

METHYLATION OF TOLUENE WITH METHANOL USING MODIFIED HZSM-5 CATALYSTS: EFFECT OF STEAMING

*Weerachit Pulsawas^a and Thirasak Rirksomboon^{*a,b}*

^a The Petroleum and Petrochemical College, Chulalongkorn University, Bangkok, Thailand

^b Center of Excellence on Petrochemical and Materials Technology, Bangkok, Thailand

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ABSTRACT

Toluene produced from both catalytic reforming and cracking of naphtha is surplus and lower in value when compared with other produced aromatics, e.g., benzene, xylenes, etc. To augment a more value of toluene, methylation of toluene with methanol is a promising route to convert toluene into xylenes. HZSM-5-based catalysts have been used for this reaction because of its superior properties in shape selectivity and proper catalytic activity. In this study, the modified HZSM-5 catalysts were utilized for such a reaction aiming toward higher *p*-xylene selectivity. The parent HZSM-5 was synthesized by hydrothermal treatment with SiO₂/Al₂O₃ molar ratio of ca. 200 and then sequentially modified by two modification methods; (i) dealumination with steam and (ii) chemical liquid deposition (CLD) with tetraethyl-orthosilicate (TEOS). Under the following reaction conditions; a constant temperature of 450 °C, atmospheric pressure, WHSV of 12 h⁻¹, and T/M molar ratio of 4:1, the toluene conversion and *p*-xylene selectivity attained at 365 min on stream were 11.8% and 65.6%, respectively, for the parent HZSM-5 catalyst whereas were 9.9% and 86.5%, respectively, for the modified one.

*t.rirksomboon@unb.ca

INTRODUCTION

Xylenes is an important intermediate chemical among fastest growing petrochemicals especially on *p*-xylene which was mainly produced via catalytic reforming and thermal cracking of naphtha along with other aromatics such as benzene and toluene. For *p*-xylene, it was used for terephthalic acid and terephthalates productions for polyester synthesis. So it is very useful and valuable compared to others. The cost of separating xylenes is very expensive because of its very close boiling point commercially operated by moving-bed adsorption and fractional crystallization. Since toluene is produced in excess relative to the market demand compared to other aromatics, toluene disproportionation and methylation were used as alternative routes (Ahn *et al.*, 2015). However, benzene as a co-product presented in toluene disproportionation, and the relatively high cost of product separation making it less attractive (Wu *et al.*, 2014).

In toluene methylation, HZSM5 zeolites have been widely studied due to its medium pore geometries and shape selective with *p*-xylene yielding high catalytic activity. To more improve selectivity of HZSM5, the modification of HZSM-5 is needed. Some modification method such as dealumination via steaming treatment (Almutairi *et al.*, 2013), silylation by chemical liquid deposition (CLD) of tetraethyl orthosilicate (TEOS) onto the zeolite surface (Ahn *et al.*, 2014) have been reported.

In this work, we propose the methylation of toluene with methanol using HZSM-5 with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of ca. 200 modified by silylation and combination of steaming and silylation to maximize the *p*-xylene selectivity.

EXPERIMENTAL

A. Catalyst Preparation

HZSM-5 samples were synthesized from hydrogel solutions with the following molar composition $10\text{Na}_2\text{O}:200\text{SiO}_2:\text{Al}_2\text{O}_3:20\text{TPABr}:7800\text{H}_2\text{O}$. The silica and aluminium sources were obtained from 40 wt% Ludox (Sigma-Aldrich) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Ajax Finechem), respectively. The resultant gel was placed into an autoclave for hydrothermal treatment and heated in an oven at a temperature of 140 °C for 72 h. The resultant gel was washed by deionized water, dried at 120 °C overnight and calcined at 550 °C for 5 h. The as-synthesized ZSM-5 is ion-exchanged with 1 M NH_4NO_3 (Ajax Finechem) solution for three times at 80 °C, and then washed with distilled water. The resultant zeolite was dried overnight at 120 °C and calcined at 550 °C for 5 h to obtain the parent HZSM-5 catalyst.

The silylated HZSM-5 catalysts were modified as follows; 1 g of parent HZSM-5 was stirred with 1 ml of tetraethyl-orthosilicate (Aldrich) and 10 ml of cyclohexane (RCI Labscan) for 7 h denoted as xCLD-HZ5 catalyst where x is the number of cycle of silylation. The combined treatment of CLD-steaming sequence was prepared as follows: firstly the parent HZSM-5 catalyst was steamed at water partial pressure of 10 – 40 kPa using nitrogen flow of 100 ml/min. Then the steamed HZSM-5 was silylated denoted as xCL-S(y/z)-HZ5 catalysts where y is the water partial pressure and z is the steaming temperature.

B. Catalyst Characterization

The morphology of the catalysts was characterized by field emission scanning electron microscope (FESEM, Hitachi S4800). The $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio was measured by x-ray fluorescence spectrometer (XRF, PANalytical Axios). The acidity of the catalysts was measured by temperature-programmed desorption of NH_3 and isopropylamine. The crystallinity of the catalysts was characterized by x-ray diffraction spectrometer (XRD, Rigaku Smartlab). The surface area and pore volume was measured using by surface analyser (BET, Quantachrome Autosorb 1-MP). The coke deposition of spent catalysts was measured by temperature-programmed oxidation.

C. Activity Testing

The catalytic activity studied on methylation of toluene with methanol was carried out at atmospheric pressure using a fixed-bed continuous down-flow reactor. The reactor has 6 mm in outside diameter with 1mm in thickness and 40 cm in length. 80 mg of catalyst was packed and placed into an electric furnace. Then, the mixture of toluene and methanol with

molar ratio of 4:1 was introduced into the reactor with reaction temperature of 450 °C using a syringe pump carried by flowing nitrogen of 40 ml/min.

RESULTS AND DISCUSSION

The synthesized parent HZSM-5 catalyst possesses MFI structure identified by XRD as illustrated in Fig. 1. The silylation of external surface of HZSM-5 catalysts exhibited a significant decrease in intensity of crystal planes (200) and (051) and a slight decrease in intensity of crystal planes (011) and (501). Nevertheless, the variation of steaming conditions did not affect its structure. The morphology of the HZSM-5 catalysts appears as an irregular hexagonal prism with rectangular insertion having about 1.01 x 2.22 x 0.27 μm and well uniformed shapes as shown in Fig. 2.

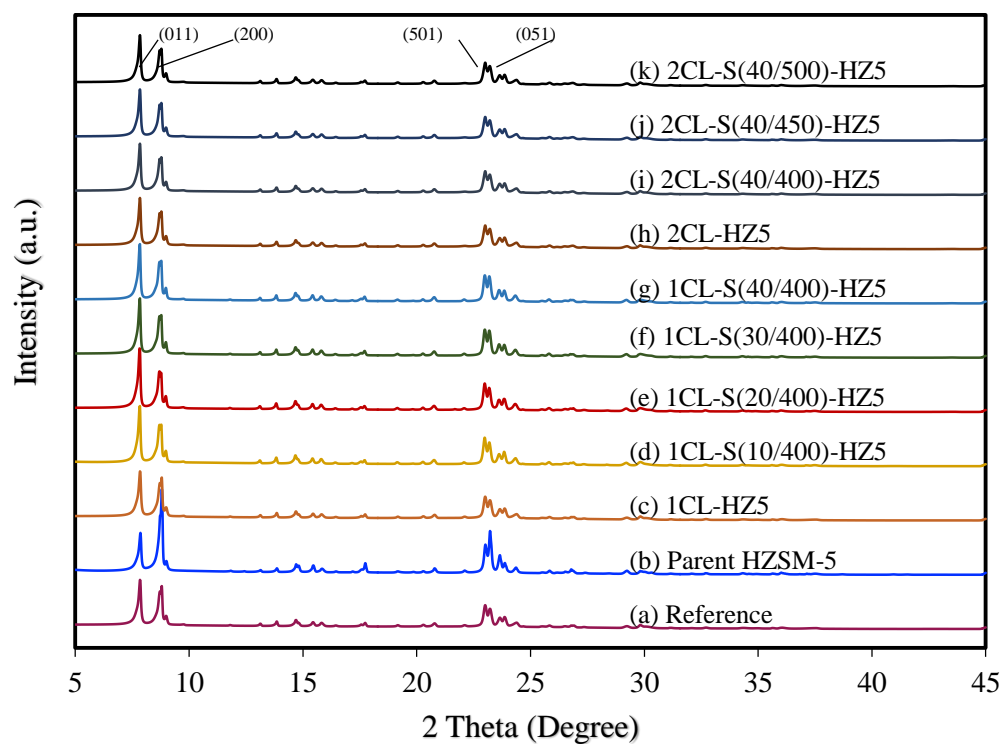


Figure 1 XRD patterns of the parent and modified HZSM-5 catalysts.

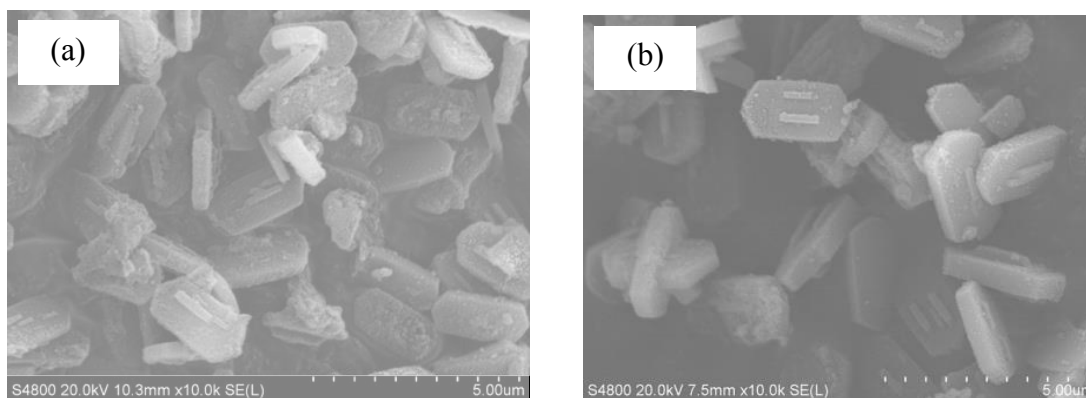


Figure 2 FESEM images of (a) parent HZSM-5 and (b) 2CL-S(40/450)-HZ5

Their textural properties and acidity types are summarized in Table 1. Its parent BET surface area (S_{BET}) was decreased from 323 to 302 and 271 m^2/g for 1CL-HZ5 and 2CL-HZ5, respectively, resulting from the silylation (CLD). In addition to the decreases in BET surface area (S_{BET}) and micropore volume (V_{mi}), Brönsted acid sites were decreased with increasing the water partial pressure resulting in the augmentation of Lewis acid site to total acidity ratio (L/T).

Because the Brönsted acid sites were demolished as an increased severity of steaming conditions, it was suggested that the significant increase of Lewis acid sites corresponding to extra-framework aluminum species generated (Fan *et. al.*, 2006) would cause the blockage of the micropore channels. Besides, severe steaming (40kPa) at high temperatures led to an increase in total pore volume (V_{tot}).

Table 1 Textural properties and acidity of the parent and modified catalysts

Catalyst	S_{BET} (m^2/g)	V_{mi} (cm^3/g)	V_{tot} (cm^3/g)	Total Acidity (T) ($mmol/g$)	Brönsted Acid Site (B) ($mmol/g$)	Lewis Acid Site (L) ($mmol/g$)	L/T Ratio
Parent HZSM-5	323	0.121	0.274	0.156	0.109	0.047	0.301
1CL-HZ5	302	0.111	0.254	0.140	0.094	0.046	0.328
2CL-HZ5	271	0.105	0.220	0.129	0.083	0.046	0.356
1CL-S(10/400)-HZ5	301	0.120	0.254	0.139	0.091	0.048	0.345
1CL-S(20/400)-HZ5	300	0.116	0.254	0.137	0.086	0.051	0.372
1CL-S(30/400)-HZ5	300	0.114	0.256	0.138	0.083	0.055	0.399
1CL-S(40/400)-HZ5	299	0.113	0.256	0.138	0.076	0.062	0.449
2CL-S(40/400)-HZ5	269	0.105	0.223	0.128	0.080	0.048	0.375
2CL-S(40/450)-HZ5	269	0.105	0.224	0.127	0.075	0.052	0.409
2CL-S(40/500)-HZ5	270	0.106	0.231	0.128	0.071	0.047	0.367

^a Determined by t-plot method, ^b Determined by NH₃-TPD, ^c Determined by IPA-TPD

Figure 3 shows the *p*-xylene selectivity, xylenes selectivity, toluene conversion and methanol conversion of parent and modified catalysts with the variations of water partial pressure and steaming temperature. There is no significant change of toluene conversion being ca.12% by modifying the external surface with CLD, however, the *p*-xylene selectivity was enhanced from 65.6% to 72.9% and 79.5% for 1CL-HZ5 and 2CL-HZ5, respectively. The results revealed that the *p*-xylene selectivity was increased with increasing a steam partial pressure as shown in Fig. 3a. The catalyst treated by steam with its partial pressure of 40 kPa followed by single CLD (CL-S(40/400)-HZ5) gave relatively high *p*-xylene selectivity of 75.1%. This is because of a slight blockage of the diffusional paths caused by extra-framework aluminum species for high steam partial pressure (Vasques *et. al*, 1989). The effect of steaming temperature on catalytic activity for the catalysts treated by twice CLDs (2CL-S(40/xxx)-HZ5) is presented in Fig. 3b. As observed, the 2CL-S(40/450)-HZ5 catalyst exhibited the highest *p*-xylene selectivity of 86.5% partly contributed by the L/T ratio of 0.409.

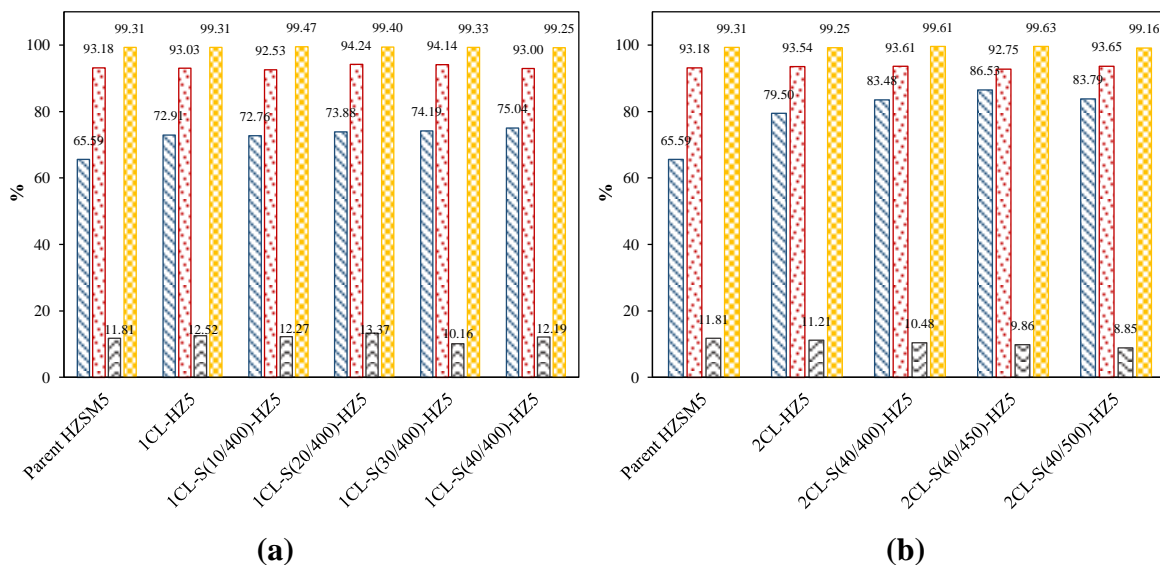


Figure 3 *p*-xylene selectivity (▨), Xylenes selectivity (⋯), toluene conversion (▩), and methanol conversion (⊞) of various catalysts (a) different water partial pressures and (b) different steaming temperatures.

CONCLUSIONS

The enhancement of *p*-xylene selectivity was successfully achieved by the sequential steaming-dealumination and CLD modifications. The influences of steam partial pressure and temperature were investigated. It can be concluded that an appropriate steaming-dealumination helps not only augment the Lewis acid sites but also agglomerate the extra-framework aluminum species to diminish the diffusional pores resulting in enhancement of

p-xylene selectivity. The 2CL-S(40/450)-HZ5 catalyst yielded the highest *p*-xylene selectivity of 86.5% with toluene conversion of 9.9% under reaction conditions: 450 °C, WHSV of 12 h⁻¹, and T/M ratio of 4/1.

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