



Growth of Hierarchically Structured High-Surface Area Alumina on FeCralloy® Rods



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ABSTRACT

The formation of metastable alumina phases due to the oxidation of commercial FeCralloy® rods (0.5 mm thickness) at various temperatures and time periods has been examined. This structured layer acts as an anchor to bind additional coatings of alumina via wash-coat techniques, thereby improving the layer thickness and increasing adhesion of the catalytic surface. Optimisation of the layer thickness and catalytic properties were conducted, using a range of analytical systems [scanning electron microscope (SEM), energy dispersive X-ray (EDX) and X-ray diffraction (XRD)]. The modified FeCralloy® rods were tested in a fixed bed reactor rig to assess the impact on yield for the dehydrogenation of methylcyclohexane.

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1. Introduction

Modern car-exhaust systems use catalysts supported on ceramic monoliths. The last decade has seen a move towards metallic monoliths affording improved conversion and selectivity [1]. The use of catalysts supported on metal for packed bed catalytic reactions are limited [2]. A structured catalyst with an alumina wash coat deposited on a highly conductive support, such as a FeCralloy®, has the potential to eliminate the heat transfer limitations in catalytic processes [1,3–5]. An adherent alumina wash coat on metal supports remains a challenge both ensuring that the support is anchored when thermal cycling is inherent in the operation of fixed bed reactors and ensuring that sufficient active catalyst is available to maintain required conversions.

The growth of transient metastable alumina (θ -, γ -) on foils when oxidised at temperatures of 1073 K–1273 K for varied time periods has been reported [6–8]. During the phase transformation of the transient alumina, there are particular oxidation parameters which result in the growth of a γ -Al₂O₃ layer which has properties of high surface area and porosity. The structured morphology helps improve the adherence of a coating layer and also forms a base for synthesis of other supported catalysts [9].

Adhesion of coatings on non-porous structures such as FeCralloy® is non-trivial. Coating deposition is usually conducted by dip coating, spray coating or brush coating [9]. Dip coating is by far the most common method due to its ability to produce uniform and repeatable results. There are also known correlations between the thickness of the layer, viscosity of the medium and withdrawal speed. The coatings

can either incorporate the catalyst directly or act as a support upon which the catalytic phase may be deposited within. Meille and Pallier [2] achieved a very thin layer of alumina deposited on FeCralloy® fibres however, there were significant cracks observed even in such a thin layer. The coated fibres were further impregnated with platinum; this step was not found to be detrimental to the integrity of the coating. It was also found that the precursor to alumina to produce the sol should not be thermally pre-treated. From the observations it was proposed that thermal pre-treatment of the precursor eliminates hydroxyl groups, thus reducing the potential number of surface chemical bonds between the sol and support – the result being non-uniform non-adherent layers. The sol's viscosity was also found to play a crucial role in the thickness developed. The viscosity was controlled by changing the alumina concentration and pH of the sol.

This paper aims to give a better understanding of the growth of the γ -Al₂O₃ layer by the controlled oxidation of FeCralloy® rods followed by a one-step hybrid deposition method. The prepared catalyst was loaded with 1% (by mass) platinum and its catalytic activity was assessed by testing it for dehydrogenation of methylcyclohexane.

2. Experimental

2.1. Material

FeCralloy® rods of thickness 0.5 mm with a chemical composition (by mass) of 72.8% Fe, 22% Cr, 5% Al, 0.1% Y and 0.1% Si, were used. The wires were commercially manufactured and supplied by GoodFellow (UK). The rods were annealed in a continuous furnace at 1373 K prior to being supplied.

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2.2. Method

2.2.1. Support oxidation

Prior to subjecting the samples to any oxidation, the surface of alloy rods was roughened to remove any oxide layer which may have formed during the annealing process. Also, previous work has shown that an increase in surface texture enhances the growth of the oxide layer [10]. A three step chemical treatment described by Wu *et al.* [11] was carried out to remove any silicon deposits which might have occurred during sandpapering. The rods were first subjected to an alkali wash for 10 min followed by acid wash for the same time. The final step was an ultrasonic bath in acetone for 30 min followed by an ultrasonic bath in de-ionised water. These treated rods were calcined in a Thermo Gravimetric Analyzer (TGA) at 1073 K–1473 K for different time periods (0.5 h–16 h) under flowing air ($0.83 \text{ cm}^3 \cdot \text{s}^{-1}$), to obtain the optimum conditions which favour for the growth of a uniform $\gamma\text{-Al}_2\text{O}_3$ layer on the surface.

2.2.2. Coating deposition

The oxidised rods (calcined at the optimum temperature) were loaded with multiple alumina washcoats through the method of dip coating. A one step deposition method as suggested by Liu *et al.* [12] was employed. To improve the adherence of the washcoat layer, a binder sol was prepared which is added to the washcoat slurry to increase the loading. The binder sol comprised of 4% (mass fraction) boehmite powder (DISPERAL®, supplied by Sasol) dispersed in 16% (mass fraction) conc. HNO_3 and 80% [the oxidised rods (calcined at the optimum temperature)] were loaded with multiple alumina washcoats through the method of dip coating. A one step deposition method as suggested by Liu *et al.* [12] was employed. To improve the adherence of the washcoat layer, a binder sol was prepared which is added to the washcoat slurry to increase the loading. The binder sol comprised of 4% (mass fraction) boehmite powder (DISPERAL®, supplied by Sasol) dispersed in 16% (mass fraction) conc. HNO_3 and 80% (mass fraction) distilled water. The slurry was prepared by dispersing 23% of the binder sol prepared in 23% $\gamma\text{-Al}_2\text{O}_3$ (PURALOX®, supplied by Sasol) powder and 54% (mass fraction) distilled water followed by vigorous stirring at 298 K for 24 h. The calcined FeCralloy rods were cut into strips of 2.5 cm and fitted onto PTFE blocks (Fig. 1). These blocks were immersed into the prepared slurry and were withdrawn at a constant speed of $0.05 \text{ cm} \cdot \text{s}^{-1}$. The coated rods were flash dried at 393 K prior to loading with two additional washcoats. The coated samples were calcined at 923 K for 2 h to reveal a well adherent alumina layer. The total mass of the alumina coating (on the coated rods tested in an experimental run) was found to be 0.1 g.

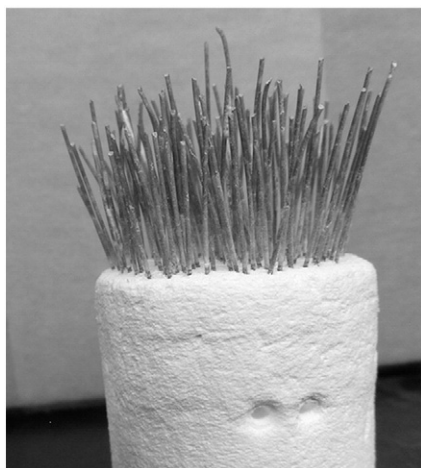


Fig. 1. FeCralloy® rods washcoated with alumina layer.

2.3. Support characterisation

2.3.1. Surface morphology

The varied surface morphology of the oxidised wire samples was analysed using an environmental scanning electron microscope (Quanta 200 FEI). Each rod sample was examined using the ESEM under high vacuum conditions and coated with gold by the method of physical vapour deposition to enable improved image quality. All samples were analysed at an accelerated voltage of 30.0 kV at magnifications ranging from 50 times to 25,000 times the original size.

2.3.2. Chemical analysis

Using an energy dispersive X-ray spectrometer (EDAX Genesis), an elemental analysis was done on the surface of the oxidised samples to obtain an indication of the varied surface composition. Multiple spots were analysed to ensure uniformity and also to obtain an average elemental composition. All the samples were embedded vertically in an electro-conductive resin, Demote 70™. The resin was then cut and polished to a 1 μm finish. This standard technique was employed to establish the thickness of the oxide layer. This method ensures analysis being done on a flat surface rather than a curved surface thus confirming that the EDX relative intensity signals are from the thin oxide layer and not the underlying alloy substrate. Using a back scattering electron detector a line scan was done across the oxide layer around the wire surface to estimate the thickness of the oxide layer. Samples were analysed at an accelerated voltage of 30.0 kV under high vacuum conditions and chamber pressure of $8.9 \times 10^{-4} \text{ Pa}$.

2.3.3. Phase analysis

Using the Philips X'Pert PRO, X-ray diffraction experiments were performed on the samples in the 2θ range of 0.52 rad–0.87 rad and a scanning speed of $2.618 \times 10^{-6} \text{ rad} \cdot \text{s}^{-1}$. Slit widths of 0.004 rad and 0.008 rad were used for all the experiments. A qualitative chemical phase analysis was performed on the oxide layer grown on the alloy rods. X'Pert Data viewer programme was used to analyse the results obtained from the XRD scan.

2.4. Catalytic testing

The alumina coated FeCralloy® rods were loaded with 1% (by mass) platinum by the method of wet impregnation. The Pt precursor was a $0.0001 \text{ mol} \cdot \text{L}^{-1}$ hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$). The coated rods were added to this solution and gently stirred 30 min at 305 K. This mixture was gently heated to 343 K and constantly stirred for 2 h and then heated up to 393 K and left to dry overnight. The rods were tested for dehydrogenation of methylcyclohexane (MCH) in the experimental set up shown in Fig. 2. The design specifications of reactor used for dehydrogenation are listed in Table 1. The activity of the structured catalyst was tested under a range of operating conditions as described in Table 2.

The prepared structured catalyst rods were loaded uniformly into the middle zone ($L = 0.05 \text{ m}$) of the reactor ($\text{ID} = 0.011 \text{ m}$) and the top zone ($L = 0.2 \text{ m}$) was packed with carborundum ($d = 0.1 \text{ mm}$) to act as a feed pre-heater and distributor. Part of the bottom zone of the reactor was filled with carborundum and was connected to the separation unit of the experimental rig external to the furnace. The three zones in the reactor were separated with quartz wool to prevent the catalyst from moving into the voids between the carborundum. The total length of the catalyst bed was 5 cm and the total mass of the catalyst bed was 9.54 g.

Prior to catalysis, the rods were activated by the method of calcination and reduction which were done *in-situ*. The catalyst was calcined at 773 K for 6 h under flowing air ($0.83 \text{ cm}^3 \cdot \text{s}^{-1}$) and reduced at 723 K for 16 h in H_2 ($0.83 \text{ cm}^3 \cdot \text{s}^{-1}$). To obtain a detailed quantitative assessment of the selectivity towards the formation of toluene at various operating conditions, all samples were analysed in a GC–MS (Agilent Technologies, Model-6890 N) equipped with a HP-5MS capillary column ($50 \text{ m} \times 0.00025$

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