

## Selective Cracking of Light Olefins to Ethene and Propene

Abeer Arjah<sup>ab\*</sup>, Mohammed Al-Bahar<sup>ab</sup>, Chaozhou Li<sup>b</sup>, Arthur A. Garforth<sup>b</sup>

<sup>a</sup> Chemicals Division, Research and Development Centre, Saudi Aramco, Dhahran, Saudi Arabia

<sup>b</sup> School of Chemical Engineering and Analytical science, The University of Manchester, UK, M13 9PL

abeer.arjah@postgrad.manchester.ac.uk

Catalytic cracking of olefins is becoming a more crucial process to produce valuable platform chemicals in the chemical industry such as ethane and propene. Steam cracking and fluid catalytic cracking can no longer meet the required demand of propene and ethene. Previous research has found that catalytic cracking showed the best results when an acidic mesoporous ZSM-5 catalyst was used. This paper reports the use of ZSM-5 with Si/Al=15, 40 and 70 and post synthetically modified large crystal ZSM-5 and silylated large crystal ZSM-5 (Si/Al = 70). The different catalysts were tested using variable flowrates and temperatures.

### 1. Introduction

Ethene and propene are two very important building blocks in the petrochemical industry (Miyaji, et al., 2013) with over 60 million tons of polyethylene made every year (The University of York, 2014). There are three main sources of ethene: steam cracking of ethane, propane and naphtha and catalytic cracking of gas oil that comes from crude oil in the FCC process (The University of York, 2014).

Propene is also a very important hydrocarbon being the basis of many chemicals and with around 67% being used to make polypropylene (Lin, et al., 2014). There is a very high demand for propene around the world and the demand is increasing (Figure 1) with an increasing gap between the supply of propene and the demand (Akah & Al-Gharami, 2015). This investigation aims to close the gap by increasing selectivity when catalytically cracking pentene and butene to ethene and propene reducing undesired side products. Catalytic cracking is a complicated reaction that is not very selective to the production of the desired product. Numerous side reactions occur, along with the main cracking reaction, which need to be suppressed. Some of these side reactions are dehydrogenation, aromatization and hydrogen transfer (Lin, et al., 2014).

The main focus of this research investigates the effect of Si/Al ratio, ZSM-5 crystal size and the effect of reducing activity through liquid phase silica deposition to decrease side reactions.

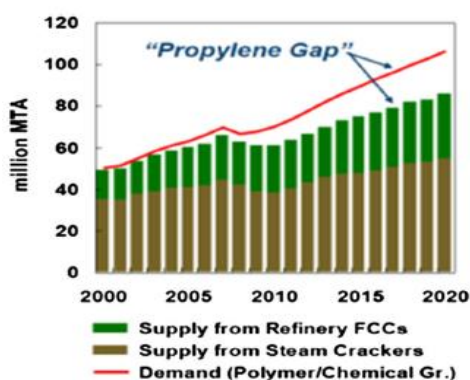


Figure 1: Propene gap, (Akah & Al-Gharami, 2015)

## 2. Materials and Methods

A mixed feed of trans- and cis-2-pentene (30:70) was used and the amount of hydrocarbon feed entering the reactor was controlled using a bubbler saturator and high purity helium. Owing to the volatility of the mixed feed (i.e. boiling point of 37 °C), the chiller was operated -17.7 °C and pentene supplied to the reactor held constant at 13.3 mol% in flowing helium (typically 40, 80 and 120 ml/min).

All catalysts were first pressed and pelleted (250 – 400 microns) before loading. 0.1g of catalyst into the glass reactor and positioned in the stable temperature zone of the furnace. After every run the catalyst was regenerated by allowing air to flow through the reactor at 450 °C for 4 hours. The normal sized ZSM-5 crystals were supplied by Zeolyst with Si/Al ratios of 15, 40 and 70. The large crystal ZSM-5 with a Si/Al ratio around 70 was synthesised in-house and modified by silylation using TEOS (Chen, et al., 1988).

### 2.1 Analysis

All products were in the gas phase and were analysed directly from the reactor using a Varian 3400 GC fitted with a 50 m x 0.32 mm PLOT Al<sub>2</sub>O<sub>3</sub>/KCl capillary column with FID detector. The GC was calibrated using a standard of 1 mole% made up of C<sub>1</sub>-C<sub>5</sub>. The typical error was about ±1.5%. Each sample was done once and was not duplicated. From the GC analysis, the conversion and the C<sub>2</sub>= and C<sub>3</sub>= selectivities were calculated using the Eq(1)-(3):

$$\text{Conversion (mol\%)} = 100 - (\text{cis-2-pentene} + \text{trans-2-pentene})_{\text{out (mol\%)}} \quad (1)$$

$$C_2^= \text{ Selectivity} = \frac{C_2^= (\text{out, mol\%})}{\text{Conversion}_{(\text{mol\%})}} \quad (2)$$

$$C_3^= \text{ Selectivity} = \frac{C_3^= (\text{out, mol\%})}{\text{Conversion}_{(\text{mol\%})}} \quad (3)$$

## 3. Results and Discussion

Key process parameters were tested such as flow rate and temperature. The acidity was varied and the crystal size altered as stated (normal = 0.5 microns, large crystal = 30 microns). Further post synthetic modified larger crystals were also tested and details are reported below in Table 1.

Table 1: Summary of Process Parameters Tested.

	450°C						550°C	
	Normal Crystal ZSM-5			Large Crystal	Silylated Large Crystal	Normal ZSM-5		
He Flow rate (ml/min)	W/F (g*hr/mol)	WHSV (h <sup>-1</sup> )	Si/Al=15	Si/Al=40	Si/Al=70	Si/Al≈70	Si/Al≈70	Si/Al=70
40	37	10	✓	✓	✓	✓	✓	✓
80	19	20	✓	✓	✓	✓	✓	✓
120	12	30	✓	✓	✓	✓	✓	✓

### 3.1 Effect of Catalyst Acidity (Si/Al ratio)

The effect of varying the acidity was studied by testing three Si/Al ratios (15, 40 and 70) at a constant WHSV (i.e. a constant helium flow rate, 80 ml/min) at 450 °C. Overall the conversions were very high at greater than 95%, however, clear differences in selectivity were observed. The best catalyst for olefin cracking was determined to be the most acidic ZSM-5 catalyst with Si/Al ratio of 15 with a decrease with decreasing acidity. The increase in Si/Al ratio significantly increased the C<sub>3</sub>= with little difference when changing from Si/Al = 40 to the further dealuminated catalyst. Conversely, the selectivity decreased for C<sub>2</sub>= with nearly a 50% reduction for the most dealuminated catalyst, as shown in Figures 2-4.

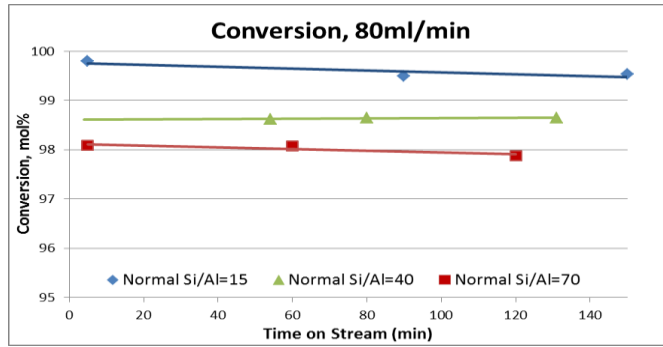


Figure 2: Effect of Si/Al ratio on Conversion, 80ml/min at 450°C

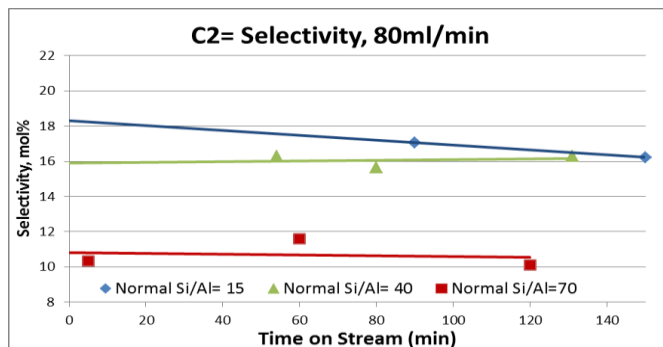


Figure 3: Effect of Si/Al ratio on C<sub>2</sub>= Selectivity, 80ml/min at 450°C

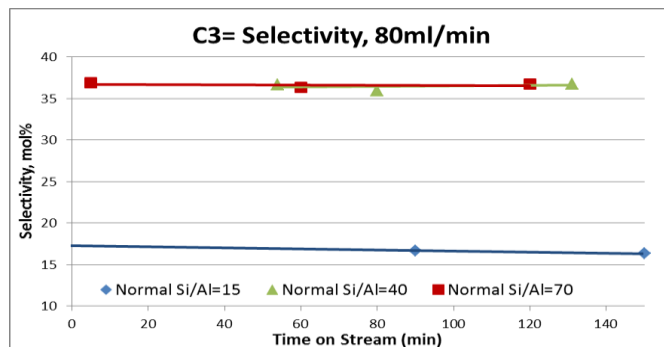


Figure 4: Effect of Si/Al ratio on C<sub>3</sub>= Selectivity, 80ml/min at 450°C

### 3.2 Effect of Weight Hourly Space Velocity (WHSV)

The weight hourly space velocity is:

**Errore. L'origine riferimento non è stata trovata.** 
$$\text{WHSV} = \frac{\text{Weight of } C_5}{\text{Weight of Catalyst}} * \frac{\text{g/hr}}{\text{g}} = \text{hr}^{-1} \quad (4)$$

This is determined by the flowrate entering the reactor. The WHSV determines the contact time with the catalyst, for example, the higher the WHSV means a faster flow rate and therefore less contact time. The less the hydrocarbon comes in contact with the catalyst the less side reactions take place and therefore should lead to higher C<sub>3</sub>= and C<sub>2</sub>= selectivity. Three WHSVs were tested 10, 20 and 30 h<sup>-1</sup> equivalent to a helium flow of 40, 80 and 120 ml/min using ZSM-5 with Si/Al ratio of 15 and a constant temperature of 450°C. As it is evident in the Figure 5, the conversions remain unchanged at very high mol% even as the WHSV increased. Meanwhile both C<sub>2</sub>= and C<sub>3</sub>= selectivity increased with the increase in WHSV, as is shown in Figure 6 and Figure 7.

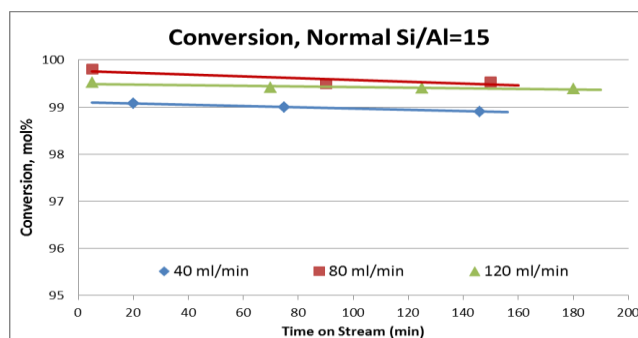


Figure 5: Effect of WHSV on Conversion, Si/Al=15 at 450°C

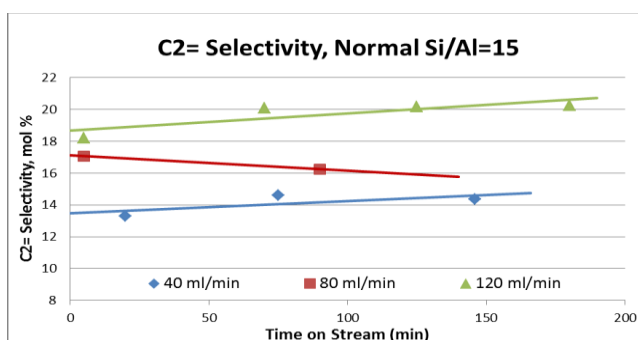


Figure 6: Effect of WHSV on C<sub>2</sub>= Selectivity, Si/Al=15 at 450°C

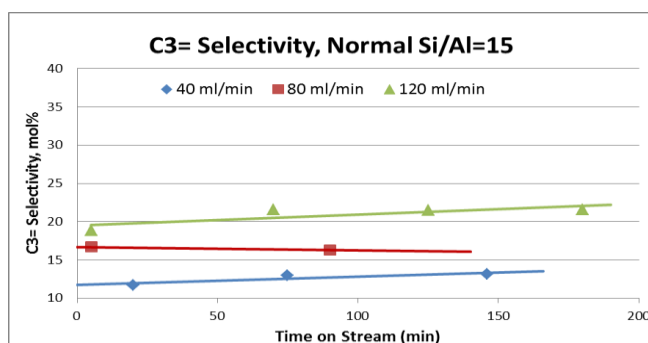


Figure 7: Effect of WHSV on C<sub>3</sub>= Selectivity, Si/Al=15 at 450°C

### 3.3 Effect of Large Crystal and Silylated Large Crystal ZSM-5

In an attempt to increase selectivity, large crystals of ZSM-5 were considered. Larger crystals have increased path length for diffusion and reduced external surface area. The cracking reactions occurring on the surface of the catalyst cause larger molecules to form reducing selectivity; as there is no diffusion control, the opportunity for the production of secondary products such as oligomerisation and subsequent ring closure lead to the formation of coke. Increasing the crystal size would in theory decrease the external surface area therefore reducing over reaction. Furthermore, increasing the crystal size also increases the path length of the catalyst pores therefore increasing the diffusion control and restricting the formation of bulky intermediates hence potentially increasing the selectivity towards lighter compounds.

As stated, the reactions often take place on the very active crystal external surface as well as within the pores of the catalyst. In order to reduce the activity of the surface, the surface was coated with a deactivating agent. Chemical liquid deposition (CLD) of silica was carried out using tetraethyl orthosilicate (TEOS) otherwise known as silylation. Conversion remained very high with both the large crystal ZSM-5 prior to and post silylation as shown in Figure 8. As for the C<sub>2</sub>= selectivity, Figure 9, both the large crystal and the silylated large crystal ZSM-5 increased selectivity by about 5% over the normal size ZSM-5 (Si/Al=70). The same behaviour

was noticed for the  $C_3=$  selectivity with the large crystal and silylated large crystal in increasing with both modifications.

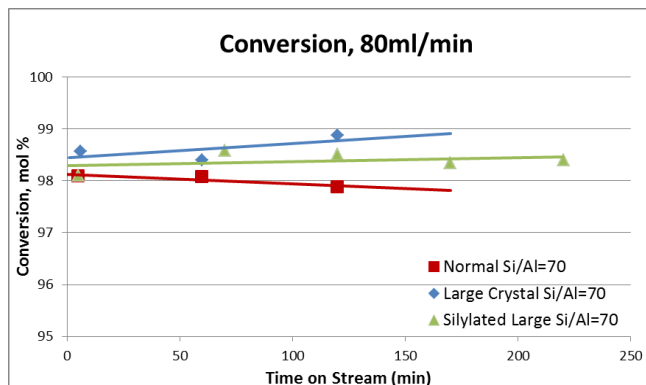


Figure 8: Effect of Large Crystal and Silylated Large Crystal on Conversion, Si/Al=15 at 450°C

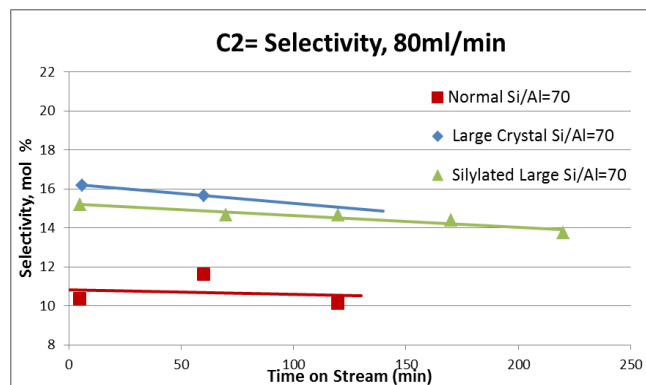


Figure 9: Effect of Large Crystal and Silylated Large Crystal on  $C_2=$  Selectivity, Si/Al=15 at 450°C

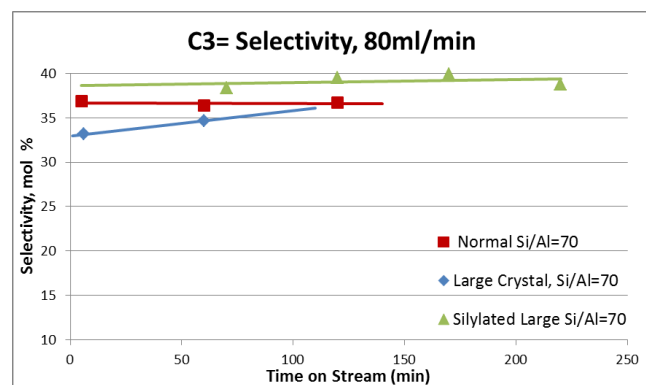


Figure 10: Effect of Large Crystal and Silylated Large Crystal on  $C_3=$  Selectivity, Si/Al=15 at 450°C

### 3.4 Effect of Temperature

The typical process temperature for fluid catalytic cracking (FCC) were used as a guide to determine the most fitting temperatures at which the olefin cracking was to be carried out. Previous research showed that a decrease in conversion and an increase in  $C_2=$  and  $C_3=$  with an increase in temperature (Zhu, et al., 2005). This behaviour was observed until a temperature of 620 °C after which the selectivity of both began to decrease. An increase in temperature suppressed the alkene hydrogen transfer reaction which leads to less undesired by-products such as  $C_1-C_5+$ . A temperature increase above 620 °C can lead to an increase in cracking reactions and an increase in aromatization of  $C_5+$  cyclization. Aromatics form when  $C_3$  and  $C_4s$

dimerize or oligomerise to form longer chains which then back bite to form ring structure. To study the temperature effect two temperatures were tested (450 and 550°C) at a constant 80ml/min flow rate and constant Si/Al ratio= 70. It was noticed that when the temperature increased the conversion remained very high over 6 hours. With the temperature increase, the C<sub>2</sub>= selectivity almost doubled from an 8% to a 16%. The C<sub>3</sub>= selectivity also increased with the increase in temperature from a 30% to almost 40%.

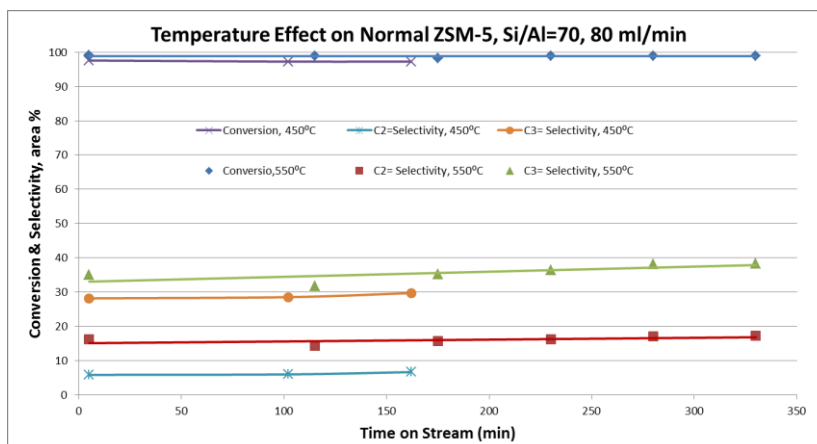


Figure 11: Effect of Temperature on Conversion, C<sub>2</sub>= Selectivity and C<sub>3</sub>= Selectivity, Si/Al=70 & 80ml/min

#### 4. Conclusions

Overall conversion for all catalysts was high at about 95%+ with only a slight decrease in conversion with time due to mild coking. As the flow rate was increased and contact time reduced, both C<sub>2</sub>= and C<sub>3</sub>= selectivity increased. When the Si/Al ratio was increased, conversion decreased along with C<sub>2</sub>= selectivity, but C<sub>3</sub>= selectivity improved markedly. Both larger crystal and silylated ZSM-5 showed improvement in C<sub>2</sub>= selectivity over the smaller crystal, Si/Al = 70, with similar C<sub>3</sub>= selectivity. The best results were observed for the silylated large crystal ZSM-5 and at elevated temperatures. Further research is focusing on this catalyst with additional phosphorus modification.

#### Acknowledgements

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