, experiments on the glass insert which had not been fired demonstrated that the unfired glass surface provided the necessary nucleation centres for $Al(OH)_3$ formation and the resulting layer had similar thickness (ca. 50 μm) to those found with the α-alumina substrates. Further characterisation work of the layers obtained was therefore restricted to the use of the unfired substrates. Fig. 2 shows the pictures of initial unfired glass substrate and the substrate surface after porous alumina deposition.

3.3. XRD analysis of coating obtained on the unfired glass inserts

Fig. 3 presents the X-ray diffraction patterns of (a) the deposited $Al(OH)_3$ layer and (b) the coating after calcination. The results for the $Al(OH)_3$ layer obtained after the deposition–precipitation process (Fig. 3a) showed that the layer resulting from precipitation consisted of the mixture of bayerite crystal

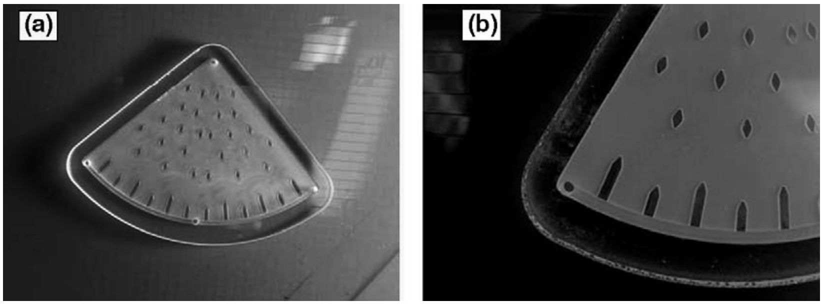

Fig. 2. Optical images of a unfired glass insert (a) and the insert surface after alumina deposition (b).

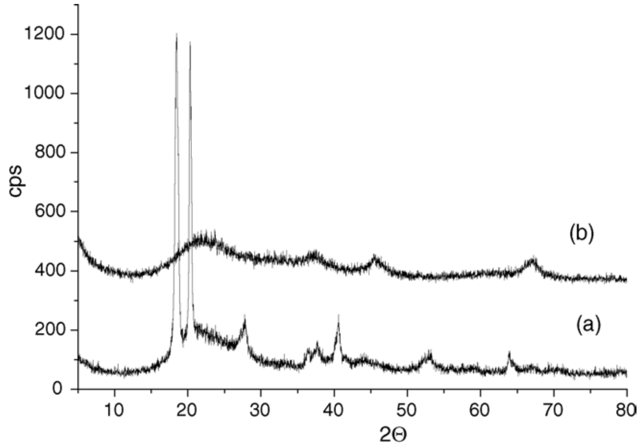

Fig. 3. XRD pattern of the deposited layer (a) dried at 120 °C and (b) calcined at 450 °C.

modification (JCPDS-ICDD Card No.: 20-0011) with gibbsite (JCPDS-ICDD Card No.: 33-0018). As will be shown later the morphology of the deposited film is typical for the bayerite precipitation and presence of gibbsite cold be explained by irreversible transformation of bayerite after precipitation. This result is an agreement with data from the Bayer process [13] which gives the precipitation of bayerite in the room temperature region.

The diffraction pattern of the calcined coating (Fig. 3b) shows that all the aluminium hydroxide was decomposed during the calcinations step and that the final product of the transformation under the conditions used was γ-Al_2O_3 (JCPDS-ICDD Card No.: 29-0063). This transformation of $Al(OH)_3$ is consistent with the well-documented thermal transformation of aluminium hydroxide as described, for instance, in Ref. [14].

3.4. SEM analysis of uncoated and coated unfired glass inserts

Fig. 4(a) shows a SEM image of the unfired glass surface. This substrate has a rough surface with many apparent chips introduced as a consequence of machining. (No such roughness was seen with fired substrates.) Those surface 'chips' are probably responsible for providing nucleation points for $Al(OH)_3$ precipitation since, as noted above, the smooth glass surface did not show any sign of $Al(OH)_3$ precipitation.

Fig. 4(b) and (c) show the surface morphology of the precipitated $Al(OH)_3$ layer at two different magnifications. The surface is made up of spherical particles with a morphology which has the appearance of balls of twined cord ('clews'). Such clew-like crystallites are typical of the bayerite precipitated from cold solutions [13] and so the result helps confirm the XRD identification of bayerite in the precipitated $Al(OH)_3$.

The surface morphology of the calcined alumina layer is shown in Fig. 4(d). Comparing the morphologies of the calcined and uncalcined layers, it is clear that calcination results in the formation of cracks in the surface of the initial spherical agglomerates of $Al(OH)_3$. Those cracks are likely to be due to changes in density occurring during the dehydration process since the specific volumes of bayerite/gibbsite mixture and γ-Al_2O_3 are different. The presence of those cracks appears not to reduce the all-over adhesion of the layer as long as the layer thickness is less than 70 μm.

3.5. BET analysis of coating obtained on the unfired glass inserts

To perform BET analysis of the final layer material, the porous layer was mechanically removed from the substrate

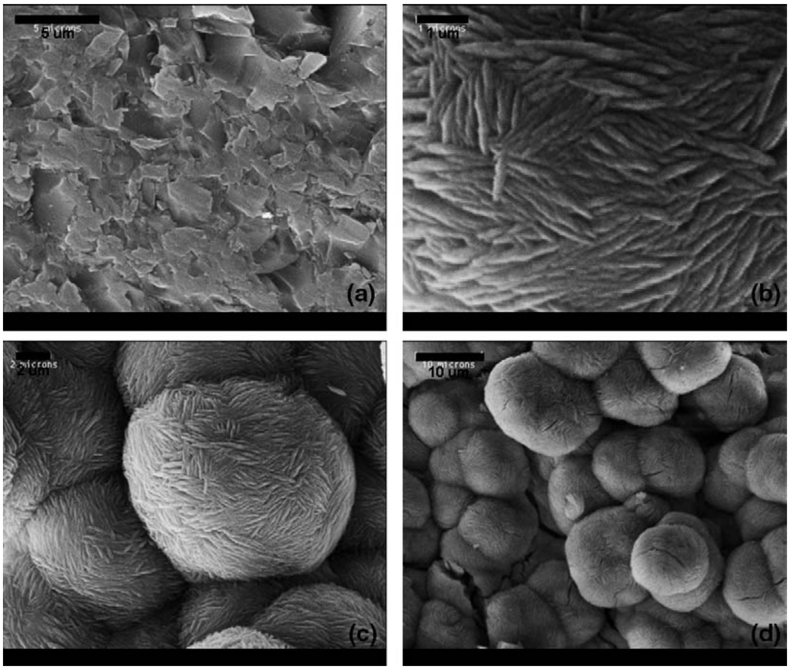

Fig. 4. SEM images of (a) the unfired milled glass surface, (b) and (c) the deposited layer dried at 120 °C and (d) the deposited layer calcined at 450 °C.

surface by scraping it. The specific surface area of the final porous coating was found to be in the range of 120–130 m^2/g. Such a value is in the range of the typical surface area for γ-Al_2O_3 calcined under the conditions used here [15].

4. Conclusion

In this article, we describe the results of the application of the deposition–precipitation technique for the preparation of microreactor inserts covered with porous catalysts. The technique developed is compatible with the microreactor material used (Borofloat 33 glass) and its shape. The catalytic coating prepared demonstrated adhesion suitable for liquid application. The porous γ-alumina coating prepared by this technique has characteristics similar to those of γ-alumina powder and can therefore be used as a support for a variety of different catalysts. The glass inserts that were coated as described in presented article were used in a mesh multiphase microreactor with integrated solid catalyst [16]. The detailed kinetic investigation of the hydrogenation of the double bond in α-methylstyrene (to give cumene) in mentioned reactor was presented in following work [17].

Acknowledgments

We wish to thank the UE for support of this work under contract (KEMMiC) and our partners in that project for useful discussions. We also thank Dr. Mitch Loan for helpful advice on aluminium hydroxide precipitation and transformation.

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