Fundamental Aspects in the Deposition of $\gamma$Al$_2$O$_3$ Layers on Ceramic and Metallic Supports for Preparation of Structured Catalysts


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1. INTRODUCTION

Structured catalysts are nowadays used on a large scale in several important environmental applications, including catalytic combustors, SCR De-NOx processes and catalytic mufflers; application of structured catalysts to chemical processes is also receiving attention. We present herein a procedure for the deposition of $\gamma$-Al$_2$O$_3$–based catalytic coatings onto ceramic and metallic structured supports, as well as a systematic investigation of the main related preparation variables.

2. PREPARATION OF COATED SAMPLES

Deposition of $\gamma$-Al$_2$O$_3$ coatings onto Al supports in the form of slabs and onto $\alpha$-Al$_2$O$_3$ tubes was performed according to the following two steps procedure:

a) Deposition of a bohemite primer: The primer was prepared by dispersing 10% w/w of a commercial aluminium hydroxide powder (DISPERAL®, Condea Chemie) in a 0.4% w/w HNO$_3$ aqueous solution (corresponding to 0.0635 mol/l solution). The supports were dipped in such a dispersion and dried at room temperature for 30 - 40 minutes.

b) Deposition of the $\gamma$-Al$_2$O$_3$ washcoat. A commercial submicronic $\gamma$-Al$_2$O$_3$ (Sumitomo ALKPG-0015) was dispersed in HNO$_3$ aqueous solution, with variable concentrations of HNO$_3$ and H$_2$O. After mixing for about 16 hours the dispersions were suitable for deposition. The various supports were dipped in the dispersion, withdrawn at a constant speed of 3 cm/min, and then flash heated (5 minutes) at 280°C in oven to obtain a well adherent coating layer.

3. RESULTS AND DISCUSSION

The prepared samples were characterised by gravimetric analyses, SEM images, BET analyses and rheologic measurements. The influence of the main preparation variables is discussed in the following.

Effect of HNO$_3$ concentration in the slurry

We have investigated a range of HNO$_3$ concentrations in the slurry between 0.36 and 8.65 mmol/g HNO$_3$/Al$_2$O$_3$ (from 0.1125 mol/l to 2.7 mol/l solution) at constant H$_2$O/Al$_2$O$_3$ = 3.2 w/w ratio. The resulting slurries were used to coat aluminium slabs and $\alpha$-Al$_2$O$_3$ tubes. As shown in Figure 1, the plot of the coating load per unit surface area versus the HNO$_3$ concentration in the slurry goes through a maximum at 4.33 mmol/g (1.35 mol/l). The deposited layers with an acid/alumina ratio greater than or equal to 3.6 mmol/g (1.125 mol/l) were poorly adherent. The results of the rheologic measurements are helpful in interpreting the data in Figure 1. From the flow curves we can observe that for HNO$_3$/Al$_2$O$_3$ ratios less than or equal to 2.16 mmol/g (0.675 mol/l) the slurries exhibited a Newtonian behaviour, the viscosity remaining constant with increasing shear rate. For greater HNO$_3$/Al$_2$O$_3$ ratios the slurries became non-Newtonian, their viscosities decreasing with increasing shear rate (shear-thinning behaviour). Remarkably, if viscosity values are plotted versus the HNO$_3$/Al$_2$O$_3$ ratio at a constant shear rate (Figure 2), we obtain the same trend exhibited by the coating load (Figure 1), again with
a maximum at the HNO3/Al2O3 ratio of 4.33 mmol/g (1.35 mol/l). This correlation points out the key role of the slurry flow behaviour in determining the thickness and the adherence of the coating layer. Slurries prepared with variable H2O/Al2O3 ratios were used to coat aluminium slabs as well as α-Al2O3 tube pieces. The coating layers were well adherent in all cases except for the smallest H2O/Al2O3 ratio = 2.8 w/w. Probably in this case there is a lack of dispersing medium for the alumina particles, so that the resulting slurry is not adequate for the deposition process. The coating load per unit surface area decreases with increasing H2O/Al2O3 ratio, and reaches an asymptote for ratios greater than 3.3 g/g. Between the coating loads deposited onto various samples and the corresponding coating thickness there is the linear correlation. Accordingly, the deposited layers have the same density value of about 0.9 g/cm³, estimated from the slope of the regression line.

Have been studied also the effect of withdrawal velocity, resulting in a major amount of coating load increasing the velocity.

**Coating Adherence** The adherence of the flash heated coatings has been evaluated according to a method described in the patent literature [2], based on the measurement of the weight loss caused by exposure to ultrasounds. The coated slabs were immersed in petroleum ether inside a sealed beaker, and then treated in an ultrasound bath for 30 minutes. The samples obtained from slurries with HNO3/Al2O3 ≤ 2.2 mmol/g showed no weight loss; samples associated with HNO3/Al2O3 ratios of 2.9 mmol/g gave 11% weight loss; samples with higher ratios gave weight losses greater than 25%. Plotting the weight loss versus the HNO3 concentration again resulted in a maximum at HNO3/Al2O3 = 4.33 mmol/g. Accordingly, optimal adherence is achieved for HNO3/Al2O3 ratios less than 2.9 mmol/g. We investigated also the influence of calcination temperature on the adherence of the coating layers. Fecralloy® slabs were coated as described above using a slurry with HNO3/Al2O3 ratio of 2.9 mmol/g. Calcinations temperatures of 400°C, 700°C, and 900°C for 10 h resulted in weight losses of 1.6%, 0.8% and 0.08%, respectively. This suggests that increasing the calcination temperature improves the layer adherence.

**Catalytic activity** CO oxidation and CH₄ oxidation have been taken as a model reactions for our structured catalysts. The catalytic activity showed for the two reactions was good, comparable with the activity of a powder catalyst with the same composition.