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Reactivity of mesoporous ZSM-5 zeolite towards Friedel-Crafts acylation of anisole and propionic anhydride

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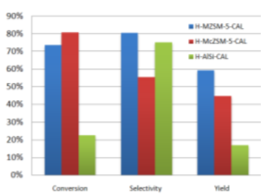
GRAPHICAL ABSTRACT



ABSTRACT

ZSM-5 zeolite is known as solid acid catalyst for many organic reactions. ZSM-5 zeolite is a microporous aluminosilicate catalyst which is not suitable for reactionsinvolving large molecules. Therefore, ZSM-5 with mesopores size needs to be synthesized. In this study, mesoporous ZSM-5 were synthesized in the presence and absence of sucrose as mesotemplate. As comparison, microporous ZSM-5 was also synthesized using standard method. The samples were characterized using XRD, FTIR and nitrogen adsorption analysis. Results from XRD and FTIR of sample with sucrose template showed the formation of crystalline ZSM-5 structure while sample without sucrose showed amorphous phase. Nitrogen adsorption analysis showed that the synthesized mesoporous ZSM-5 has mesoporous structure with type IV isotherm which the average pore is in the range of 4-6 nm and the BET surface area was 400 m^2/g. The reactivity of all synthesized samples was tested in Friedel-Craft acylation of anisole and propionic anhydride to produce the main product, p-methoxypropiophenone and the side product, propionic acid. Results proved that synthesized mesoporous ZSM-5 with sucrose is the best catalyst in term of conversion and selectivity with 73.66% and 80.45% respectively as compared to sample without sucrose has comparable selectivity, 75.11% but low conversion, 22.63%. In contrast, microporous ZSM-5 has comparable conversion, 80.81% but low selectivity, 55.53%. This indicates that acidity and mesoporosity are responsible enhanced reactivity of ZSM-5 catalyst for Friedel-Crafts reaction involving large molecule.

Keywords: mesoporous ZSM-5 zeolite, microporous ZSM-5, mesoporous, aluminosilicate, Friedel-Crafts acylation reaction

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1. INTRODUCTION

Zeolite Socony Mobil-5 popularly known as ZSM-5, was first synthesized by Argauer and Landolt in 1972. ZSM-5 has framework with type mordenite framework inverted (MFI) form, which is analuminosilicate zeolite belonging to the Pentasil family, composed of several Pentasil units linked together by oxygen bridges to form Pentasil chains [1]. Figure 1 shows the Pentasil unit of ZSM-5 consisting of eight of five-membered rings. The oxygen bridges are interconnected with Pentasil chains, which forming corrugated sheets with 10-ring holes. Like the Pentasil units, each 10-ring hole has Al or Si as vertices with an O assumed to be bonded between each vertex. The estimated pore size of the channel running parallel with the corrugations is 0.54–0.56 nm.ZSM-5 and its molecular sieves provide the periodically sized microporous structure, which parts of the structure are active sites.

Microporous molecular sieves especially ZSM-5, is important aspect in acid catalysis because of their peculiar pore structure and strong intrinsic acidities. These unique properties leave zeolite with wide as applications as catalyst in petrochemical industry such as in the processes of hydrocarbon, cracking and so on [2]. However, the limitation of micropores ZSM-5 is that it is strongly hinder the diffusion of large molecules and this causing the acceleration of catalyst deactivation in the reaction [3]. Hence, researchers have focused on the synthesis of nanocrystal of hierarchically structured zeolite consisting the mixture of micro and mesoporous structure [2].

Hierarchical zeolite, containing both micropores and mesopores structure which is believed could improves catalytic performance by shortening the diffusion paths and making more active sites exposed and accessible to gust molecule at the same mass of zeolite. Hierarchical zeolite has high hydrothermal stability, string acidity and large mesopores structure. The introduction of mesoporous is a convenient and effective method.

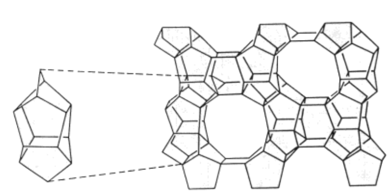


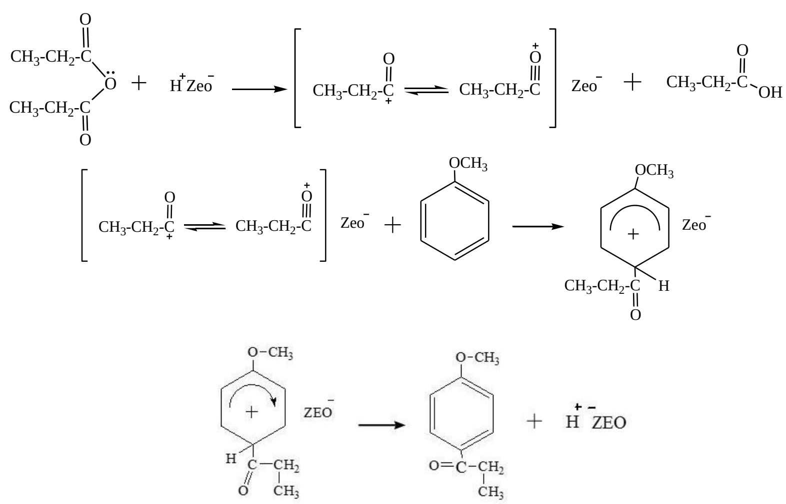
Fig. The pentasil unit of ZSM-5framework

This research emphasized on synthesizing and characterizing mesoporous ZSM-5 in the presence of sucrose as mesotemplate agent and tested their catalytic performance in Friedel-Crafts acylation involving large molecules. As comparison microporous ZSM-5 was also applied for the catalytic testing to study the effect of porosity towards the reactivity of the catalysts for the Friedel-Crafts reaction. The reaction proceeds in the presence of acidity provided by the ZSM-5 (Scheme 1) while porosity of catalyst determined selectivity of the catalyst. High percentage of conversion, selectivity and yield is said to be the best catalyst for the Friedel-Crafts acylation reaction.

2. EXPERIMENTS

The experiment focused on the synthesis of mesoporous ZSM-5, followed by characterization of the all synthesized samples using XRD, FTIR and N_2 adsorption. The reactivity of samples as a catalyst was then tested in Friedel-Crafts acylation reaction of anisole and propionic anhydride.

Mesoporous ZSM-5 with composition of 1 Al_2O_3 : 50 SiO_2: 8 TPAOH: 1500 H_2O was synthesized using sol-gel method in the presence of sucrose as template [4]. Aluminium sulfate octadecahydrate ($Al_2(SO_4)_3.18H_2O$) (0.28 g, Riedel-de-Haën) and tetrapropylammonium hydroxide solution (TPAOH 20%, 6.25 mL, Merck Schuchardt) were dissolved in distilled water (3.75 mL) under stirring to obtain a clear and homogenous solution. Tetraethyl orthosilicate (TEOS, 5 mL, Aldrich) was then dropped into the solution under vigorous stirring and left stirred for 6 hours. The mixture was allowed to age at 100º C for 16 hours in static condition. The mixture was then mixed with sucrose solution (15 mL, GCE), followed by 30 minutes stirring. The resulted suspension was transferred Teflon bottle and kept at 100°C in an oven for 48 hours. The solid formed was filtered, washed with distilled water and allowed to dry for overnight at 60°C. Finally, the powder was calcined in air at 550°C for 6 hours. The sample obtained was denoted as MZSM5-CAL. The synthesis was repeated without the presence of sucrose and denoted as mesoporous aluminosilicate. As comparison microporous ZSM-5 was synthesized following the method reported by Kadja *et al.* [5]. The sample was denoted as McZSM-5. Sample was characterized using XRD, FTIR and N_2 adsorption analysis.



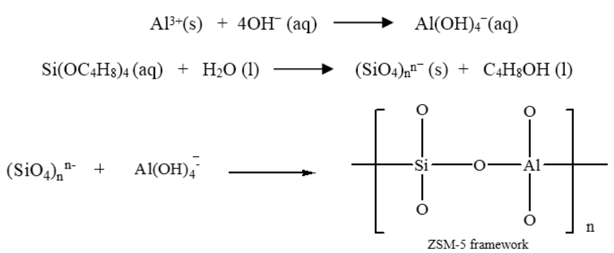
Scheme 1 Proposed mechanism of Friedel-Crafts acylation of anisole and propionic anhydride

For catalytic testing, the synthesized sample needs to be protonated in order to create the acidity in the catalyst. The sample was ion exchanged using 1M NH_4NO_3 to convert all to NH_4-formed. Before reaction, the sample was activated at 500°C for 3 hours. The reaction was carried out by using 50 mL two necked round bottom flask equipped with condenser. The ZSM-5 catalyst (0.3g), anisole (5.46 g, 50 mmol, Merck and propionic anhydride (5.46 g, 50 mmol, Merck) were put in flask. The flask was placed in oil bath at 120°C and the reaction was run for 24 hours. The liquid product was sampled out at 5 min, 2 hours and 24 hours and analysed using FID gas chromatography using ULTRA 1 column. The proposed mechanism of Friedel-Crafts acylation reaction of anisole and propionic anhydride is shown in Scheme 1. The reactivity of the catalyst was reported in term of percentage of conversion, selectivity and yield.

3. RESULTS AND DISCUSSION

3.1 Formation of mesoporous ZSM-5

Mesoporous ZSM-5 had been synthesized using sol-gel method. Sol-gel method able to produce nano-size particle as it provides high surface area catalyst and also prevent problems with co-precipitation. Since the method used is sol-gel method, then the best precursor is metal alkoxide, which is TEOS. Silica is a good in making zeolite catalyst because it provides high surface area meanwhile aluminium is used due its low cost and easily to get. Tetrapropylammonium hydroxide solution (TPAOH) act as molecular template for ZSM-5 [6]. Scheme 2 shows the process occurred during the formation of ZSM-5 framework. Sucrose was used as mesotemplate due to the big structure in which suitable for fabricating hierarchical ZSM-5 with a chainlike morphology [7].



Scheme 2 Process that occurred during the formation of ZSM-5 zeolite framework.

3.2 Characterization of sample by XRD

XRD is commonly used to identify the phase and crystallinity of the solid obtained. Figure 2(a) showed the standard XRD pattern from International Zeolite Association for ZSM-5 phase and 2(b) shows the XRD pattern of as synthesized mesoporous ZSM-5 obtained from the experiment, while Figure 2(c) and (d) show XRD patterns of microporous ZSM-5 and aluminosilicate respectively. According to International Zeolite Association, ZSM-5 falls under MFI family framework type coordinates the peaks of ZSM-5 should consist of two intense peak at 2θ 7.94° and 9.00° followed by two small peaks at 2θ 45.22° and 45.74°. Both mesoporous ZSM-5 and microporous ZSM-5 showed high intensity at peaks that correspond to ZSM-5 based on the standard data from (JCPDS 44-0003)[8] indicating that the synthesized samples have ZSM-5 phase. As for mesoporous aluminosilicate, it only showed low intensity at peaksthat correspond to the peaks XRD pattern of ZSM-5. This indicates that for mesoporous aluminosilicate has the crystal structure but the percentage is very low, hence it can be as classified as amorphous structure.

3.3 Characterization of sample by FTIR

FTIR provides qualitative and quantitative analysis for both organic and inorganic sample. It is used to determine the type of bond and functional groups exist in the sample. Basically, zeolite has typical pattern for structural vibration in infrared spectrum. The pattern mostly consists of several main peaks corresponding to the structural framework which are the asymmetric and

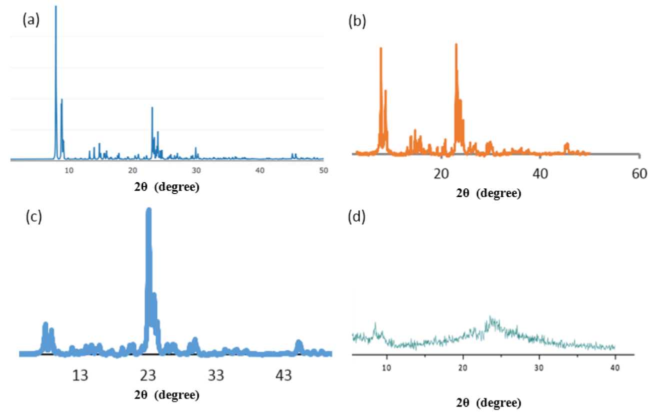


Fig. 2 (a) XRD pattern from International Zeolite Association (b) XRD pattern of mesoporous ZSM-5 (c) XRD pattern of microporous ZSM-5 and (d) XRD pattern of mesoporous aluminosilicate

symmetric stretching peaks of tetrahedral TO_4 (T= Al,Si) at 1400-1000 cm^{-1} and 750-650 cm^{-1} respectively and T-O bending at 500-400 cm^{-1}[6]. The IR measurement was obtained in the wavenumber range between 4000 cm^{-1} to 400 cm^{-1} and the KBr method was used to prepare the sample before being analysed.

Figure 3(a) shows the spectra of mesoporous ZSM-5 before calcined (MZSM5-NC) and after calcined (MZSM5-CAL). The only different between these two samples is MZSM5-NC has a peak at 1473.54 cm^{-1}, meanwhile the peak is not present in MZSM5-CAL. This shows that the impurities and unwanted species especially the organic template species has been completely removed from the compound. Figure 3(b) shows the spectra of mesoporous ZSM-5 after calcined (MZSM5-CAL) and after protonated with NH_4NO_3, (H-MZSM-5). H-MZSM-5 has broader peaks because more hydrogen bond (OH) is present in the form of hydroxyl nest, which formed in the structure during protonation. Figure 3(c) shows the spectra of protonated samples of mesoporous ZSM-5 (H-MZSM-5), microporous ZSM-5 (H-McZSM-5) and mesoporous aluminosilicate (H-AlSi). Only H-AlSi shows different pattern than the other ZSM-5 samples at the range 550-570 cm^{-1}. This is because aluminosilicate is considered amorphous according to XRD result and it does not have the 5-ring secondary building units characteristic for ZSM-5 framework thus no vibration is observed in this IR range.

3.4 Characterization of mesoporous ZSM-5 by N_2 adsorption analysis

The type of pore, BET surface area, pore volume and pore width of the resulted solid were determined by nitrogen adsorption-desorption analysis. Figure 4(a) shows the adsorption isotherm of MZSM-5-CAL, Figure 4(b) for the t-plot of MZSM-5-CAL and Figure 4(c) for BJH desorption pore volume of MZSM-5-CAL. The isotherm of the MZSM-5-CAL falls within type IV according to IUPAC classification group which shows that pore that falls in mesoporous size range. t-Plot was used to determine the microporous surface area of the samples. Based on Figure 4(b), this shows that MZSM-5-CAL consists of a mixture of microporous and mesoporous. The microporous volume is 0.047396 cm^3/g and micropores area is 108 m^2/g. The BET surface area of MZSM-5-CAL is 397 m^2/g. The maximum pore width distribution of MZSM-5-CAL is *ca.* 55.26 Å with pore volume 0.01751 cm^3/g meanwhile the other pore width distribution of MZSM-5-CAL *ca.* 67.78Å with pore volume 0.00973561 cm^3/g.

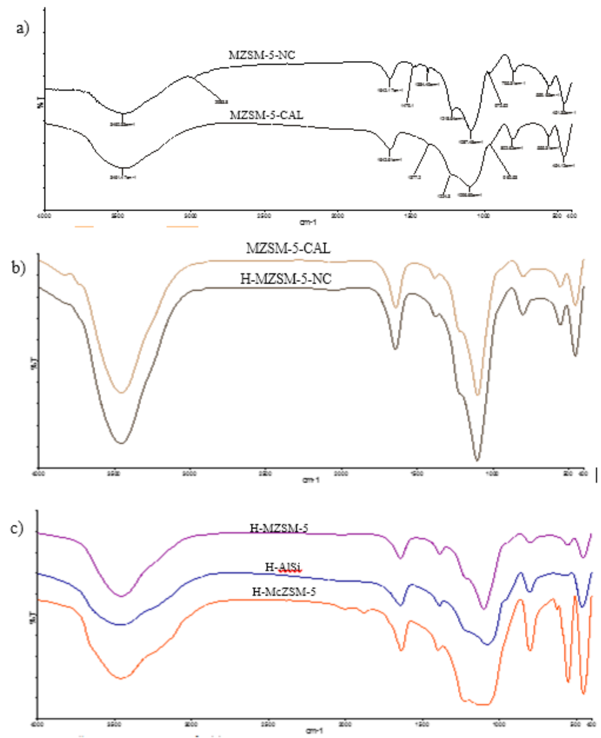


Fig. 3FTIR spectra of (a) MZSM5-NC and MZSM5-CAL, (b) MZSM5-CAL and H-MZSM5, and (c) H-ZSM-5, H-AlSi and H-McZSM-5

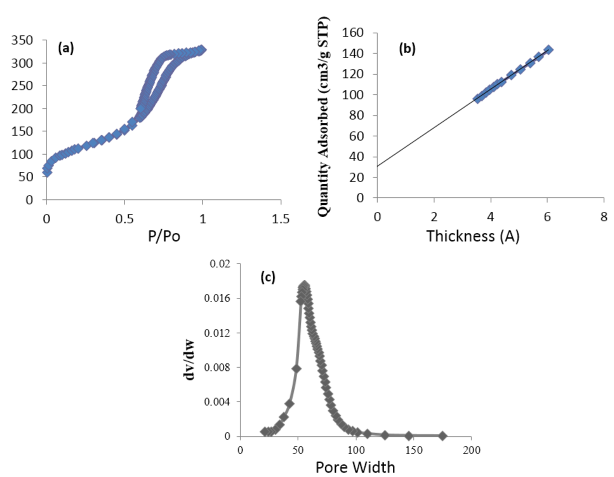


Fig. 4 (a) Adsorption isotherm of MZSM-5-CAL, (b) t-plot of MZSM-5-CAL and (c) BJH desorption pore volume of MZSM-5-CAL

As for sample mesoporous aluminosilicate H-AlSi-CAL, the sample showed mesoporous character with adsorption isotherm of the type IV with BET surface area of 700 m^2/g, with t-plot showing the intercepted line at 0 indicating a mesoporous character[9], while H-McZSM-5-CAL also showed type IV isotherm with low BET surface area of 43.2 m^2/g but showed microporosity character, based on the t-plot which intercepted on the y axis [10].

3.5 Protonation of samples

Samples need to be protonated in order to create acidity in the as-synthesized ZSM-5 catalyst. Protonation step had been done by ion exchanged with NH_4NO_3 to change it to ammonium form ZSM-5, followed by calcination at 400°C.

$$NH_4\text{-ZSM-5(s)} \longrightarrow \text{HZSM-5(s)} + NH_3\text{(g)}$$

Common acid like HCl can also be used to create acidity in ZSM-5. However, this kind of acid has major drawback by leaving behind Cl^-, which is poisonous to the catalyst. The ion could destroy the framework structure of zeolite catalyst. In the NH_4-form, calcination resulted in the evolution of NH_3, leaving H^+ attached to zeolite catalyst and not poisonous to the catalyst.

3.6 Testing of the catalyst in Friedel-Crafts acylation reaction

Reactivity of samples (H-MZSM-5, H-McZSM-5 and H-AlSi) as catalyst has been tested in Friedel-Crafts acylation reaction using anisole and propionic anhydride. According to the theory, the reaction of anisole and propionic anhydride will produce *p*-methoxypropiophenone as the main product and propionic acid as side product. This study investigates the effect of different type of porosity of the catalysts for the formation of desire product, which is *p*-methoxypropiophenone over side-product, propionic acid. Figure 6 shows the gas chromatogram of the reaction products using H-MZSM-5 for 24 hours.

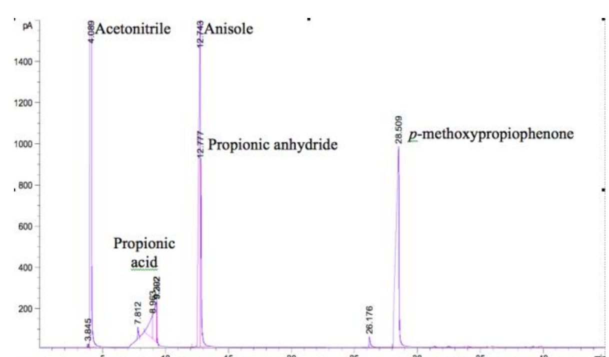


Fig. 6 Gas chromatogram using H-MZSM-5 at 24 hours reaction

The pattern of the gas chromatogram of the product from reaction using H-McZSM-5 and H-AlSi are similar only different in intensities of the peaks

3.7 Effect of Acidity and Porosity of Catalyst in Friedel Crafts reaction.

p-Methoxypropiophenone is the desired product for Friedel-Crafts acylation of anisole and propionic anhydride. Figure 7 shows the percentage of conversion, selectivity and yield for each catalyst sample. Reactivity of the catalyst is shown by the percentage of conversion which depends on the number of active sites as in this reaction provides by the acidity of the catalyst. While the selectivity and yield is based on the desired product, *p*-methoxypropiophenone over propionic acid. Only H-MZSM-5 and H-McZSM-5 catalysts showed high conversion as both have ZSM-5 framework structure consisting of framework acidity which is known to have high strength in acidity. In contrast, H-AlSi showed low conversion, indicating that it has low strength of acid due to its amorphous structure, in order to catalyse the acylation reaction. In term of selectivity, the mesoporosity plays a role in selecting the desired product. This is shown by H-MZSM-5 and H-AlSi catalysts that give higher selectivity as compared microporous H-McZSM-5, has the lowest selectivity towards the desired product due to the micropore size of the pore of channel provided by H-McZSM-5 in the range of 0.54–0.56 nm, which is small for big product like *p*-methoxypropiophenone to pass through it. This proved that mesoporous ZSM-5, H-MZSM-5 having both mesoporosity and high strength acidity is the most reactive catalyst for this Friedel-Crafts acylation reaction as it could convert anisole to products well and able to choose desired product, *p*-methoxypropiophenone efficiently as well as gives higher percentage of yield in the reaction.

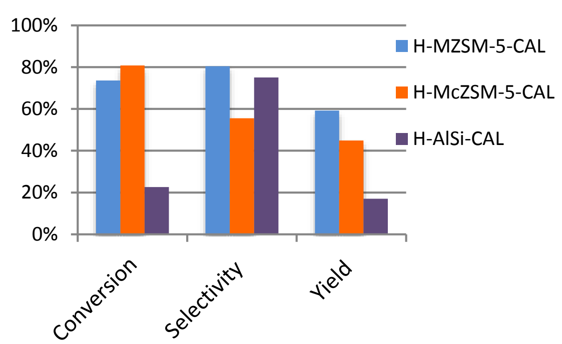


Fig. 7 Percentage of conversion, selectivity and yield for each sample

4. CONCLUSION

Mesoporous ZSM-5 with molar composition $1Al_2O_3$: $50SiO_2$: 8TPAOH: $1500H_2O$ was successfully synthesized using sucrose as mesotemplate based on the XRD result. Both mesoporous and microporous ZSM-5 show the pattern of FTIR spectra for crystalline ZSM-5 except for aluminosilicate due to its amorphous phase. For nitrogen adsorption, synthesized ZSM-5 shows mesoporous structure with type IV isotherm, having both mesoporous and microporous structure with BET surface area for the synthesized mesoporous ZSM-5 is 400 m^2/g. The activity study of catalyst in Friedel-craft acylation reaction of anisole and propionic anhydride showed that mesoporous ZSM-5 the most reactive giving the highest conversation, selectivity and yield for the main product *p*-methoxypropiophenone. Microporous ZSM-5 reveals to have comparable conversion but low selectivity for this reaction due to the pore size of its channel, while aluminosilicate proves to have comparable selectivity but low conversion due to its amorphous structure. In conclusion, combination of acidity and mesoporosity are essential for the reactivity of catalyst for Friedel-Crafts acylation reaction.

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