Toluene side chain alkylation with methanol over silica catalyst

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Abstract. MSN and SiO₂ catalyst were investigated on side chain toluene alkylation with methanol reaction. Characterization of the catalyst were carried out by XRD, N₂ physisorption analysis, FTIR spectroscopy. A pyrrole adsorption FTIR study reveals shifting of perturbed NH stretching increasing slightly in MSN compared to SiO₂ catalyst revealed that MSN possessed higher basic sites than SiO₂. N₂ adsorption desorption isotherm analysis showed that MSN possessed higher surface area than SiO₂ as well as increased the amount of mesopores in catalyst. The catalytic side chain toluene alkylation with methanol reaction was conducted in the range of 523K-673K under atmospheric pressure. MSN exhibits the highest catalytic performance compared to SiO₂ catalyst.

1. Introduction
Production of polymer materials like styrene-butadiene-styrene (SBS) rubber, polystyrene and resin has gained much courtesy from community nowadays [1]. Styrene monomer serve as the starting material for the production of commercial polymers and commercially derived from the Friedel Craft Alkylation of benzene with ethylene. However, multistep of styrene creation in this process and higher consumption of energy due to difficulty of obligation of ethylbenzene products ratio. Plus, operation of this reaction occurred at higher temperature which more than 550 ºC limits its applications [2]. To address these obliges, current researcher moves to alternative side chain toluene alkylation with methanol as it provide reliable way to obtain styrene products. Unfortunately, attempts to design robust catalyst for this reaction still remained being an obstacle which until now the yield of styrene obtained still not reached satisfaction level (< 20%) due to ineffectively catalyst used and rapid deactivation of the catalyst [1–3].

Side chain toluene alkylation with methanol was extensively known required basic sites and Lewis acid sites to accelerate the reaction [4]. Owning the basic sites in the catalyst may proceed the styrene product to convert into ethylbenzene consequently from hydrogen carrier gas or originated from resulted hydrogen molecule formation from decomposition of formaldehyde. Thus, ethylbenzene product formation in this process is inevitable. Additionally, Bronsted acid sites in catalyst will lead to the occurrence of side reaction and emerging of xylene and hydrocarbon product [5]. Hence, it is crucial
to design a catalyst which possessed the criteria to be good catalyst for toluene side chain alkylation to attain higher selectivity of desired products.

Based on the literature, many efforts of evolving catalyst have been done to evaluate the catalytic performance of side chain alkylation. The effort involving alteration of the Cs-X with variety of elements together with metal or non-metal besides changing the preparation method such as ion exchange, impregnation ad physical mixing [6]. Up to now, no documentation reported on the use of silica catalyst to evaluate side chain alkylation. Herein, the metal free of SiO$_2$ and MSN catalyst were applied in order to inspect the catalytic performance from both catalyst towards toluene side chain alkylation with methanol.

2. Experimental

Mesoporous MSN were prepared referring to the previous work [7]. The cetyltrimethylammonium bromide, CTAB (surfactant), ammonium hydroxide solution, NH$_4$OH and ethylene glycol (EG) were mixed in water (700mL). The molar composition of them were 0.0032:0.2:0.2:01 respectively. The mixture was mixed for 30 minutes together with heating until clear and homogenous solution observed. After that, 1 mmol of 3-aminopropyltriethoxysilane (APTES) and 1.2 mmol tetraethylorthosilicate (TEOS) were slowly added under vigorous stirring for 2 hours until whitely solution observed. The mixture underwent centrifugation and washed with distilled water. The product underwent drying process overnight at 383K followed by calcination process at 823K for 3 hours to eliminate the surfactant.

Catalytic side chain toluene alkylation with methanol was conducted in reactor known as micro catalytic pulse within temperature 523–673 K. Initially, air stream was flew on 200 mg of catalyst for 1 hour at 723K and cooling to desired temperature after catalyst treatment. As soon as temperature was stable, toluene and methanol mixture was injected into the reactor at a flow rate 40 mL/min at reactant ratio of 1. The gas chromatograph equipped with a FID (7820N Agilent Gas Chromatograph) was used to analyze the outlet gas. The conversion of methanol and toluene ($X_{\text{methanol}}$ and $X_{\text{toluene}}$), selectivity of styrene, ethylbenzene, and other product as well as yield of styrene and ethylbenzene were calculated using equations:

$$X_{\text{methanol}} = \frac{\sum \text{all products}}{\sum \text{all products} + \text{methanol}}$$  (1)

$$X_{\text{toluene}} = \frac{\sum \text{all products}}{\sum \text{all products} + \text{toluene}}$$  (2)

$$S_{\text{styrene}} = \frac{\sum \text{styrene}}{\sum \text{all products}} \times 100\%$$  (3)

$$S_{\text{ethylbenzene}} = \frac{\sum \text{ethylbenzene}}{\sum \text{all products}} \times 100\%$$  (4)

$$Y_{\text{styrene}} = \frac{S_{\text{styrene}}}{100} \times X_{\text{toluene}}$$  (5)

$$Y_{\text{ethylbenzene}} = \frac{S_{\text{ethylbenzene}}}{100} \times X_{\text{toluene}}$$  (6)
3. Results and discussions

3.1 Crystallinity and textural properties of catalysts
Low angle XRD pattern was shown in Figure 1. MSN catalyst exhibited three respective peaks at 2θ = 2.4, 4.05, and 4.7º indicate the p6mm hexagonal symmetry in the mesostructured silica of the MSN [8–10]. While, no diffraction peak below than 2θ=10 was observed in SiO₂.

![Figure 1. Low angle XRD diffractogram of MSN and SiO₂.](image)

Isotherm with type II was revealed in SiO₂ with H3 hysteresis loop corresponded to macroporous with irregular system of pores material [11]. Meanwhile, MSN catalyst showed isotherm type IV with an hysteresis loop H1 reflected to the attributes of mesoporous materials with exceptionally uniform round and hollow pores [8,9]. Capillary condensation with two steps at P/Po = 0.3 was found in MSN catalyst due to mesoporous (intra- particles) in MSN and (P/Po = 0.9) which at high partial pressure attributed to interparticle textural porosity [9]. Besides, SiO₂ catalyst demonstrated a little narrow capillary condensation with steady slant at high partial pressure which revealed to the nearness of pores with multidimensional tube-shaped channels [7–9].

![Figure 2. Isotherm data and pore size distribution of catalyst (A) SiO₂ (B) MSN.](image)
As per the isotherm results, the (NLDFT) method was applied for pore distribution identification. It was proved the existence of mesopore in both catalysts. A narrow peak distribution with 4-5nm in MSN attributed to the pores which originated from self-assembly of surfactant during the synthesis procedure. The lessened of micropore volume in MSN due to the increment of mesopores volume in that catalyst. SiO$_2$ catalyst pore distribution was much lower compared to MSN likely because of amorphous structure of SiO$_2$ [7]. MSN catalyst possessing high pore volume as well as surface area (851 m$^2$/g) than SiO$_2$ which have 473 m$^2$/g surface area as analyzed in Table 1.

Table 1 Properties of catalysts.

| Catalyst | Surface area (m$^2$/g) | Mesopore volume (cm$^3$/g) | Micropore volume (cm$^3$/g) | Total pore volume (cm$^3$/g) |
|----------|------------------------|---------------------------|-----------------------------|-----------------------------|
| SiO$_2$  | 473                    | 0.75                      | 0.06                        | 0.81                        |
| MSN      | 851                    | 0.94                      | 0.01                        | 1.04                        |

3.2 Chemical properties of catalysts

Highest peak intensity in SiO$_2$ observed in Figure 2A clarified SiO$_2$ catalyst owned high basicity. The band at 3800–3400 cm$^{-1}$ which was indexed to the vibration of the NH band stretching in pyrrole which binding with the oxygen structure through hydrogen bonding and connection by via aromatic system with the non-framework cations which happened concurrently and impact one another [11,12]. The shifting of peak intensity of each catalyst was identified in order to determine the basic sites of each catalysts. The intensity peak at 3436 and 3409 cm$^{-1}$ for SiO$_2$ and 3459 cm$^{-1}$ for MSN catalyst. According to the former study, the strength of the catalysts was observed by the interaction of H atom with basic sites in pyrrole [12,13]. MSN catalyst has revealed the deviation of stretching of NH vibration, $\Delta V$ (NH) = −71 cm$^{-1}$ and $\Delta V$ (NH) = −94 and -121 cm$^{-1}$ for SiO$_2$. As observed, SiO$_2$ has two type of basic sites indicated that presence of two difference nature of basic sites. Thus, it proved that SiO$_2$ have strength basic sites rather than MSN.

![Figure 3](image_url)

Figure 3. (A) FTIR pyrrole for both catalyst (B and C) FTIR spectra in evacuated system for SiO$_2$ and MSN catalyst.

FTIR results in evacuated system in both MSN and SiO$_2$ catalysts were shown in Figure 3B and 3C. Commonly, spectra of both catalysts demonstrated the presence of five bands at 3740, 3700, 3660, 3610, 3545 and broad band at 3480 cm$^{-1}$. It were corresponded to the terminal silanol group,
perturbation of OH through lattice defects, hydroxyl group species, bridging hydroxyl, perturbation of H-bond interaction with the mesoporous channels and silanol group respectively [8–11,14,15]. According to the result observed, it showed that the intensity of every single peak in FTIR spectra in evacuated system augmented two times from SiO$_2$ to MSN catalyst.

### 3.3 Catalytic testing

Evaluation catalytic performance of side chain toluene alkylation with methanol was performed at temperature range of 523–673 K using micro catalytic pulse reactor. The methanol conversion, toluene conversion and the yield of the ethylbenzene with styrene product was portrayed in Figure 4. As the results, Figure 4A illustrates that the methanol conversion over silica catalyst which SiO$_2$ and MSN catalyst. As temperature increased, it was found that the methanol conversion was kept increasing until over MSN catalyst which shows declining of methanol conversion at 673K. It might be due to the lower basic sites possessed in the MSN catalyst. It verified that the basic sites was consumed for the formaldehyde formation via aldol-type condensation as the temperature increase [3,4,16]. As depicted in the pyrrole probed FTIR spectroscopy (Fig 2A), it revealed that the SiO$_2$ have more basic sites rather than MSN catalyst. It could be the cause of fully converted of methanol.

![Graph A: Methanol conversion](image1)

![Graph B: Toluene conversion](image2)

![Graph C: Styrene and ethylbenzene yield](image3)

**Figure 4.** Catalytic toluene side chain alkylation performance (A) Methanol conversion (B) Toluene conversion (C) Styrene and ethylbenzene yield.

Furthermore, Fig 4B demonstrated the toluene conversion over SiO$_2$ and MSN catalyst within temperature range 523-673K. It was found that toluene conversion was slightly increased from 523K to 673K. It was due adequate amount of basic sites in SiO$_2$ resulted in higher formation of benzyl anion and 2-phenylethanol intermediates [6,17]. However, MSN catalyst showed lower conversion of toluene at each temperature compared to SiO$_2$ catalyst. It might be due to fewer basic sites in MSN as evidenced by FTIR adsorbed pyrrole. Preceding work stated that occurrence of less basic sites suppressed the ability of the basic sites to convert toluene into the benzyl anion intermediates [3,5].
Table 2 Distribution of products in side chain toluene alkylation at 523-673K.

|                    | SiO$_2$ catalyst: |                  |                  |                  |                  |
|--------------------|------------------|------------------|------------------|------------------|------------------|
|                    | Temperature (K)   | 523              | 573              | 623              | 673              |
| Methanol conversion (%) | 63.9            | 93.8             | 94.9             | 100              |
| Toluene conversion (%)  | 25.4            | 41.8             | 68.5             | 85.5             |
| Selectivity of products: |                |                  |                  |                  |                  |
| Hydrocarbon         | 0.224           | 28.4             | 90.7             | 95.7             |
| Benzene             | 95.5            | 69.6             | 7.78             | 3.98             |
| Ethylbenzene        | 0.00            | 0.00             | 0.00             | 0.00             |
| Styrene             | 4.24            | 2.08             | 1.57             | 0.335            |
| Yield of products:  |                  |                  |                  |                  |                  |
| Hydrocarbon         | 0.057           | 11.9             | 62.1             | 81.8             |
| Benzene             | 24.3            | 29.1             | 4.92             | 3.40             |
| Ethylbenzene        | 0.00            | 0.00             | 0.00             | 0.00             |
| Styrene             | 1.08            | 0.869            | 1.08             | 0.304            |
| MSN catalyst:       |                  |                  |                  |                  |                  |
|                    | Temperature (K)   | 523              | 573              | 623              | 673              |
| Methanol conversion (%) | 34.0            | 46.5             | 80.3             | 75.2             |
| Toluene conversion (%)  | 21.7            | 33.5             | 32.9             | 33.3             |
| Selectivity of products: |                |                  |                  |                  |                  |
| Hydrocarbon         | 4.83            | 29.3             | 35.3             | 42.4             |
| Benzene             | 81.1            | 66.5             | 60.5             | 49.9             |
| Ethylbenzene        | 3.91            | 1.20             | 1.19             | 2.85             |
| Styrene             | 10.1            | 3.02             | 2.98             | 4.87             |
| Yield of products:  |                  |                  |                  |                  |                  |
| Hydrocarbon         | 1.05            | 9.82             | 11.6             | 14.1             |
| Benzene             | 17.6            | 22.3             | 19.9             | 16.6             |
| Ethylbenzene        | 0.848           | 0.402            | 0.392            | 0.949            |
| Styrene             | 2.19            | 0.10             | 0.980            | 1.62             |

Fig. 4C illustrated the products of styrene and ethylbenzene which considered to be desired product in the reaction process. From the result above, it was discovered that MSN formed more styrene and ethylbenzene product. It was due to the controllable of basic sites in selectivity of styrene and ethylbenzene product in MSN. It can be proved in Table 2 which showed increase of higher desired product selectivity from 0.335 % to 7.72% styrene and ethylbenzene selectivity. From Table 2, SiO$_2$ produced more hydrocarbon product and decreasing selectivity about 44.3% at 673K in MSN catalyst.

The presence of additional basic sites would lead to the side reaction resulted in higher production of hydrocarbon and benzene product along with quenching the xylene product [5]. Remarkably, no production of styrene product observed in SiO$_2$ catalyst compared to MSN catalyst suggesting the basic sites possessed in SiO$_2$ has no ability to transfer hydrogen to form ethylbenzene. Higher hydrocarbon product by SiO$_2$ might be due to the micropores in the catalyst that will cause diffusion limitations of products. Thus, the formation of hydrocarbon product due to favourable of thermal cracking process. These outcome shows coinciding with N$_2$ adsorption-desorption result which revealed that desired product favour in high mesopore catalyst.

4. Conclusions
Catalytic performance of toluene side chain alkylation with methanol over silica catalyst (SiO$_2$ and MSN) were successfully evaluated at atmospheric pressure. The results revealed that a significant enhancement of MSN catalyst towards yield of styrene and ethylbenzene product compared to SiO$_2$. Fascinatingly, it can be summarized that basicity plays a noteworthy part in dehydrogenation of
methanol to formaldehyde and hydrogenation of styrene to form ethylbenzene in order to improve the catalytic performance. Despite of basicity, presence of mesopores also contribute to the augmentation of the selectivity styrene and ethylbenzene product. From the results obtained, it also can be clinched the basic sites in the catalyst also will lead to the formation of the hydrocarbon product and fast decomposition of formaldehyde into the carbon monoxide and hydrogen.

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