

Growing Zeolite Y on FeCrAlloy Metal

Rana Th. A. Al-Rubaye, Burcin Atilgan, Richard J. Holmes, and Arthur A. Garforth

Abstract—Structured catalysts formed from the growth of zeolites on substrates is an area of increasing interest due to the increased efficiency of the catalytic process, and the ability to provide superior heat transfer and thermal conductivity for both exothermic and endothermic processes.

However, the generation of structured catalysts represents a significant challenge when balancing the relationship variables between materials properties and catalytic performance, with the Na_2O , H_2O and Al_2O_3 gel composition paying a significant role in this dynamic, thereby affecting the both the type and range of application.

The structured catalyst films generated as part of this investigation have been characterised using a range of techniques, including X-ray diffraction (XRD), Electron microscopy (SEM), Energy Dispersive X-ray analysis (EDX) and Thermogravimetric Analysis (TGA), with the transition from oxide-on-alloy wires to hydrothermally synthesised uniformly zeolite coated surfaces being demonstrated using both SEM and XRD. The robustness of the coatings has been ascertained by subjecting these to thermal cycling (ambient to 550°C), with the results indicating that the synthesis time and gel compositions have a crucial effect on the quality of zeolite growth on the FeCrAlloy wires.

Finally, the activity of the structured catalyst was verified by a series of comparison experiments with standard zeolite Y catalysts in powdered pelleted forms.

Keywords—FeCrAlloy, Structured catalyst, and Zeolite Y.

I. INTRODUCTION

THIN layers of zeolite catalyst have previously been coated on a range of metal substrates, including stainless steel, carbon and $\alpha\text{-Al}_2\text{O}_3$, with the choice of substrate influencing the performance of the catalyst [1], however metallic substrates such as FeCrAlloy offer high mechanical resistance, high thermal conductivity and the use of wires as the catalyst support presents a low pressure drop in relation to standard packed bed catalysts [2]. One of the major advantages of using a FeCrAlloy support is that the aluminium can be oxidised at high temperatures to form a thin film of aluminium oxide

(Al_2O_3) on the surface [3, 4], and this oxide layer can then be used to anchor and subsequently grow an active zeolite phase [5]. The surface growth and development of a structured catalyst thus provides a significant enhancement on the surface area available for any catalysis reactions, with the ability to vary the physical properties (residence time, dispersion, stability, heat and mass transfer and pressure drop across the bed) via growth conditions improving the range of processes and applications compatible with the system [6, 7].

The method of attachment of the Zeolite crystal onto the FeCrAlloy surface can be achieved through a number of routes. The first is the use of a dip coating method, which uses a binder to glue pre-synthesised zeolite crystals to the metal surface. An alternative method is the use of an in-situ growth of the zeolite crystals onto the substrate using the alumina formed on the metal surface as a partial source of Al required for the zeolite preparation [8]. In all cases, the pre-treatment step is crucial, as it requires the formation of uniformly thin aluminium oxide layer on the metal surface. This film then increases the wetting of the support by the synthesis gel mixture and/or promotes the nucleation of zeolite crystals [9-15].

As such, this paper presents a study of the effects of both the zeolite gel composition and in-situ zeolite gel crystallisation time for zeolite Y film formation, with an evaluation of their catalytic performance for n-heptane cracking.

II. EXPERIMENTAL

A. Support Pre-Treatment

FeCrAlloy annealed wires (0.5 mm diameter) were supplied by GoodFellows with a pre-determined chemical composition by weight of Fe 72.8%, Cr 22%, Al 5%, Y 0.1%, and Zr 0.1 %.

The pre-treatment process was as follows; Oxide removal using No.100 glass paper; immersion in 0.1M KOH at 25°C for 10 minutes, followed by 0.1M HNO_3 solution at 80°C for 5 min [13]. The wires were then rinsed with de-ionised water, placed in acetone and ultrasonicated for 10 minutes (Cam sonix C080T) and finally placed in de-ionised water and ultrasonicated for 10 minutes.

Thermal pre-treatment of the wires was conducted in a muffle furnace (Progen Scientific), ramped at a rate of $10^\circ\text{C}/\text{min}$ and held at 1000°C 4h. The wire samples were suspended over a stainless steel support to ensure even oxidation of the surfaces and then removed from the furnace and rapidly cooled to ambient temperature.

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B. Preparing of the Structured Catalyst

The zeolite Y precursor gel was prepared from sodium aluminate (Fisher Scientific), colloidal silica (Ludox AS-40) and sodium hydroxide (Sigma-Aldrich), with the composition range was carefully controlled within the range shown in the literature [16] with the starting gel composition being $3.3\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10\text{SiO}_2:120\text{H}_2\text{O}$. The pre-treated FeCrAlloy support wires were cut into lengths (2.5 cm) and inserted vertically into the gel mixture, with the synthesis performed under autogenous pressure at 100°C for 4 days. The compositions were investigated and are summarised in Table I. By varying the amounts of the sodium aluminate (Fisher Scientific), Colloidal silica (Ludox AS-40 from Sigma-Aldrich) and sodium hydroxide (Sigma-Aldrich) use, it was possible to change the starting gel composition to be $x\text{Na}_2\text{O}:y\text{Al}_2\text{O}_3:10\text{SiO}_2:z\text{H}_2\text{O}$, where as the $x=2.3\text{--}4.3$, $y=0.75\text{--}1.25$, and $z=120\text{--}240$ in molar ratios (Table I), and in order to allow comparison with the literature, the gel compositions used in this work are highlighted in Fig1.

After the hydrothermal synthesis, both the zeolite gel precipitated in the autoclave and the coated wires were removed, rinsed and then ultrasonicated in de-ionised water for 10 min, where the as-made Na-Y zeolite powder (1 g) and all the structured zeolite were ion exchanged using a 0.5M ammonium nitrate solution (NH_4NO_3 , purity > 98% Sigma-Aldrich) at 80°C under constant reflux conditions with constant stirring (60–100 rpm) for 1 hour. These were then washed thoroughly with deionised water and dried at 100°C .

Post ion-exchange, the zeolite Y powder and structured zeolites were shown to have 3%Na content and were subjected to dealumination in order to produce an ultra-stable form of the zeolite Y. The dealumination process was performed using acidified ammonia nitrate, and the $\text{NH}_4\text{-Y}$ powder or structured $\text{NH}_4\text{-Y}$ zeolites were mixed with an ammonium nitrate solution (15% wt.) and the pH adjusted from 4.1 to 2.48 by the addition of HNO_3 (70%wt., Camlab Chemical, UK)[17].

TABLE I
DIFFERENT MOLAR COMPOSITIONS OF THE NaY GELS

COMPOSITION	NaAlO_2 (g)	NaOH (g)	Ludox (g)	H_2O (g)
$2.3\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10\text{SiO}_2:120\text{H}_2\text{O}$	1	0.52	7.52	6.02
$2.7\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10\text{SiO}_2:120\text{H}_2\text{O}$	1	0.68	7.52	5.98
$3.0\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10\text{SiO}_2:120\text{H}_2\text{O}$	1	0.80	7.52	5.95
$3.3\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10\text{SiO}_2:120\text{H}_2\text{O}$	1	0.92	7.52	5.92
$4.3\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10\text{SiO}_2:120\text{H}_2\text{O}$	1	1.32	7.52	5.84
$3.3\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10\text{SiO}_2:180\text{H}_2\text{O}$	1	0.92	7.52	11.35
$3.3\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10\text{SiO}_2:240\text{H}_2\text{O}$	1	0.92	7.52	16.67
$3.3\text{Na}_2\text{O}:0.75\text{Al}_2\text{O}_3:10\text{SiO}_2:120\text{H}_2\text{O}$	1	1.35	10.04	7.93
$3.3\text{Na}_2\text{O}:1.25\text{Al}_2\text{O}_3:10\text{SiO}_2:120\text{H}_2\text{O}$	1	0.65	6.02	4.72

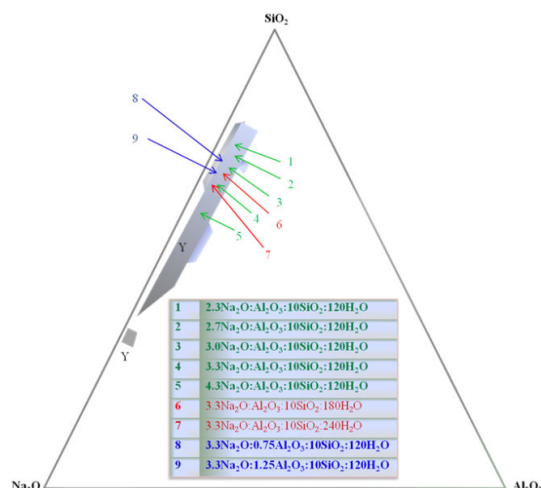


Fig. 1 Different molar compositions of the NaY gels

III. CHARACTERISATION

The crystal growth of the zeolite on the wire surface was compared with the crystal growth in the bulk phase using a Philips X' Pert PRO X-ray diffraction meter scanning $0.000832^\circ/\text{min}$ slit widths $1/8^\circ$ and $1/4^\circ$ over a 2θ range of $3^\circ\text{--}50^\circ$. The powder zeolite samples were analysed similarly however a faster scanning rate of $0.0289^\circ/\text{min}$ was used.

Calcination and adhesion of the zeolite layers for all samples was studied using thermogravimetric analyzer (Q5000-IR TA Instruments), and calcination was carried out by heating in air (25 ml/min) from ambient at a rate of $1^\circ\text{C}/\text{min}$ to 550°C where the temperature was held for 480 min. The adhesion of the zeolite layers was tested by thermal cycling selected wires between ambient to 550°C at $10^\circ\text{C}/\text{min}$. The wires were held at both the high and low temperatures for 30 minutes and the process was repeated five times.

Surface morphology and chemical analysis were carried out on gold-coated powder and wires samples under high vacuum using the Quanta200 FEI scanning electron microscopy and the Genesis software.

Energy Dispersive Spectrometry EDS spectroscopy was used to identify elements and count the impinging X-rays based upon their characteristic energy levels [18]. Since, a well polished surface is required for quantitative/qualitative analysis and concentration maps, two techniques were used. Firstly, the external surface of the wire was analysed directly using X-ray spot analysis on carbon or gold-coated samples. Secondly the analysis of the elements dispersed across different layers of the metal, oxide layer and coated zeolite was carried out. Wires samples were prepared by immersion vertically in a resin and then sectioned with diamond saw to obtain a clean surface. This surface was then ground with SiC sandpaper and polished with Al_2O_3 in order to obtain a smooth flat surface. The samples were then rinsed with alcohol to remove contamination and finally carbon or gold-coated.

IV. CATALYTIC CRACKING PERFORMANCE OF CATALYTIC FILMS

The behavior of the structured and pelleted catalysts was studied using a well characterised n-heptane cracking reaction in a 4 mm i.d. quartz reactor. Bundles of the USY structured catalyst wires were loaded into a reactor (2.5 cm length x 0.05 cm diameter) with a zeolite equivalent weight for Y of 0.03 gm. For comparison, the same bed length of pelleted USY zeolite catalyst of 1 gm (425–500µm pellets) were tested. The catalysts under test were sandwiched between two layers of quartz wool and the microreactor was located in the middle of the furnace (Carbolite MTF 12/12A). The catalysts were activated prior to the cracking by heating from 25°C to 550°C in air (1°C/min, 25ml/min) and held isothermally at 550°C for 16 hours. The n-heptane (99.99% Fluka) was supplied by flowing nitrogen through three bubblers connected in series and placed in an ice bath to maintain a constant temperature. All the stainless steel pipes connected between the reactor and the GC were lagged with heating wire (Electrothermal PLC, UK) and maintained at approximately 110°C to avoid any condensation of the reactant and products. A Varian 3400 FID GC fitted with a PLOT $\text{Al}_2\text{O}_3/\text{KCl}$ capillary column (50m×0.32 mm i.d.) was connected to the reactor and samples analysed at regular intervals between 5 and 125 min. All catalysts were studied at 450°C with a W/F= 42 g.h/ mol and the activity and selectivity reported.

V. RESULTS

A. Optimum the Gel Composition of Zeolite Na-Y Gel

Synthesis of zeolite Na-Y was performed using aluminosilicates gels of the general mole composition $x\text{Na}_2\text{O}:y\text{Al}_2\text{O}_3:10\text{SiO}_2:z\text{H}_2\text{O}$; where $x=2.3-4.3$, $y=0.75-1.25$, $z=120-240$ to study the properties of the zeolite growing on FeCrAlloy. For all the samples the crystallisation time was 4 days for the powder and structured zeolite.

The XRD data of the Na_2O molar ratio changed between 2.3 and 4.3 for powder samples confirmed the presence of zeolite Na-Y. Phase-pure zeolite Na-Y was obtained from gel composed of $2.7\text{Na}_2\text{O}$, $3.0\text{Na}_2\text{O}$ and $3.3\text{Na}_2\text{O}$. However; the composition of the 4 day aged sample presented different XRD patterns because of the forming of different phases. The XRD patterns in Fig (2) illustrated the crystallisation of Faujasite (FAU), and Na-P1 (GIS) type zeolites together for the $4.3\text{Na}_2\text{O}$. Comparison of crystallinities in Table II Na_2O enhanced the crystal growth of the zeolite Na-Y however at higher Na_2O values the picture was more confusing. For the structured zeolite, the zeolite films were hard to characterise with the ratio being less than $4.3\text{Na}_2\text{O}$ and at $4.3\text{Na}_2\text{O}$ ratio the major phase was the Na-P1 (GIS) type zeolites as shown in Fig 2.

TABLE II
DIFFERENT GEL COMPOSITIONS EFFECT ON THE CHARACTERISATION PROPERTIES

COMPOSITION CHANGE OF THE GEL COMPOSITION				
Na_2O Ratio	2.3	2.7	3	3.3
H_2O Ratio	120	120	120	120
Al_2O_3 Ratio	1	1	1	1
Crystallinity %	34	47	67	100
Si/Al Ratio	2.97	2.86	2.76	2.47
Weight gain %	0.1	0.5	0.2	0.6
Cumulative coverage (g/m^2)	1.3	4.8	2.0	5.3
Na_2O Ratio	2.3	2.7	3	3.3
H_2O Ratio	120	120	120	120

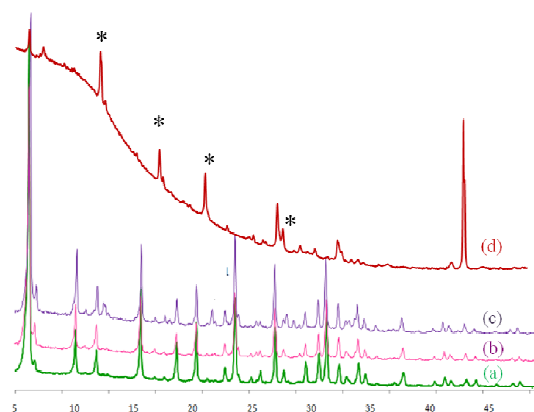


Fig. 2 XRD patterns the crystallisation of different phases for (a) $2.3\text{Na}_2\text{O}$, (b) $3.3\text{Na}_2\text{O}$, (c) $4.3\text{Na}_2\text{O}$ molar ratio for powder compared with (d) $4.3\text{Na}_2\text{O}$ structured catalyst. Impurities in the zeolite Y phase are highlighted (*)

It was shown that the crystallisation rate decreased zeolite Na-Y when there was an increase in the H_2O mole ratio using the formula; $3.3\text{Na}_2\text{O}:\text{Al}_2\text{O}_3:10\text{SiO}_2:z\text{H}_2\text{O}$ where the $z=120, 180$ and 240 , and the effects of modifying the aluminium ratio for the synthesised zeolite Na-Y was monitored using the aluminium molar ratios of 0.75, 1 and 1.25. The samples were prepared following the same procedure as for the composition study in order to ensure that the properties of the each zeolite Na-Y sample remained constant for both the zeolite powder and the structured zeolite. The crystallisation time of 4 days was found to be suitable in order to produce a pure phase of the zeolite Na-Y, with the crystallinity of the zeolite Na-Y seen to be decreased when there was an increase in the Al_2O_3 ratio in the gel composition. The growth on the metal surface was determined using the XRD with the pure zeolite Na-Y phase detected at a typical low angle reflection of ($2\theta = 6.1 - 10.4^\circ$) for $0.75\text{Al}_2\text{O}_3$ (Fig 3).

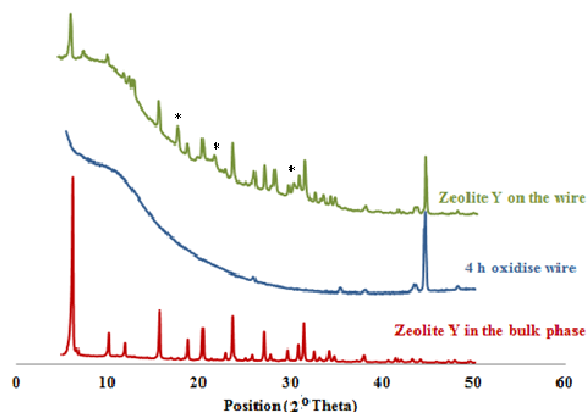


Fig. 3 XRD patterns of wire surface oxidised for 4 h, structured zeolite and zeolite Y in the bulk phase with 0.75 Al_2O_3 ratios for both. Impurities in the zeolite Y phase are highlighted (*)

SEM analyses of powder samples demonstrated that there was no significant change in the crystal size and morphology when increasing the Na_2O and H_2O . Whereas, in the Al_2O_3 ratio case, increasing Al_2O_3 ratio from 0.75 to 1.25, resulted in crystals forming with sharp edges and small sizes (Fig 4). The SEM images of the structured zeolite in Fig 5 illustrate that the zeolite crystals growth on FeCrAlloy has the same size and shape as the zeolites found in the bulk phase. However, the zeolite coverage (namely the increase in the mass of pure zeolite film grown on the FeCrAlloy and thus the surface area of the FeCrAlloy wires (g/m^2)) was different depending on the ratios of Na_2O and Al_2O_3 (Table II). Higher ratios of Na_2O led to thicker and eventually lumpier coatings with major formation of Na-P1 (GIS) type zeolites suggesting that a combination of coating and alumina dissolution was occurring.

The ESEM verified a scarce development of crystals was uniformly distributed on the FeCrAlloy wire surface with the change of the coverage and layer thickness attributed to the deposition of new small crystals on top of the existing ones.

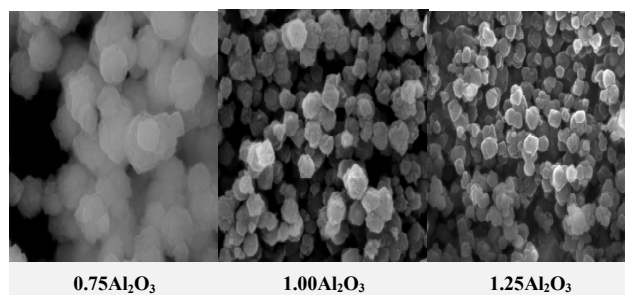


Fig. 4 SEM images of zeolite powder for different composition ($3.3\text{Na}_2\text{O}:\text{yAl}_2\text{O}_3:10\text{SiO}_2:120\text{H}_2\text{O}$; $\text{y}=0.75 - 1.0 - 1.25$)

The EDAX results for the different Na_2O mole ratio for both zeolite powder and structured zeolite samples demonstrated that by increasing the Na_2O and the Al_2O_3 ratios the Si/Al ratio is decreased from 2.97 to 2.07 and from 2.69 to 2.38, respectively, whilst the change in the H_2O ratio had no effect on the Si/Al ratio.

As was expected from the pure zeolite preparation, the amount of Na_2O had a significant effect on the crystallisation on the alloy support, with higher Na_2O leading to thicker and eventually lumpier coatings with Na-P1 (GIS) type zeolites. Again water increase had little effect, but an increase in the molar ratio of Al_2O_3 in the composition affected the morphology and the structure of the zeolite coating surface and thus led to the formation of zeolite Y pure phase with trace impurities.

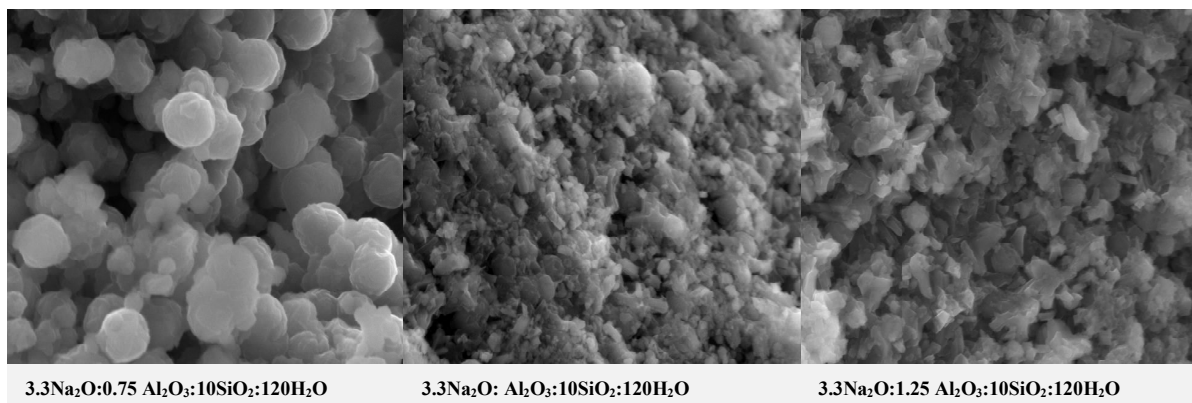


Fig. 5 SEM images of zeolite powder for different composition ($3.3\text{Na}_2\text{O}:\text{yAl}_2\text{O}_3:10\text{SiO}_2:120\text{H}_2\text{O}$; $\text{y}=0.75 - 1.0 - 1.25$)

B. Calcination of Zeolite Na-Y

The calcination of the powder and structured Na-Y zeolite was studied by monitoring the weight loss using TGA, with the weight losses during heating is due to the loss of the

volatile components, chemisorbed water and physisorbed water (Fig. 6 and Fig. 7).

The weight loss for all samples below 250°C was due to desorption of moisture from both the powder and structured Na-Y zeolites as shown in Fig 6. For powder and structured Na-Y zeolite the major reduction was 19.36% and 1.46% due

to loss water and volatile materials from zeolite framework structure. This was confirmed in the derivative thermogravimetric graphs (Fig. 7), which show small peaks below 250°C.

The weight loss from the Na-Y zeolite powder framework was 19.36%, while in the structured zeolite framework was 1.46%, where it was found that the weight of the Na-Y zeolite layer on the FeCrAlloy was approximately 8.1% of the total weight of the structured catalyst. Study of the morphology and the crystals size of the powder and structured Na-Y zeolite showed there was no noticeable change in the crystals size nor shape after the calcination process for the powder and structured Na-Y zeolite.

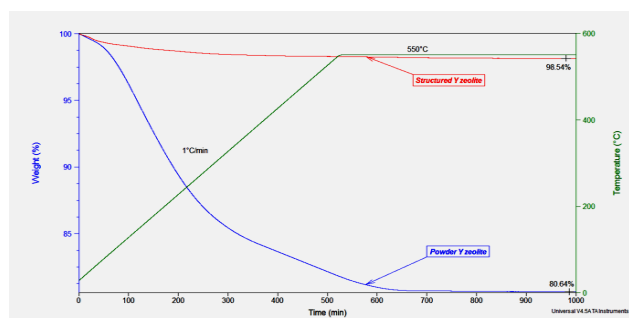


Fig. 6 Thermal thermogravimetric analysis for the calcination of powder and structured Na-Y

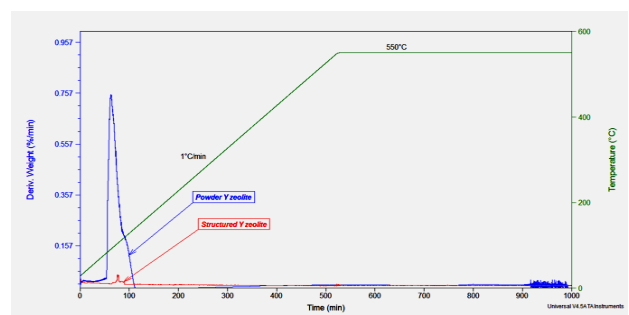


Fig. 7 Derivative thermogravimetric analysis for the calcination of powder and structured Na-Y

C. Catalyst Test for Y Pelleted and Structured Catalyst

The Si/Al ratio for post synthetically modified powder and structured zeolite Y structured increased from 2.7 to approximately 8 (as determined by SEM/EDAX), with the catalytic activity of Y pellets (425–500µm) and bundles of structured Y catalyst grown on wires determined using n-heptane cracking in a fixed bed micro-reactor. The conversion of n-C₇ for an equivalent amount of catalyst at 450°C and W/F=42 g.h/mol for the two experiments and is presented in Fig. 8. As expected both catalysts deactivate rapidly with the pelleted Y catalyst showing the greater activity.

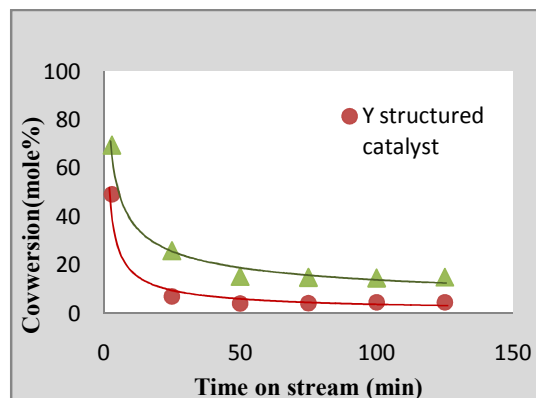


Fig. 8 Conversion of n-C₇ cracking for pelleted and structured USY at 450°C

Despite the higher conversion of the pelleted Y catalyst, the product selectivities of both catalysts at 450°C were quite similar with C₃= and C₄= being the major products with negligible amounts of C₁ and C₅. The strongest sites deactivated first [19], and as such there was a rapid decrease in i-C₄ production accompanied by a rapid increase in C₃= and C₄= with time. Both catalysts behaved similarly and it was not too surprisingly apparent that the activation energy of 56 kJ mol⁻¹ was determined for both.

VI. DISCUSSION AND CONCLUSIONS

Zeolite Y was successfully synthesised using a variety of gel compositions. After 4 days, when the Na₂O amount was increased, the XRD of the 4.3Na₂O:Al₂O₃:10SiO₂:120H₂O sample illustrated the crystallisation of Faujasite (FAU), and Na-P1 (GIS) type zeolites together. Altering the Al₂O₃ content in the gel also had an effect on the rate of crystallisation, the crystal size and the morphology, as the Al₂O₃ molar ratio in the composition increased, the crystal size decreased.

As was expected from the pure zeolite preparation, the amount of Na₂O has a significant effect on the crystallisation on the alloy support, with higher Na₂O concentrations leading to thicker and eventually lumpier coatings with Na-P1 (GIS) type zeolites. Again water increase had little effect but an increase in the molar ratio of Al₂O₃ in the composition affects the morphology and the structure of the zeolite coating surface and thus led to the formation of zeolite Y pure phase with trace of impurities. Finally n-C₇ cracking revealed lower cracking activities for the structured catalysts with the most likely explanation being that the imperfect packing of the fixed bed micro-reactor allowed some degree of channelling of the reactant resulting in lower conversions. However, the acid-leached zeolite Y (Si/Al = 8) structured catalysts showed similar product selectivities to their Pelleted counterparts. Increased i-C₄ yields indicated more secondary reactions in the case of the Pelleted catalysts supporting the lower activity observed for the structured catalysts. Apparent activation energies of approximately 60 kJmol⁻¹ for all catalysts suggested similar reaction mechanisms and that the surface reaction was controlling.

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REFERENCES

- [1] J. Jansen, et al., "Zeolitic coatings and their potential use in catalysis," *Microporous and Mesoporous Materials*, vol. 21, pp. 213-226, 1998.
- [2] J. M. Zamaro, et al., "ZSM5 growth on a FeCrAl steel support. Coating characteristics upon the catalytic behavior in the NO_x SCR," *Microporous and Mesoporous Materials*, vol. 115, pp. 113-122, 2008.
- [3] C. Badini and F. Laurella, "Oxidation of FeCrAl alloy: influence of temperature and atmosphere on scale growth rate and mechanism," *Surface and coatings technology*, vol. 135, pp. 291-298, 2001.
- [4] J. E. Samad, et al., "Structured catalysts via multiple stage thermal oxidation synthesis of FeCrAl alloy sintered microfibers," *Chemical Engineering Journal*, vol. 168, pp. 470-476, 2011.
- [5] I. Yuranov, et al., "Zeolite/sintered metal fibers composites as effective structured catalysts," *Applied Catalysis A: General*, vol. 281, pp. 55-60, 2005.
- [6] M. Tatlier, "Adsorption Heat Pumps Utilizing Zeolite Coatings Grown on Metal Surfaces.," Master, Istanbul Technical University, Turkey, 2001.
- [7] A. Dabrowski, *Adsorption and its applications in industry and environmental protection* vol. 120: Elsevier, 1999.
- [8] V. Meille, "Review on methods to deposit catalysts on structured surfaces," *Applied Catalysis A: General*, vol. 315, pp. 1-17, 2006.
- [9] R. Munoz, et al., "Zeolite Y coatings on Al-2024-T3 substrate by a three-step synthesis method," *Microporous and Mesoporous Materials*, vol. 86, pp. 243-248, 2005.
- [10] Z. Wang, et al., "Synthesis of thin silicalite-1 films on steel supports using a seeding method," *Microporous and Mesoporous Materials*, vol. 52, pp. 191-197, 2002.
- [11] S. Mintova, et al., "Adhesivity of molecular sieve films on metal substrates," *Zeolites*, vol. 17, pp. 462-465, 1996.
- [12] X. Wu, et al., "Influence of an aluminized intermediate layer on the adhesion of a γ -Al₂O₃ washcoat on FeCrAl," *Surface and coatings technology*, vol. 190, pp. 434-439, 2005.
- [13] M. Valentini, et al., "The deposition of γ -Al₂O₃ layers on ceramic and metallic supports for the preparation of structured catalysts," *Catalysis today*, vol. 69, pp. 307-314, 2001.
- [14] M. Mies, et al., "Hydrothermal synthesis and characterization of ZSM-5 coatings on a molybdenum support and scale-up for application in micro reactors," *Catalysis today*, vol. 110, pp. 38-46, 2005.
- [15] J. Čejka, *Introduction to zeolite science and practice* vol. 168: Elsevier Science, 2007.
- [16] A. Kostinko John, "Factors Influencing the Synthesis of Zeolites A, X, and Y," in *Intrazeolite Chemistry*. vol. 218, ed: AMERICAN CHEMICAL SOCIETY, 1983, pp. 3-19.
- [17] J. G. Vassilakis and D. F. Best, "Novel zeolite compositions derived from zeolite Y," ed: Google Patents, 1991.
- [18] G. Danilatos, "Review and outline of environmental SEM at present," *Journal of Microscopy*, vol. 162, pp. 391-402, 2011.
- [19] P. A. Jacobs and J. A. Martens, "Introduction to acid catalysis with zeolites in hydrocarbon reactions," *Studies in Surface Science and Catalysis*, vol. 58, pp. 445-496, 1991.