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Generation of Catalytic Films of Alumina and Zeolites on FeCralloy Rods

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FeCralloy rods (0.5 mm thickness) were subjected to high temperature thermal oxidation to produce a metastable alumina phase. This structured layer acts as an anchor to bind additional coatings of alumina via washcoat techniques, thereby improving the layer thickness and increasing adhesion of the catalytic surface. In addition, thin films of structured zeolite catalysts (ZSM-5 and Zeolite Y) were grown onto the surface of a metal substrate using in-situ hydrothermal synthesis. All catalysts were fully characterised by SEM, EDX and XRD. The cracking of n-heptane over structured catalysts for both ZSM-5 and Zeolite Y showed very similar product selectivity compared with similar traditional pelleted catalyst forms. The alumina coated FeCralloy rods were impregnated with 1 wt. % platinum and tested in a fixed bed reactor to assess the impact on yield for the dehydrogenation of methylcyclohexane and compared with conventional 1 wt. % Pt/Al_2O_3 pellets. This paper demonstrates that structured catalysts can be manufactured with excellent alumina and zeolite adherence and when suitably activated/modified gives comparable catalytic results to the pelleted powder forms. These coated structured catalysts enhance temperature distribution in highly exothermic and endothermic catalysed processes in addition to improving the mass transfer properties of the reactor system.

1. Introduction

Catalytic films deposited on a highly conductive support, such as a FeCralloy, have the potential to eliminate the heat transfer limitations of catalytic processes. An adherent catalytic layer on metal supports remains a challenge. It is imperative the catalytic layer remains anchored when thermal cycling is inherent in the operation of fixed bed reactors, to ensure sufficient active catalyst is available to maintain required conversions. The growth of transient metastable aluminas (θ-, γ-) on foils when oxidised at temperatures of 800 °C - 1000 °C for varied time periods has been reported (Jedlinski, 1997). During the phase transformation of the transient aluminas, there are particular oxidation parameters which result in the growth of a γ-Al_2O_3 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 source of alumina for the synthesis of zeolite films. The porous transient alumina later acts as an anchor for an adherent alumina washcoat and the growth of zeolite films which are further tested for dehydrogenation of methylcyclohexane and n-heptane cracking respectively.

2. Experimental

2.1 Thermal Oxidation of FeCralloy

FeCralloy rods of thickness 0.5 mm with a chemical composition (in wt. %) of 72.8 % Fe, 22 % Cr, 5 % Al, 0.1 % Y and 0.1 % Si, were used. The rods were commercially manufactured and supplied by GoodFellow. Prior to thermal oxidation, the surface of the alloy rods was roughened using medium grade sandpaper, to remove any oxide layer which may have formed whilst being manufactured. Previous work has suggested that an increase in surface texture enhances the growth of the oxide layer (Zhang et al., 2009). Following this, a three step chemical treatment described by Wu et al was carried out to remove any silicon deposits which

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might have occurred during surface roughening (Wu et al., 2001). The rods were first subjected to an alkali wash for 10 min followed by an 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. A detailed study on the varied thermal oxidation conditions of FeCralloy rods has been previously reported by Rallan and Garforth, and the optimum oxidation conditions were reported to be 950 °C for 10 h (Rallan and Garforth, 2014). The FeCralloy rods prior to catalytic layer deposition, were oxidised at 950 °C for 10 h.

2.2 Deposition of alumina layer

The oxidised rods were loaded with multiple alumina washcoats through the method of dipcoating. A one step deposition method as suggested by Liu (Liu et al., 2003) was employed. To improve the adherence of the washcoat layer, a binder sol was prepared which was added to the washcoat slurry to increase the loading. The binder sol comprised of 4 % w/w boehmite powder (DISPERAL, supplied by Sasol) dispersed in 16 % w/w concentrated HNO_3 and 80 % w/w distilled water. The slurry was prepared by dispersing 23 % w/w of the binder sol prepared in 23 % w/w γ-Al_2O_3 (PURALOX, supplied by Sasol) powder and 54 % w/w distilled water. After vigorous stirring at 25 °C for 24 h, the rods were immersed into the prepared sol and were withdrawn at a constant speed of 3 cm/min. The coated rods were flash dried at 120 °C prior to loading with two additional washcoats. The coated samples were calcined at 650 °C for 2 h. The washcoating procedure was further repeated with a 48 h aged sol. The alumina coated FeCralloy rods were loaded with 1 wt. % Platinum by the method of wet impregnation. The Pt precursor was a 0.0001M hexachloroplatanic acid ($H_2PtCl_6.6H_2O$). Prior to catalysis, the rods were activated by the method of calcination and reduction, which were done in-situ. The catalyst was calcined at 500 °C for 6 h under flowing air (50 ml/min) and reduced at 450 °C for 16 h in H_2 (50 ml/min).

2.3 Synthesis of ZSM-5 layer

The application of zeolite crystals onto a metal surface to form a structured catalyst can be achieved through different methods. The method of dip coating uses a binder to attach already synthesized zeolite crystals to the metal surface. In-situ growth is a method of growing zeolite crystals onto the substrate using the alumina formed on the metal surface as a part source of Al required for the zeolite preparation (Meille, 2006). The thermally treated FeCralloy support rods were cut into strips of 2.5 cm and vertically inserted into a PTFE-lined autoclave following which hydrothermal zeolite synthesis was performed. ZSM-5 was synthesized using a seeding and feedstock gel, where a seeding gel with a molar composition of 4.5 Na_2O: 3.0 TPAOH: 60 SiO_2: 1200 H_2O was prepared using colloidal silica (Ludox AS-40 supplied by Sigma-Aldrich), sodium hydroxide (Sigma-Aldrich) and tetrapropylammonium hydroxide (1M, Sigma-Aldrich) (Chou et al., 2006). The seeding gel was aged overnight at 100 °C . 3.2 g of the seeding gel was added to a feedstock which had a molar composition of 6.5 Na_2O: 2 Al_2O_3: 60 SiO_2: 1916 H_2O. This was prepared by dissolving sodium aluminate (Fisher Scientific) and sodium hydroxide (Sigma-Aldrich) in de-ionised water and adding colloidal silica (Ludox AS-40). The gel was then poured into a PTFE-lined autoclave, heated to 180 °C in an oven and held at temperature for 4 - 48 h. Post hydrothermal synthesis, the zeolite precipitated in the autoclave and the coated rods were removed, rinsed and ultrasonicated in de-ionised water for 10 min. The coated rods were then heated in a muffle furnace (Carbolite Corp) from 25 °C to 550 °C at 1 °C/min and held at 550 °C for 16 h to remove the structure directing template and finally the zeolite powder (1 g) and the structured zeolites were ion exchanged using a 0.5M ammonium nitrate solution (NH_4NO_3, purity>98 % supplied by Sigma-Aldrich) at 80 °C with constant agitation (60 - 100 rpm) for 1 h. Finally the rods were filtered and then washed thoroughly with de-ionised water and dried at 100 °C.

2.4 Synthesis of Zeolite-Y layer

The Zeolite Y precursor solution was prepared from sodium aluminate (Fisher Scientific), colloidal silica (Ludox AS-40) and sodium hydroxide. The precursor solution (3.3 Na_2O: 0.75Al_2O: 10 SiO_2: 120 H_2O) was aged overnight at room temperature. The synthesis gel was then poured into a PTFE-lined autoclave, containing the thermally treated FeCralloy rods and placed in an oven at 100 °C for between 8 - 72 h. After hydrothermal synthesis, the zeolite precipitated in the autoclave and the coated rods were removed, rinsed and then ultrasonicated in de-ionised water for 10 minutes. The synthesized zeolite layer (Na content of 3 wt. %) was further subjected to a de-alumination to produce the ultra-stable form of Zeolite Y. The de-alumination process was performed using acidified ammonia nitrate. The NH_4-Y powder or structured NH4-Y zeolite was mixed with an ammonium nitrate solution (15 wt. %) and the pH adjusted from 4.1 to 2.5 by the addition of HNO_3 (70 wt. %, supplied by Camlab chemical, 0.4 g/g of exchanged zeolite). The slurry was further heated to 85 °C and held for 1 h. Then the powder and structured Y zeolite were washed and dried at 100 °C (Vassilakis and Best, 1991). Finally, the de-aluminated catalysts were ion exchanged once more following the procedure above to reduce the Na content to less than 0.5 wt. %.

3. Catalyst Characterization

3.1 SEM and EDX analysis

The varied surface morphology of the oxidised rod samples was analysed using an Environmental Scanning Electron Microscope *(Quanta 200 FEI)*. Each sample was examined using the SEM 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 30.0kV at magnifications ranging from 50 times to 25,000 times the original size. Figure 1(a & b) describes the change in surface morphology of the FeCralloy after roughening in with sandpaper. The rods oxidised at 950 °C for 10 h resulted in a platelet morphology as shown in Figure 1(c). Previous work has suggested that this platelet morphology can be associated with growth of transient aluminas (Badini and Laurella, 2001). SEM analysis of the alumina coated rods showed a uniform well adhered alumina layer (Figure 2) and similarly for the zeolite layers (Figure 3). The morphology of the zeolites grown on FeCralloy was identical to that of the the zeolites synthesised under the normal hydrothermal conditions (Chou et al., 2006).

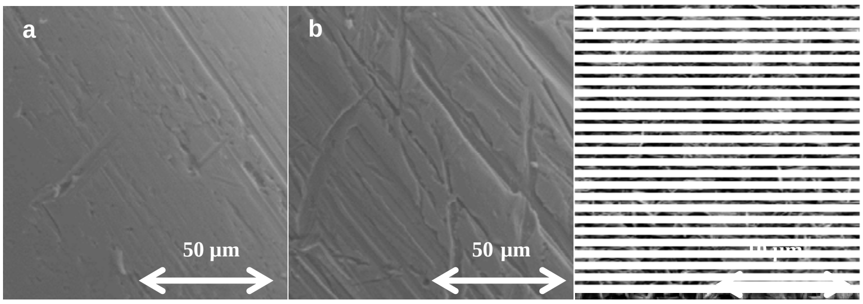

Figure 1 : SEM images of the FeCralloy rods a) as supplied, b) post surface roughening, and, c) after thermal pre-treatment

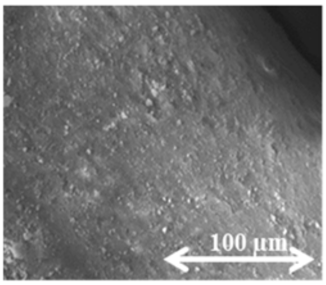

Figure 2 : SEM analysis of the alumina coated FeCralloy rod following multiple alumina washcoating

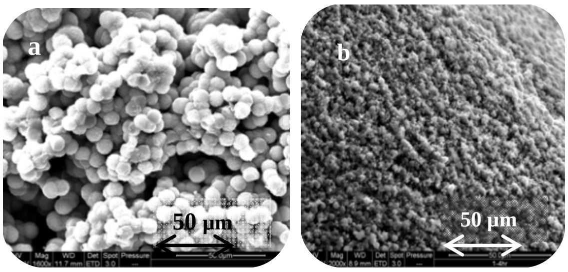

Figure 3 : SEM analysis of zeolites grown on the FeCralloy rods a) ZSM-5 and b) Zeolite Y

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 any change in surface composition. All the samples were embedded vertically in an electro-conductive resin. This technique ensured analysis was being done on a flat surface rather than a curved surface thus confirming that the EDX relative intensity signals were from the thin films and not the underlying alloy substrate. The Si/Al ratio of the ZSM-5 layer was found to be 11 and for the zeolite Y layer the value was 2.8. Post synthetic modification of zeolite Y by acid leaching raised the Si/Al ratio to approximately 8 (measured by EDX and MASNMR).

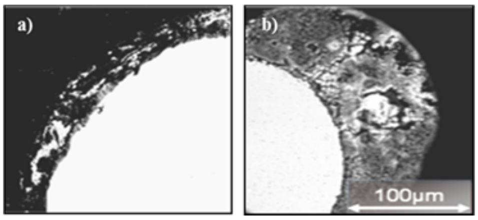

Figure 4 : BSE images showing the thickness of the layers grown on the FeCralloy rods after 72 h crystallisation time a) Zeolite Y (20 - 25 µm) and b) ZSM-5 (100 - 120 µm)

The coated rods were embedded in a resin and using back scattering electron imaging (BSE) mode it was possible to obtain the thickness of the different catalytic layers (Table 1). BSE images gave a proper understanding of the zeolite layers that were grown on the surface of the rods which can be seen in Figure 4, noting that the thickness of the ZSM-5 layer was approximately four times thicker than that of Zeolite Y. The alumina washcoat layer was found to be approximately 6 µm thick.

Table 1 : Thickness of layers supported on the FeCralloy rods as a function of synthesis time

Layer		Thickness (µm)
Transient Alumina Layer		3.7
Alumina Washcoat		6
ZSM-5 synthesised at different crystallisation times	4 h	5
	8 h	10
	12 h	50
	20 h	120
	72 h	147
Zeolite Y synthesised at different crystallisation times	8 h	2
	16 h	4
	24 h	4
	48 h	21
	72 h	23

3.2 XRD characterization

Using the Philips X'Pert PRO X-Ray Diffraction experiments were performed on the samples in the 2θ range of 0° - 50° and a scanning speed of 0.009 °/min. Slit widths of 1/4° and 1/2° were used for all the experiments. X'Pert Data viewer programme was used to analyse the results obtained from the XRD scan. XRD was performed to study the crystal growth of the zeolite on the rod surface and compared with the crystal growth in the bulk phase. These analyses confirmed that the increase in crystallisation time leads to an increase in the intensity of the XRD peaks of ZSM-5. It is worth noting that ZSM-5 crystallization starts earlier on the alumina-rich metal surface (12 h) whilst forming slower in the bulk. Following the growth of zeolite Y on the rods by XRD was more challenging due to the slow growth rate, but the typical reflection of the low angle (2θ = 6.1° - 10.4°) for the Zeolite Y was noticeable after 16 h. XRD pattern of zeolite Y on the rod showed the presence of small amounts of other phases after 72 h (potentially GIS, GME, CHA). A detailed XRD analysis of zeolite growth on the FeCralloy rods has been previously reported by Al-Rubaye and Garforth (Al-Rubaye and Garforth, 2014).

4. Catalytic Testing and Activity

4.1 Testing for dehydrogenation of Methylcyclohexane

The rods were tested for dehydrogenation of methylcyclohexane (MCH) in a fixed bed reactor. To obtain a detailed quantitative assessment of the selectivity toward the formation of toluene at various operating conditions, all samples were analysed in a GC-MS (Agilent Technologies, Model-6890N) equipped with a HP-5MS capillary column (50 m x 0.25 mm i.d.,5 % Phenyl and 95 % methylpolysiloxane). High conversions (50 % - 99 %) of MCH and increased selctivity (>98%) towards the formation of toluene were achieved at, 340 °C - 400 °C. Owing to the endothermic nature of the reaction there was an initial temperature drop of 10°C - 15°C at all reaction temperatures. The use of pelleted 1 wt. % Pt/Al_2O_3 for the same reaction conditions resulted in a temperature drop typically of 30 °C - 70 °C (Alhumaidan et al., 2010). The change in temperature profile when using structured catalysts can be seen in Figure 5. Long term life tests were performed at T=400 °C and W/F=14690 g s mol^{-1} on the developed catalyst and compared with a conventional commercial pelleted 1 wt. % Pt/Al_2O_3 catalyst (supplied by Sigma-Aldrich). This helped to gauge the stability of the prepared catalyst and to build the deactivation into the kinetic model for the system. Figure 6a describes the change in conversion over a period of 400 h. During the initial stages of the deactivation tests there appeared to be a sharp drop in conversion due to the deactivation of the more acidic sites. After a time period of 100 h the conversion stabilised.The structured catalyst showed high selectivity towards the formation of toluene (Figure 6b). The alumina coating was adherent post catalytic testing with a weight loss of only 0.8 %.

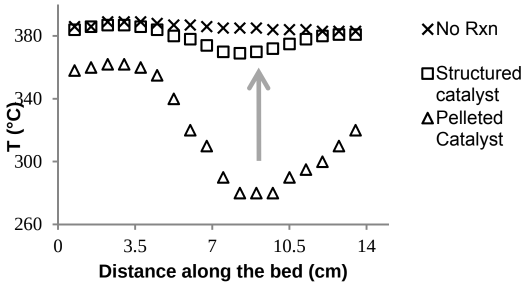

Figure 5 : Difference of temperature profile when using structured and pelleted catalysts at T=380 °C, P= 1bar and W/F= 14690 g s mol^{-1}

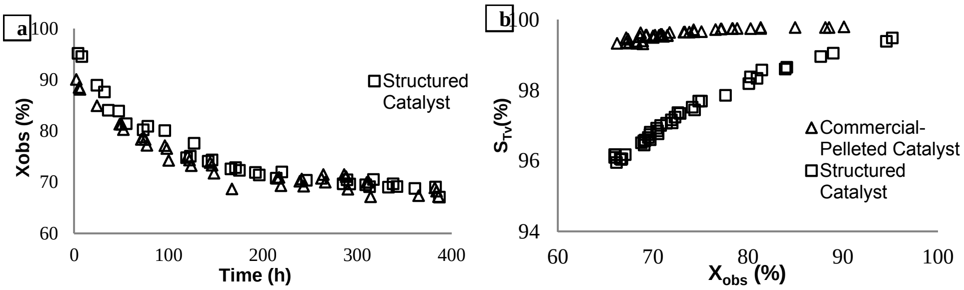

Figure 6: Long term life tests of 1wt % Pt/Al_2O_3 on FeCralloy in comparison to the conventional pelleted catalysts at T=400 °C and W/F=14690 g s mol^{-1} describing a) change in catalytic activity with time b) decreasing selectivity as the catalyst deactivates

4.2 Testing for n-heptane cracking

The catalytic activity of the zeolite films grown on the FeCralloy rods was studied by testing the developed catalysts for cracking of n-heptane. The results were compared with pelleted ZSM-5 and Zeolite Y catalysts tested under the similar range of operating conditions. To study the selectivity of the catalysts tested, all product samples were analysed using a GC-FID (Varian 3800 GC-FID) equipped with a PLOT Al_2O_3/KCl capillary column (50 m x 0.32 mm i.d.). The developed structured catalysts described similar catalytic selectivity as the conventional pelleted catalysts. The ZSM-5 catalysts are medium pore zeolites with regular 3D channels and due to the restricted space, secondary cracking reactions are limited hence neither catalyst showed deactivation. Both the ZSM-5 catalysts produced broadly the same product range with around 25 moles of propene ($C_3^=$) /100mols converted and 18 moles of butenes ($C_4^=$)/100 mols converted. The amount of secondary products was higher in the pelleted catalyst with approximately twice the moles of propane (C_3) and iso-butane (iC_4) /100 mols converted (Figure 7). As expected the wider pore Zeolite Y catalysts showed rapid deactivation over a time period of 125 min with the structured catalyst showing approximately half the catalytic activity when compared to the pelleted catalysts. This lower conversion was attributed to the non-optimised packing of the structured catalysts in the reactor which probably resulted in voids and channelling. Despite the differing conversion of the pelleted Y catalyst, the product selectivity of both catalysts at 450 °C was quite similar with respect to $C_3^=$ and $C_4^=$ being the major products and negligible amounts of C_1 and C_5. The apparent activation energy suggested that surface reaction kinetics predominated with values of 60 ± 3 kJ mol^{-1} for all catalysts.

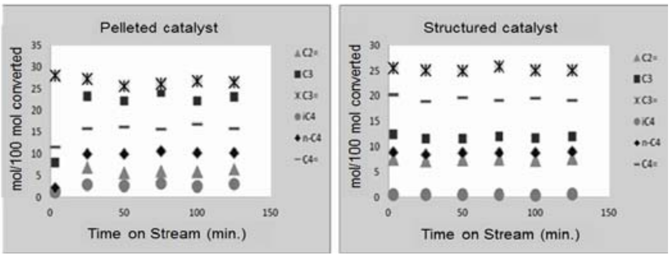

Figure 7: Selectivity of ethene ($C_2^=$), propane (C_3), propene ($C_3^=$), iso-butane (iC_4), n-butane (n-C_4) and total butenes ($C_4^=$) for pelletted and structured ZSM-5 at 450 °C

5. Conclusions

This work showed that it was possible to generate well adherent catalytic films of alumina and zeolites (ZSM-5 and Y). The developed catalysts were characterized through a range of systems such as SEM, EDX and XRD before being tested catalytically. The catalytic activity and selectivity of the catalysts compared with conventional pelleted catalyst systems tested under the same operating conditions. Although the zeolites grown on the FeCralloy rods had a lower catalytic activity when compared to the pelleted system this was predominantly a result of poor catalyst packing. The alumina loaded FeCralloy catalyst showed high activity and selectivity and helped significantly reduce the temperature drop in the reactor system when tested for a highly endothermic reaction and thus demonstrated improved heat transfer characteristics and kinetic interpretation.

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