

OLIGOMERIZATION AND LIQUEFACTION OF ETHYLENE OVER SILICA - ALUMINA SUPPORTED NICKEL CATALYST

S. A. Kareem,
Department of Chemistry, University of Ilorin, Ilorin, Nigeria

ABSTRACT

Silica - alumina support was loaded with nickel using ion-exchange method. Catalyst formed was used to oligomerize ethylene gas in a packed bed reactor operated at 100 - 300°C under a pressure of 500psi and WHSV = 2.25. GC analysis of the liquid products formed indicated the formation of even carbon number olefins in the range C₄ - C₁₂. The catalyst was found to be temperature unaffected within the operation range in their product selectivities.

INTRODUCTION

Alkenes are generally available in the industry primarily through petroleum cracking. The smaller alkenes are obtained through fractional distillation of petroleum crude and can be converted into various aliphatic compounds. The even number alkenes, or α - olefins, are normally produced by controlled ionic polymerization of ethylene using Ziegler - Natta catalysts and homogeneous catalytic reaction method. Alpha olefins in the C₆ - C₁₂ range can be consumed for octane number boosting in the petroleum industry, while the 1 - alkene portions in the C₁₂ - C₂₀ range are consumed primarily in the detergent industry¹.

Alkenes generally, and specifically the light portion, are important feed stocks for the petrochemical industries and a lot of work has been done on obtaining them through methanol conversion²⁻⁴. In the conversion of methanol to olefins, effective selectivity to light alkenes is usually achieved by modifying the zeolite, ZSM-5 structure through aluminium replacement/exchange by other metals such as Mn, Mg, Rb, Ca, Ba, etc^{5,6}.

In the work reported here, high silica zeolite obtained from CSIR (South Africa) was ion-exchanged with nickel. The ion-exchanged zeolite was then evaluated in a plug-flow reactor for ethylene conversion to higher alkenes. The reaction was carried out in a stainless steel tubular reactor, 14 inch length and 0.5 inch nominal diameter. Suggested experimental conditions from published work⁷ on ethylene oligomerization reactions are low temperature, high pressure and high weight

hourly space velocity (WHSV) for the product cuts such as desired in this work. Therefore, reaction pressure of 500psig and WHSV of 2.25 were first established at 50°C, the temperature was then varied in increments of 50°C between 100°C and 300°C in testing for catalyst oligomerization activities.

EXPERIMENTAL

Catalyst preparation

To prepare the high silica - alumina zeolite obtained from CSIR (South Africa) for nickel catalyst loading, it was first calcined at 450°C for 3 hours. It was then ion-exchanged under reflux for 6 hours in ammonium nitrate solution (1M). The ion-exchanged sample was first dried at 110°C for 3 hours and then calcined at 450°C for 3 hours. The calcined sample was then ion-exchanged under reflux for 6 hours in nickel nitrate solution (1M). The sample was finally dried at 110°C for 3 hours. About 4% (wt) nickel was loaded on the support.

Catalyst loading/evaluation

The first step in the catalyst loading/evaluation procedure was the determination of the bulk density of the catalyst. A weighed amount of the prepared catalyst was then loaded in the packed bed reaction system as shown schematically in Figure 1. The catalyst density previously determined was then coupled with reactor's cross-sectional area to determine the bed height corresponding to the weighed amount (2.196g) of the catalyst and the gas flow corresponding to the desired WHSV

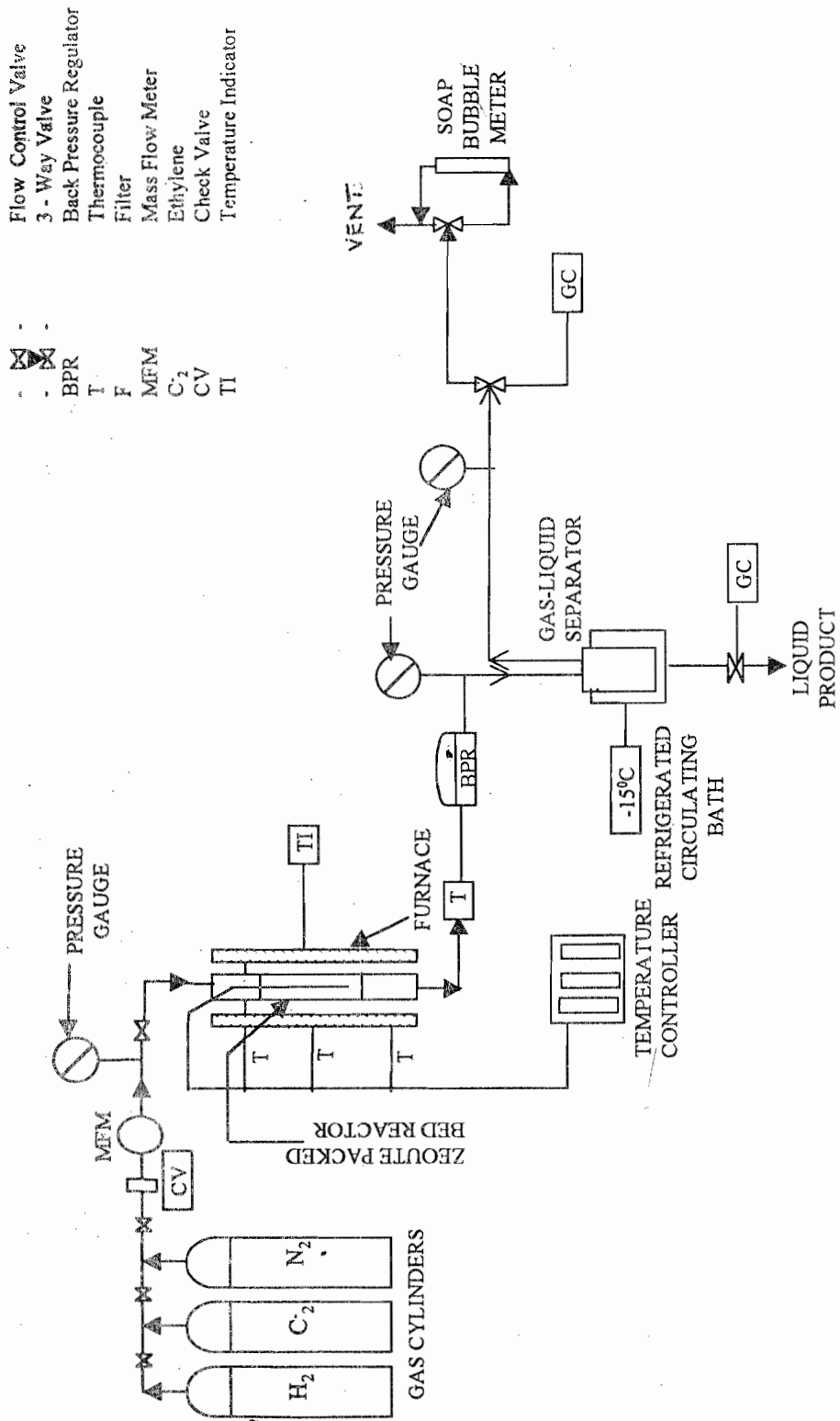


Figure 1: Schematic diagram of the packed bed reactor system for catalyst evaluation.

(2.25). Since 2.196g of catalyst was loaded, amount of ethylene gas fed through the reaction bed per hour was 0.976g (2.196g/2.25). The middle of the catalyst bed was made to coincide with the tip of thermocouple used for monitoring the reaction temperature. The reactor bed was heated to 300°C and purged with N₂ gas. The gas flow was then switched to H₂ flow for the loaded nickel reduction. Hydrogen reduction was carried out at 300°C for 3 hours under 60ml/min gas flow rate. The gas flow was then switched back to N₂ gas and temperature controller was simultaneously set to the desired reaction temperature. Once the desired reaction temperature was attained, the gas flow was switched to ethylene gas and the flow rate determined.

Initially, system stabilization was established during startup at 500psi, WHSV of 2.25 and temperature of 50°C to prevent undesired or premature reaction. After this, the temperature of the system was raised to the desired set-point and at least 1 hour was allowed for reaction stabilization before sampling the liquid and gaseous products. This study was carried out at 500psi and temperatures between 100 - 300°C. The WHSV was 2.25, based on the catalyst loading. The gas product rate was measured independently with a soap-bubble meter. Products obtained were separated into condensable and gaseous products by passing the reactor effluent stream through a gas-liquid separator maintained at -10°C. A gas chromatograph (HP 5880 analyzer) with flame ionization detector (FID) was used to analyze the gaseous product. Another gas chromatograph (HP 5880 analyzer) with thermal conductivity detector (TCD) was used to analyze the liquid product. The GC conditions were:

Initial oven temperature:	30°C
Initial time	4.0 minutes
Oven heating rate:	5° C/min
Final oven temperature:	260°C
Final time:	0.0 minute
Injection temperature:	250°C
Detection temperature:	300°C
Run time:	50 minutes

Overall, five runs were carried out, and the same catalyst activation/evaluation procedure was followed for each run. 2.196g of supported catalyst was loaded for each run.

RESULTS AND DISCUSSION

Each run was terminated either when the effluent gas flow rate from the reactor almost equaled the feed rate or when the system pressure rose up enough to trigger the back pressure regulator for each setting of the temperature. The liquid sample formed was drained and weighed hourly. At the same time, the gas stream was analyzed in the on-stream GC while also monitoring the gas flow rate. The liquid sample was analyzed by injecting sample into the sample port of the GC. To identify the peaks, 1ml of Scott Specialty standard containing C₂ - C₂₀ alpha olefins was injected manually into the GC sample port. The gas product flow rate was found to be unsteady once the oligomerization reaction commenced, an average had to be taken each time the flow rate was being determined. Excessive pressure build-up resulted in joint leakages in some of the runs and such runs had to be repeated.

For the 100°C, 500psi run, only 2.00g of liquid product was collected after 14 hours period. The reaction system leaked some liquid product between the filter and the back pressure regulator. The reactor effluent gas flow rate was measured to be 40ml/min. Although there was no system leakage experienced during the 150°C, 500psi run, the reactor effluent gas flow rate was erratic and the reaction only lasted for 6 hours. The total liquid product collected weighed 3.76g and the reactor effluent gas flow rate was measured to be 35ml/min.

The third run carried out at 200°C, 500psi lasted for 20 hours, 65.80g of liquid product was collected and the reactor effluent gas flow rate was 29ml/min. For the 250°C, 500psi run that lasted for 21 hours, 44.50g of liquid product was collected. The reactor effluent gas flow rate was measured to be 20ml/min, the system again experienced erratic gas flow rate.

The final run at 300°C, 500psi lasted for 29 hours and had to be terminated because of erratic gas flow rate in the reaction system. A total of 108.00g of liquid product was collected and the reactor effluent gas flow rates varied between an initial rate of 6ml/min (at the end of the first hour) to a maximum of 40ml/min (at the end of the fifth hour) to a minimum of 3ml/min (when the reaction was terminated). A plot of the hourly liquid product yield over the reaction period is shown for 300°C.

300psi run in Figure 2.

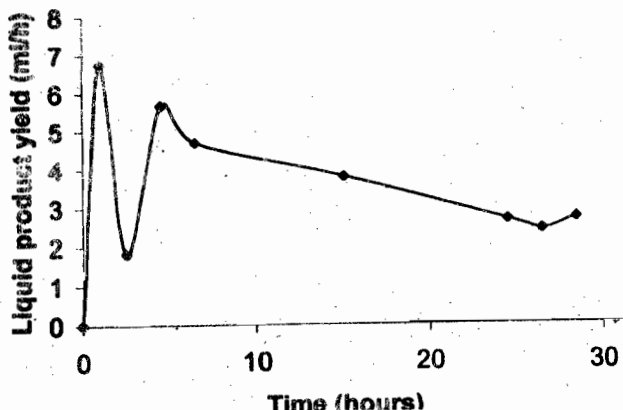


Fig. 2. Hourly liquid product yield for oligomerization reaction at 300°C, 500psi and WHSV = 2.25.

When the liquid was analyzed in the GC, the presence of isomers of even carbon number olefins in the range C₄ - C₁₂ was detected. A tabular result of the product distribution from the liquid product analysis is shown in Table 1. Because the GC instrument used cannot separate the isomers (multiple peaks at the elution time corresponding to the hydrocarbon standards), lumped values are tabulated for each carbon number detected.

Table 1. Oligomerization products selectivity variation (mole %) with reaction temperature.

Olefin	Mole % at (run temperatures (°C))				
	(100)	(150)	(200)	(250)	(300)
C ₄	0.00	29.10	23.80	27.10	37.90
C ₆	4.80	46.00	37.60	28.80	37.20
C ₈	31.20	20.00	26.30	27.10	16.20
C ₁₀	35.50	4.70	8.60	11.70	6.20
C ₁₂	28.50	0.20	3.70	5.30	2.50

In the GC analysis of the reactor effluent gas stream, only C₂ and C₄ olefins were detected. The amount of C₄ olefins increased proportionately with the reaction temperature as shown in Table 2.

Table 2. Reactor effluent gas stream compositional variation with temperature.

Olefin	Mole % at (Temperature (°C))		
	(150)	(250)	(300)
C ₂	97.10	46.50	45.20
n-C ₄	0.50	9.30	12.20
t-C ₄	1.50	26.90	25.40
c-C ₄	0.80	17.20	17.10

Because of the flow irregularities experienced during most of the runs, values tabulated represent average readings. The composition and flow-rates of the reaction effluent gas stream were non-uniform, even for the same process conditions.

One major inference from this study is that for all the temperatures investigated, purely olefin product were obtained when silica - alumina support ion-exchanged with nickel was used to oligomerize ethylene gas. The presence of isomeric co-products of 1-alkenes reduces the utility of the product directly for some uses such as detergent production; nevertheless, the liquid product lends itself to gasoline blending application for octane number boosting.

Another inference from this study is that, temperature does not change much the selectivity of the liquid product produced. Except at 100°C where C₄ olefin was not detected, at all the temperatures investigated even carbon number in the range C₄ - C₁₂ were detected as evident from Table 1. Figure 3 shows the mole percentage variation of the olefins with temperature in the liquid products. The erratic gas flow and excessive pressure build-up in the reaction system can be attributed to the formation of coke on the loaded

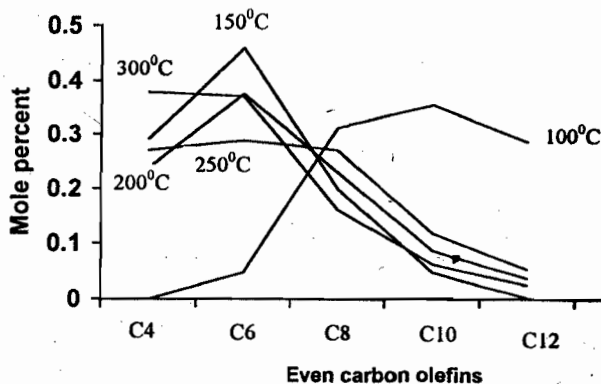


Fig. 3. Mole percent variation of the olefins with temperature in the liquid product

catalysts and consequent blocking of reaction pathway as evident from the spent catalysts when unloaded. Temperatures higher than 200°C can actually be recommended for effective runs, since coke formation was greatly unfavoured at and above 200°C.

The problem of coke formation and flow pluggage can also be solved by increasing the WHSV much higher than the 2.25 value used for this study. The residence time in the bed will be reduced and this in turn can change the composition or selectivity in the liquid product stream. The excessive pressure build-up with its concomitant long residence time in the reaction system is suspected to favour isomeric products formation.

CONCLUSION

Silica - alumina support can be ion-exchanged with nickel to synthesize catalysts that can be used to produce even carbon number olefins through ethylene oligomerization. At temperatures lower than 150°C, a lot of coke formation was observed on the spent catalysts unloaded from the reaction system and the catalysts were quickly de-activated consequently. Temperatures lower than 150°C can be considered non-ideal for ethylene oligomerization when carried out at 500psig and low WHSV such as 2.25. At temperatures 200°C and above, oligomerization reaction rate at 500psig and WHSV = 2.25 was favoured; the liquid products formed indicated very little variation in the carbon number selectivity. Coke formation was also greatly reduced on the spent catalyst unloaded from the reactor. Flow non-uniformity is suspected to be partly responsible for the formation of isomeric co-products of 1-alkenes in the liquid products. Inert particles can be mixed with the supported catalysts to obtain loose bed packing and therefore higher WHSV with respect to the active catalyst. The inert particles will effect uniform gas flow through the reaction system at reduced residence time and consequently produce different product selectivity with less isomeric content.

ACKNOWLEDGMENT

This work was carried out at the Research Institute of the King Fahd University of Petroleum and Minerals. The author appreciates the contribution of Dr. M. M. Abdillahi.

REFERENCES

1. Morrison, R. T. and Boyd, R. N., Organic Chemistry, 3rd ed., chapter 5, Allyn & Bacon, Boston, 1976.
2. Lee, W., Sapre, A. V. and Yurchak, S., European Patent 0088494A1, 1982.
3. Abdillahi, M. M., El-Nafaty, U. A. and Al-Jarallah, A. M., Applied Catalysis A: general, 1992, 91, 1.
4. Fleckenstein, T., Belendorff, K. and Fetting, F., German Chem. Eng., 1986, 9, 346.
5. Andersen, B., Fletcher, J. C. Q. and O'Connor, C. T., Proceedings of the 9th International Zeolite Conference, Boston, Mass., 1992, 2, 591.
6. Knifton, J. F., Sanderson, J. R. and Dai, P. E., Catalysis letters, 1994, 28(2-4), 223.
7. Kitada, S., Saito, K. and Ito, J., Japanese Patent JP 06, 1994, 157, 359.

accepted 12/10/2000

received 13/07/2000