Selective Toluene Disproportionation to produce para-Xylene over Modified ZSM-5

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Industrial demand for p-xylene has been increasing in recent years and the major production is by toluene disproportionation. This research studied the effect of crystal size and the modification by silica deposition on the surface of the zeolite. Shape selective catalysts have been prepared by modifying two different ZSM-5 zeolites with different crystal sizes (0.5 µm, 5 µm) by chemical liquid deposition (CLD) using TEOS (tetraethyl orthosilicate) to deposit inert silica layers. The large ZSM-5 crystals modified with two cycles of silica showed high p-xylene selectivity at typically 84 % with very low conversion. Pressure effect on the reaction was investigated. Selectivity achieved was 40 – 66 % at conversions typically 4-20 % at 10 bar.

1. Introduction

Para-xylene is used as a raw material in the production of terephthalic acid and dimethyl terephthalate important intermediates used in the production of polyester fibres and plastics (Meshram, 1987). Toluene disproportionation is one of the available processes to convert the surplus abundant toluene to the more valuable xylenes (Weitkamp and Puppe, 1999). In toluene disproportionation over ZSM-5 zeolite, xylene isomers are produced in thermodynamic equilibrium (24% p-, 50% m- and 26% o-) (Tsai et al, 1999). In 1988, Mobil's Selective Toluene Disproportionation Process (MSTD) was introduced to improve the p-xylene selectivity by toluene disproportionation (Fang et al, 1999). It was reported that p-xylene selectivity was enhanced over ZSM-5 zeolite. One of the most important properties of ZSM-5 is shape selectivity due to the channels (straight and zigzag) and pore size opening (0.55-0.57 nm) (odedairo et al, 2011). These channels produce p-xylene preferentially as it diffuses faster than the other two isomers. However, the non-selective acid sites situated on the surface allow p-xylene to isomerize leading to the thermodynamic equilibrium (Bauer et al, 2004).

Different modification methods of ZSM-5 have been studied to increase the p-xylene selectivity (Chen et al, 2004). These modification methods aimed to deactivate the non-selective external surface acid sites and potentially narrow the pores opening. To increase the selectivity towards p-xylene, ZSM-5 has been modified in various ways. Pre-coking, deposition of inert silica layer on the surface of ZSM-5 by chemical liquid deposition of organosilicon compounds such as (tetraethyl orthosilicate and polysiloxanes) and the addition of different elements and metals such as phosphorus, magnesium and nickel were used to passivate the external undesirable acid sites and narrow the pores of the zeolite to increase the selectivity towards p-xylene (Zhu et al, 2007).

Crystal size of the ZSM-5 is another parameter which could affect the diffusion rate of the xylene isomers and the selectivity to p-xylene. The effect of crystal size in alkylation of toluene with methanol reaction has been studied. The large crystals tend to slow down the diffusion of o-xylene and m-xylene as a result of the diffusion constraint implemented by the length of the crystal, leading to a reduction in the production of o-xylene and m-xylene and increase in the yield of p-xylene (Chen et al, 1988). Large crystals showed an increase in the p-xylene selectivity to about 35% without any further modifications when tested for toluene disproportionation (Paciga et al, 1997).

2. Experimental

2.1 Catalyst preparation

NH_4ZSM-5 zeolite with (Si/Al = 25) was obtained from Alfa Aesar which has a crystal size of 0.5 µm. It was calcined at 500 °C for 6 hours to obtain the acidic form HZSM-5. NaZSM-5 (Si/Al=15.5) was synthesized using feedstock and seeding gels in order to produce ZSM-5 with large crystals (5 µm). The seeding gel was prepared using colloidal silica (Ludox AS40), Sodium Hydroxide, Tetrapropylammonium hydroxide and deionised water according to a gel molar ratio of Na_2O: 3 TPAOH: 60 SiO_2: 1200 H_2O. Aging of the seeding gel was performed at 100 °C overnight. The feedstock was prepared by mixing sodium aluminate, sodium hydroxide and colloidal silica in deionised water according the gel composition 6 Na_2O: 2 Al_2O_3: 60 SiO_2: 1916 H_2O. The seeding gel was added to the feedstock gel and poured into a PTFE-lined autoclave. The autoclave was placed in an oven at 180 °C for 24 hrs. After the synthesis, the zeolite powder was washed, filtered and dried. Then, it was placed in a muffle furnace heated slowly at a rate of 3 °C to 550 °C for 8 hrs to remove the template. The catalyst was ion exchanged with ammonium nitrate solution (1 M) at 40 °C for 3 hrs, three successive times. The powder was filtered, washed and dried. At last, it was calcined at 550 °C for 6 hrs to generate the H-ZSM-5 (Rallan, 2015).

2.2 Silylation

HZSM-5 (Si/Al=25, 10g) was suspended in a solution of cyclohexane (100 ml) and tetraethyl orthosilicate (TEOS, 4 ml) to obtain a modified catalyst with 10 wt. % SiO_2. The components were mixed together for 7 hours at 40 °C. Cyclohexane was evaporated and the catalyst was dried at 120 °C. The dried sample was calcined in a muffle furnace at 550 °C at a rate of 3 °C/min for 6 hours. The one cycle of silylation with TEOS is finished. The same procedure was repeated to attain two cycles. 5 grams of HZM-5 (Si/Al = 15.5) was mixed with 50 ml cyclohexane and 5.5 ml TEOS to load 30 wt. % SiO_2 on the zeolite. The same above procedure was followed.

2.3 Catalyst characterization

X ray diffraction (XRD) (X' Pert) with scanning angle (2 theta) from 5 to 90 was used to study the structure of ZSM-5 samples. Scanning electron microscopy (SEM) was used to examine the morphology of the catalyst on Philips XL-30 instrument. The Si/Al ratio was determined by acid depletion followed by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. Comparative characterisation of the acidic OH groups (Brønsted acid sites, BAS) and Lewis acid sites (LAS) in the zeolites was carried out using transmittance FTIR measurements in the 5000-900 cm^{-1} spectral range. Pyridine (a probe molecule) was used for monitoring the relative quantities of both BAS and LAS. The intensity of the Py-BAS and Py-LAS peaks at ~ 1546 and 1455 cm^{-1} were used to compare the number of active sites in the samples, and the quantitative data are presented in Table 1.

2.4 Catalytic test

Toluene disproportionation reaction was carried out over unmodified and modified ZSM-5. The reaction was carried out in a down flow fixed bed reactor loaded with 1g of catalyst at 475 °C varying the weight hourly space velocity of toluene (WHSV) (3-100) h^{-1} and the hydrogen pressure of (1 and 10) bars. Hydrogen flow rate of 30 ml/min was kept constant throw out the whole experiment. Liquid quantitative analyses were carried out by Varian 3400 GC equipped with a 30 m X 0.32 mm Stabilwax column and FID (flame ionization detector). Toluene conversion X_T and p-xylene selectivity S_P were calculated based on the following formulae:

$$X_T = \frac{W_{T0} - W_T}{W_{T0}} \times 100 \tag{1}$$

$$S_P = \frac{W_{PX}}{W_X} \times 100 \tag{2}$$

Where W_{T0} is the weight of toluene in the feed, W_T is the weight of toluene in the product, W_{PX} is the weight of p-xylene and W_X is the weight of total xylene.

3. Results and Discussion

3.1 Catalyst characterization

The present zeolites were coated with silica successively, the Si/Al ratio increased as expected (Table 1)

Table 1: Characterisation of ZSM-5 catalysts used in this study

Sample ID	Crystal size (μm)	Number of silica modification	Si/Al*	BAS (mmol/g)	LAS (mmol/g)	B/L
S-ZSM-5	0.5	-	26.3	0.31	0.08	3.90
S-ZSM-5 1X Si	0.5	1	30	0.24	0.06	3.75
S-ZSM-5 2X Si	0.5	2	31.7	0.20	0.07	2.83
L-ZSM-5	5	-	15.5	0.37	0.17	2.15
L-ZSM-5 1X Si	5	1	16.2	0.25	0.15	1.69
L-ZSM-5 2X Si	5	2	20.1	0.20	0.13	1.52

*Si/Al was measured by ICP, BAS = Brønsted acid sites, LAS = Lewis acid sites, B/L= BAS/LAS

XRD patterns for both large and small ZSM-5 unmodified and silylated were comparable with ZSM-5 reference pattern. Patterns of silylated samples showed that the crystalline of ZSM-5 was not affected by the modification (Figure 1).
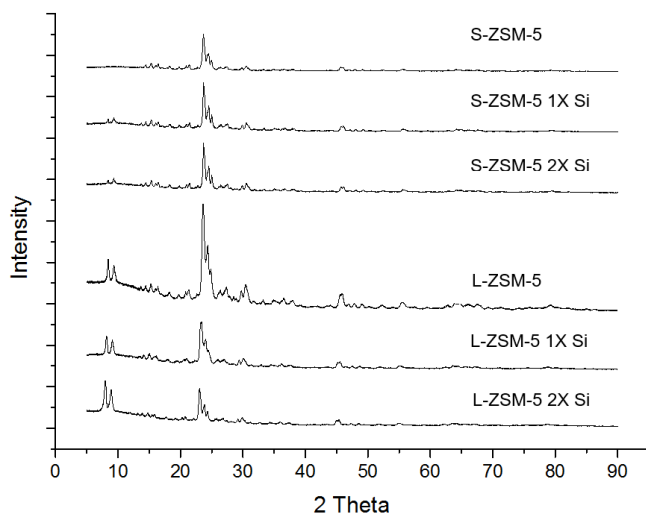

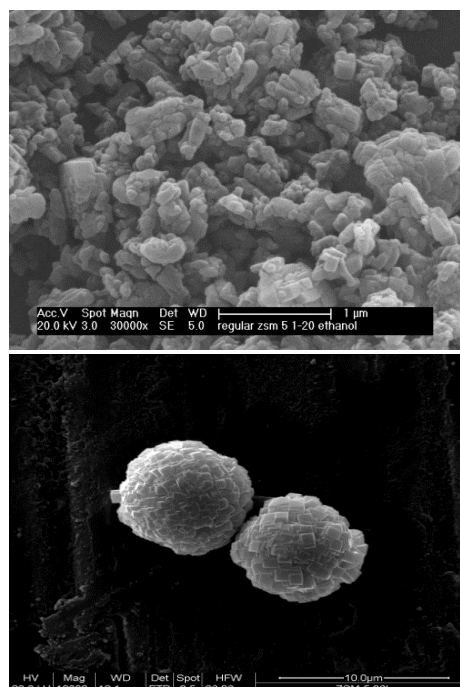Figure 1: XRD patterns of ZSM-5 samples

Figure 2: small (top) and large ZSM-5 crystals (bottom)

The crystal size and morphology of the small and large ZSM-5 are shown in Figure 2, where the ZSM-5 with small crystals ranged from 0.3 to 0.5 μm (top) and the large crystals in a spherical shape and typically crystal size of 5 μm (bottom).

3.2 Effect of crystal size of ZSM-5

It was expected that increasing the crystal size could favour the production of p-xylene as more diffusion constraints will be imposed and the external surface will be decreased at the same time. The results for the different crystal size (0.5 μm and 5 μm) shown in Table 2 did not lead to any improvement in the p-xylene selectivity at low WHSV. Increasing WHSV led to a noticeable increase in the selectivity for the large ZSM-5 crystals. Increasing the flowrate of the feed allowed less contact between the reactant molecules of toluene and the catalyst and hence less isomerisation of p-xylene to other xylenes occurred.

Table 2: Toluene disproportionation over different crystal sized ZSM-5

Reaction Conditions						
Si/Al*	26.3	15.5	26.3	15.5	26.3	15.5
Crystal size(µm)	0.5	5	0.5	5	0.5	5
WHSV(h⁻¹)	3	3	30	30	70	70
Product distribution (Wt. %)						
Benzene	9.93	8.78	3.45	4.87	1.37	2.13
Toluene	74.40	77.83	91.72	87.43	98.63	94.47
p-xylene	3.57	3.24	1.19	2.10	0.49	1.26
m-xylene	7.77	6.82	2.50	3.76	0.97	1.46
o-xylene	3.53	2.90	1.10	1.53	0.40	0.48
Benzene/Xylene	0.67	0.68	0.72	0.66	0.74	0.67
Toluene conversion (Wt. %)	25.60	22.19	8.28	12.57	3.22	5.53
p-xylene selectivity (Wt. %)	24.00	25.00	24.80	28.36	26.30	39.30

*Si/Al was measured by ICP

Increasing the pressure to 10 bar using hydrogen showed significant increase in the conversion of toluene. Pressure induces more and longer contact between the zeolite and toluene molecules meaning higher chance of feed molecules reacting over the acid sites available within ZSM-5. The difference between the reaction at 1 bar and 10 bar was clearly seen in Figure 3. Noticeably performing the reaction at high pressure increased the toluene conversion. In the case of large crystals the selectivity increased with increasing WHSV (h-1). However, it is noticeable that the selectivity was lower than the values obtained at atmospheric pressure, indicating a trade-off between conversion and selectivity.
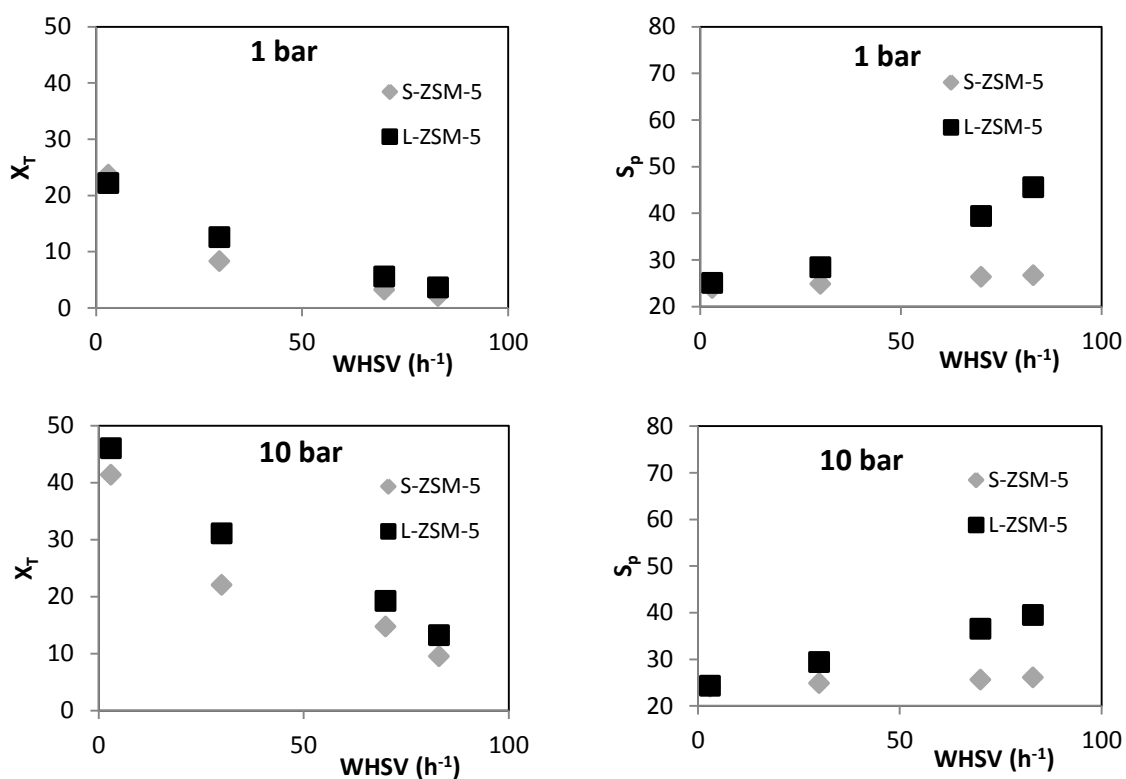

Figure 3: Effect of crystal size on toluene conversion and p-xylene selectivity at 1 and 10 bar

3.3 Effect of Silica deposition on p-xylene selectivity

Both small crystals and large crystals of ZSM-5 had been modified by chemical liquid deposition method (CLD) in order to deactivate the external undesired acid sites on the surface, responsible for xylene isomerization, by covering the surface with an inert layer of silica. All the modified catalysts gave lower toluene conversion as the addition of inert silica on the catalyst had reduced the number of external acid sites. One cycle silylation suppressed the isomerization of p-xylene to other isomers to some extent. The p-xylene selectivity had increased above the thermodynamic equilibrium value in both cases of large and small ZSM-5 crystals (Figure 4). The second cycle of silylation enhanced the selectivity further. Increasing the flow rate of toluene was accompanied by an increase in the p-xylene selectivity to 80 % at a WHSV of 83 h^{-1}. Unfortunately, the toluene conversion dropped drastically to 2 %.
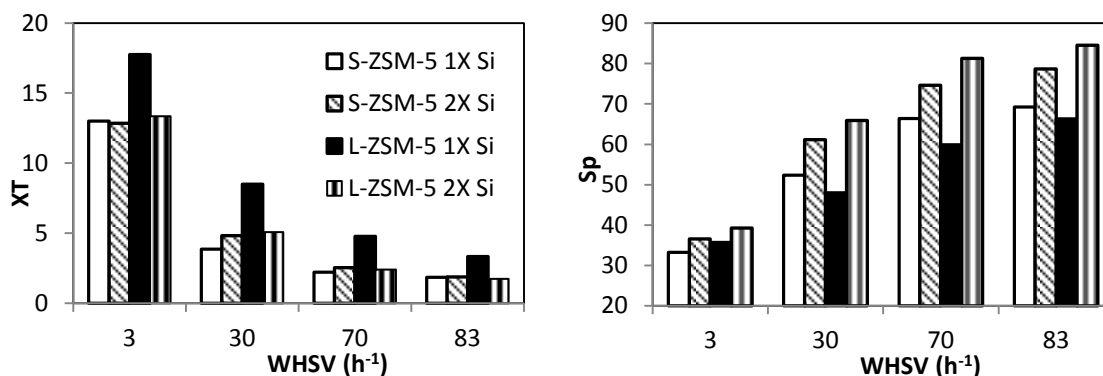

Figure 4: The effect of silylation on toluene conversion and p-xylene selectivity at 1 bar

Increasing the pressure to 10 bar almost doubled the conversion for all samples and dropped the selectivity back to the thermodynamic equilibrium value (24 %). Increasing WHSV of toluene increased the selectivity for all samples. The best selectivity was achieved by the large ZSM-5 crystal silylated twice (L-ZSM-5 2X Si) at all WHSVs reaching the highest value of about 65 % at the highest WHSV=83 h^{-1}. However, the toluene conversion decreased as the selectivity increased which is attributed to the less contact between the catalyst and the feed at high flowrates. In terms of yield, the higher the conversion of toluene the higher the p-xylene yield. however, the overall selectivity to p-xylene maybe lower. For example, testing (L-ZSM-5 2X Si) at 10 bar and a WHSV of 70 h^{-1} gave a toluene conversion of 8 % and 60 % p-xylene selectivity with overall yield of around 2.5 % in the total products. This result compares favourably with literature where (Ali et al., 2013) tested ZSM-5 catalyst silylated three times with TEOS and reported that at a toluene conversion around 10 % and p-xylene selectivity of 50 % with the yield of about 2 %. As stated, the amount of BAS and LAS acid sites were obtained by pyridine adsorption. The concentration of the Py-BAS acid sites was lower in the silylated catalysts as compared to the parent zeolite, explaining the lower conversion obtained after silica treatment.
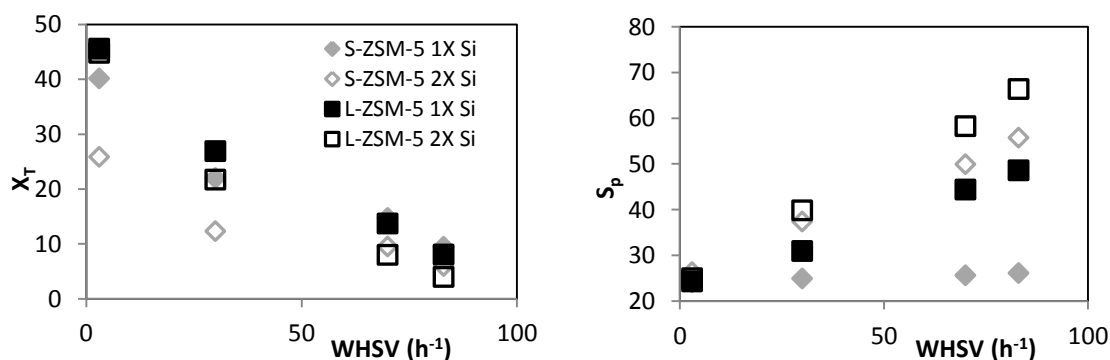

Figure 5: The effect of silylation on toluene conversion and p-xylene selectivity at 10 bar

3.4 Effect of modification on catalyst deactivation

The deactivation of unmodified small crystal ZSM-5 and silylated twice with silica was carried out for 50 hrs at 10 bar and a WHSV of 30 h^{-1}. From Figure 6, the conversion was approximately 50 % lower after silica

modification. Both catalysts showed deactivation with the modified being more rapid. In terms of p-xylene selectivity, there was no improvement over the unmodified parent catalyst. The silica treated catalyst showed an increase in p-xylene selectivity over the first few hours, stabilising at 44 % (an increase of 22 %). The catalyst remained stable with 45 % selectivity for 50 hrs. The increase in p-xylene selectivity could be attributed to the formation of coke which led to the suppression of the acid sites available for isomerisation.
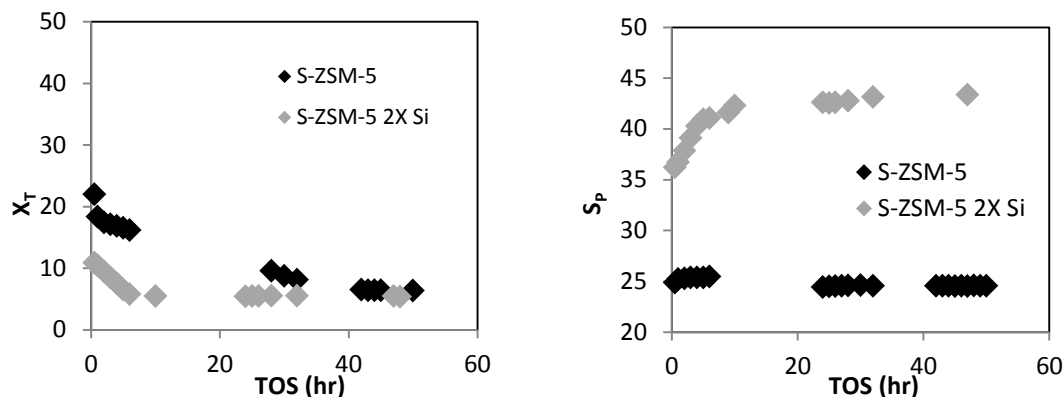

Figure 6: Effect of silylation on the deactivation of small crystals ZSM-5 at 10 bar and WHSV of 30 h^{-1}

4. Conclusions

Results showed a clear trend where increasing the crystal size increased selectivity to p-xylene without any further modification. The enhancement of p-xylene selectivity by the large crystals could be attributed to the diffusion limitation created by increased path length. Samples subjected to one cycle and two cycles silylation showed a significant increase in p-xylene selectivity to 85 % at atmospheric pressure. Increasing the pressure decreased the selectivity to 60% whereas the total conversion improved reaching 8 %. Currently work on large crystal synthesis and improved silylation is underway to improve selectivity and conversion.

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