

Methylation of Toluene To P-Xylene Using Zsm-5 Zeolite

¹*Nwanorh, K.O And ¹Ikpa, C.B.c.

Chemistry Department, Imo State University, Owerri, Nigeria.

Corresponding Author: Nwanorh

Abstract: Toluene was methylated to para-xylene using ZSM-5 zeolite. The catalyst was modified by both compaction and depositing of phosphorus. The results show that modifying with phosphorus before compacting enhances para-xylene selectivity since by this treatment ortho- and meta-xylenes easily isomerised to para-xylene.

Keywords: Toluene, para-xylene, ZSM-5, phosphorus, zeolite, selectivity.

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I. Introduction

Zeolites were first recognized by Cronstedt when he discovered stilbite in 1756[1]. He named the mineral "Zeolite" from the Greek words meaning "to boil" and "a stone" because it exhibited intumescences when heated in a blowpipe flame. In the early period of their discovery, they were mainly used in museum exhibitions. But during the late 1950's it was discovered that they had great industrial potential. This triggered off several research efforts which led to the development of commercial applications of synthetic molecular sieves of which ZSM-5, introduced by Mobil in 1972 is one.

The zeolites are sodium aluminum silicates with general composition $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{XSiO}_2 \cdot \text{YH}_2\text{O}$. They are versatile substances used as catalysts in the petrochemical industry[2]. They are the newest, and seemingly most promising substitute for phosphates as builders in detergents where they prevent soil redeposition and support washing performance[3]. By 1982 about 1.23×10^5 tons per year of zeolites were being used as detergent builders [4,5]. In refining operations, catalytic reforming is used to improve the octane number of the straight-run distillates in the gasoline boiling range. The reformate contains a substantial amount of aromatics of which the most important are benzenes, toluene, and C_8 aromatics (eg. Xylenes).

One other source of aromatic hydrocarbons in the petrochemical industry is the pyrolysis gasoline. This is a co-product of ethylene in the naphtha cracking as well as gas oil cracking. The approximate compositions of these two major sources of aromatics are as follows [6,7]:

COMPOSITIONS OF $\text{C}_6 - \text{C}_8$ AROMATICS (% WT) & MARKET DEMAND

| Component | Catalytic Reformate | Pyrolysis Gasoline | Market Demand |
|--------------|---------------------|--------------------|---------------|
| Benzene | 16 | 53 | 46 |
| Toluene | 47 | 30 | 28 |
| C_8 | 37 | 17 | 26 |

Unfortunately these C_8 aromatics are not produced in line with market demands. Of the C_8 's in the stream, para-xylene has the highest market demand even though it is the smallest component of the C_8 stream constituting only about 10%. Toluene, on the other hand, produced in large amounts, has little market demand. As a result it is converted to benzene (by dealkylation) or to the xylenes by alkylation. Since the amount of para-xylene in any equilibrium source of the xylenes is very low, and yet its demand is high, then a simple and economically viable way to its production has been the subject of this work based on ZSM-5 modifications.

Some workers [8-10] have observed that active sites in zeolites fall into three groups. The diversity of active sites therefore begs the question of whether the zeolites as synthesized are active enough, and if not, what could be done to enhance their activity. This problem has led to the modification of zeolites aimed at increasing their activities in general and selectivity towards certain products in particular.

Taylor et al [11] have carried out toluene alkylation reaction over zeolites while Chu [12] showed that modification of ZSM-5 by first steaming, and depositing phosphorus and magnesium afforded over 90% para isomer. Chandavar et al [13] also did propylation of benzene over ZSM-5 modified with phosphorus and boron. In all cases none has investigated the physical alongside chemical modifications.

This work thus involves the study of the chemical modification of ZSM-5 zeolite using a phosphorus containing compound. This is followed by physical modifications which involves pelleting under different pressures.

II. Experimental

Chemical modification

The ZSM-5 used for this work had a silica/alumina ratio of about 19. Since it normally comes in the sodium form, the sodium was exchanged with ammonium using ammonium sulphate maintained at 110°C. The toluene and methanol used were of 99% purity and thus further purification was not necessary.

Apparatus

The reactor was a fixed-bed cylindrical quartz tube measuring 1.0 x 50cm and contains a quartz sinter 25cm along its length. The system was electrically heated by a furnace 20cm long which formed a jacket over the reactor. Connected to the reactor were air and water condensers, a U-tube with tiny glass rings to trap escaping liquid, a syringe and pump to deliver definite and constant volume of reactant, a column of quartz wool along the length of the reactor immediately above the catalyst to act as an evaporating medium so that the reactants reach the catalyst as vapour.

Procedure

1.0g of the modified and calcined ZSM-5 catalyst was placed in the reactor and a quartz wool was inserted above it. The syringe needle was pushed through the Teflon seal of the side arm and nitrogen was passed at the rate of $5\text{cm}^3\text{min}^{-1}$. When bubbles of nitrogen were seen in the water of the gas collecting cylinder, heating was started to activate it by raising the temperature in three steps – 10°C; 70°C and 110°C. At each step, equilibrium time of 1.5hr was allowed. The temperature was programmed to remain at 110°C for seven hours, then 450°C for four hours, and finally 600°C for four hours.

Finally, the solution of toluene and methanol in the molar ratio of 2:1 was delivered by the syringe and pump which delivers about 10.5g hr^{-1} of solution. The solution was carried down by nitrogen. It was first preheated and vaporized by the quartz wool and the nitrogen-toluene-methanol mixture entered the catalyst bed as a thoroughly mixed vapour.

The product left the catalyst in the form of cloudy vapour and the condensable portion was collected in a receiver below while the non-condensable part passed through the U-tube to the gas collector. Samples were collected after 30, 90, 150, 210, and 255 minutes. The aqueous phase was separated from the organic phase and analyzed using a gas chromatograph (Hewlette Packard 5790) having a flame ionization detector.

III. Results And Discussion

The results show that phosphorus uptake is determined by the compactness of the zeolite. It was found that the powder catalyst picked up more phosphorus than the pellets formed at 1.59 ton cm^{-2} pressure which in turn picked up more phosphorus than that formed at 4.77 ton cm^{-2} . This means that the channel structure of the zeolite was compressed leading to decreased rate of phosphate entry into the channel. The zeolite aggregates possess pores which facilitate the diffusivity of ions into the crystal channels. Under pressure these inter-crystalline pores are reduced by the compact nature of the pellet. As the pressure of pelleting increases, the compactness increases thus reducing the diffusibility of phosphorus into the crystals. The inter-crystalline pores are reduced under pressure thus hindering phosphorus penetration into the channels of the crystal. This is borne out of the fact that for two catalysts pelleted at the same pressure, the coke level on the catalyst was low when the phosphorus content was high. As shown, in figure 1, selectivity for *p*-xylene was enhanced by modifying the zeolite before compaction. This further supports the proposition that the pore size of the channels is reduced by physical modification. This is so since the two catalysts have the same phosphorus content, thus the difference is that in powder modified zeolite, the phosphorus enters the channels system while when subjected to compaction the channel size is reduced thereby restricting entry of phosphorus. The bulk of phosphorus is thus on the outside.

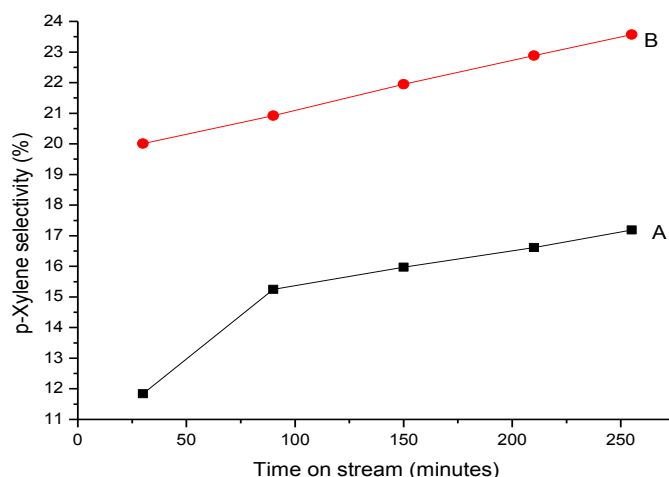


Fig. 1: Effect of modifying zeolite powder and pellets on *p*-xylene selectivity

Key: A = Zeolite powder modified before pelleting.
 B = Zeolite pelleted before modifying.

Figure 2 indicates that phosphorus modification reduces benzene selectivity considerably, while selectivity for *p*-xylene increases with phosphorus content (fig. 3). This shows that there is an optimum phosphorus level for selectivity modification. At phosphorus content of 4% benzene selectivity is virtually zero. This is further supported by the *p*-xylene selectivity factor which increases in the same line (fig. 4).

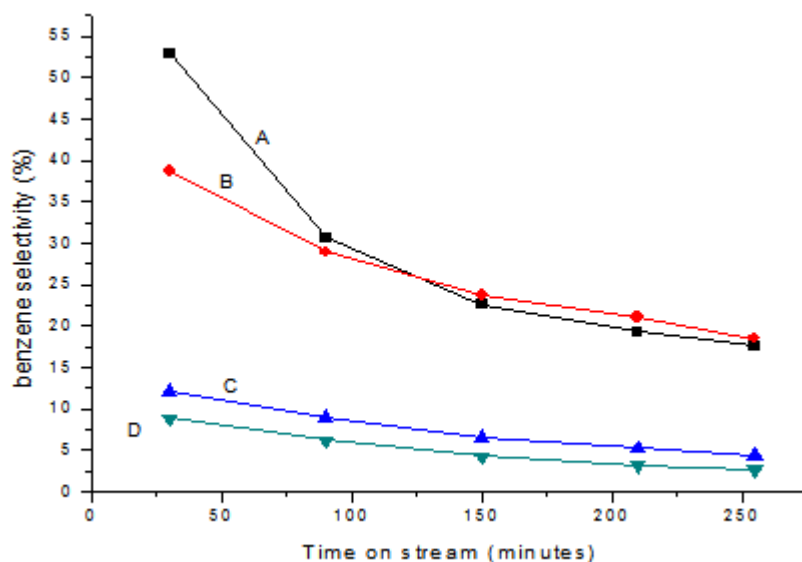


Fig. 2. Effect of phosphorous level on benzene selectivity

Key: A = Parent HZSM-5 catalyst. B = Low Phosphorus catalyst
 C = Medium Phosphorus catalyst. D = High Phosphorus catalyst

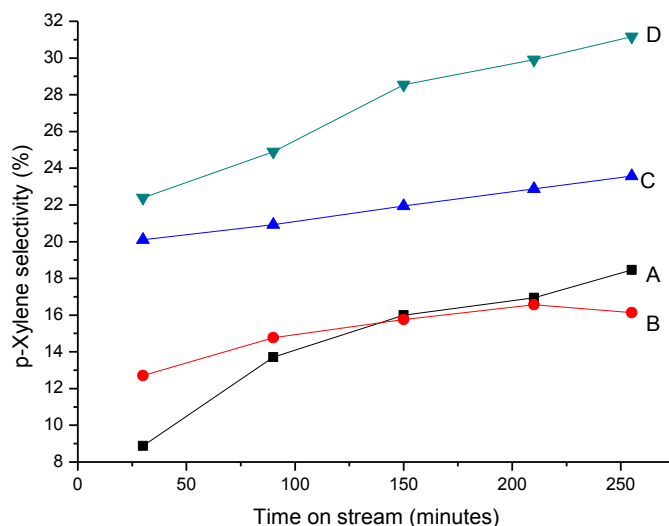


Fig 3: Effect of phosphorous level on *p*-Xylene selectivity.
 Key: A = Parent HZSM-5 catalyst. B = Low Phosphorus catalyst
 C = Medium Phosphorus catalyst. D = High Phosphorus catalyst

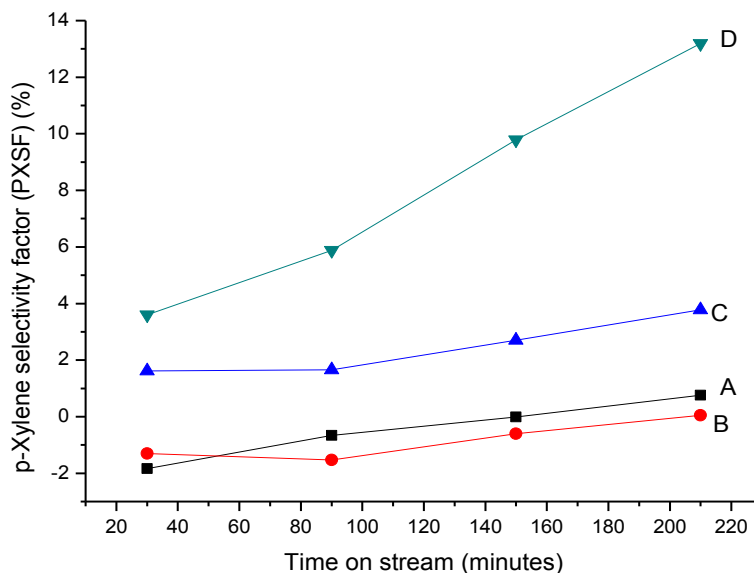


Fig.4: Effect of phosphorous level on *p*-Xylene selectivity factor (PXSF).

Key: A = Parent HZSM-5 catalyst. B = Low Phosphorus catalyst
 C = Medium Phosphorus catalyst. D = High Phosphorus catalyst

That isomerisation of *o*- and *m*-xylenes to *p*-xylene takes place within the channel is evidenced by the decrease in selectivity towards these isomers as shown in figures 5 and 6.

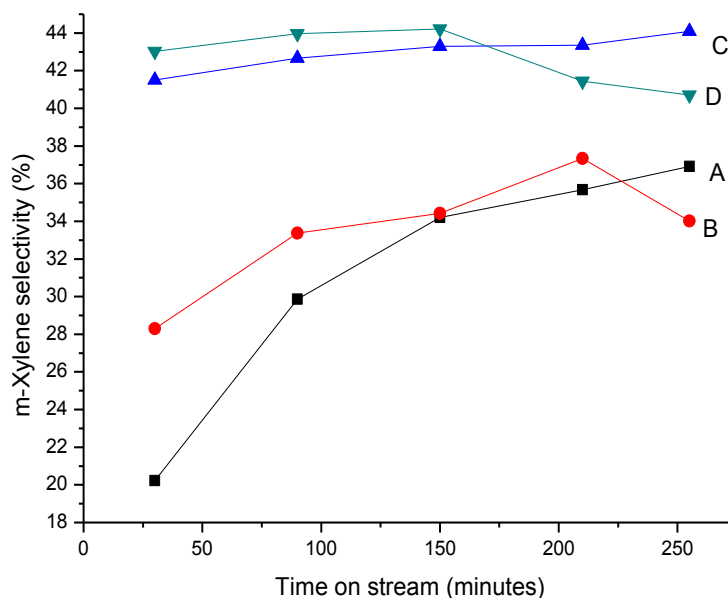


Fig. 5: Effect of Phosphorous level on *m*-Xylene selectivity
 Key: A = Parent HZSM-5 catalyst B = Low Phosphorus catalyst
 C = Medium Phosphorus catalyst. D = High Phosphorus catalyst

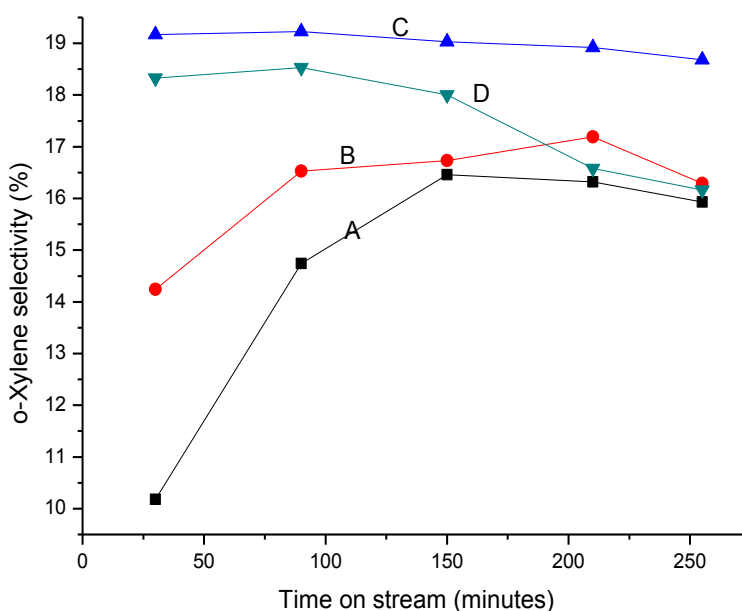


Fig. 6: Effect of Phosphorous level on *o*-Xylene selectivity

Key: A = Parent HZSM-5 catalyst. B = Low Phosphorus catalyst
 C = Medium Phosphorus catalyst. D = High Phosphorus catalyst

Physical reduction of channel pore is further illustrated when the un-modified zeolite was pelleted at two different pressures. The amount of gas produced on high pressure pellets was lower (1670 cm³) than that on low pressure pellets (2040 cm³) while coke deposit was in the reverse order 8.4% and 11.7% respectively.

IV. Conclusion

The methylation of toluene yields *para*-xylene as the primary product. The *ortho* and *meta*-xylenes co-produced isomerise to *p*-xylene as a result of reduction of the pore size added with the deposition of phosphorus to enhance *p*-xylene selectivity.

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