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Synthesis of Ruthenium Supported on Protonated Fibrous Silica ZSM-5 for Methanol to Olefin Reaction

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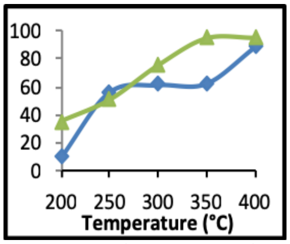
GRAPHICAL ABSTRACT



Conversion of methanol to olefin

ABSTRACT

Olefins are unsaturated alkene and essential raw materials in petrochemical and polymer industries. As the global crude oil prices rise, future generations will experience a serious raw material crisis. Producing olefins from non-oil sources are considered as the most effective ways to overcome the crisis. Conversion of methanol to olefins is one of the most economical methods since this reaction only involves a cheap starting chemical which is methanol. The fibrous morphological zeolite catalyst (FZSM-5) has been successfully prepared using microwaves assisted hydrothermal methods followed by protonation and ruthenium loaded on protonated fibrous silica ZSM-5 (Ru/HFZSM-5) by impregnation method. The catalyst is characterized by field emission scanning electron microscopy (FESEM), nitrogen physisorption analysis and pyridine-Fourier transform infrared (FTIR). The FESEM result showed ZSM-5 (HFZSM-5) fibrous silica having ZSM-5 structure and spherical morphology with dendrimeric silica fibers evenly distributed. Furthermore, the increase in the surface area of both catalysts is shown by the analysis of nitrogen physisorption from 470.43 m²/g to 474.60 m²/g for HFZSM-5 and Ru/HFZSM-5 respectively. The addition of metals into the HFZSM-5 catalyst increases the acidity of the catalyst as shown in the pyridine-FTIR spectra. The catalytic performance was tested at 200 – 400 °C under atmospheric pressure. Increased acidity of Ru/HFSZSM-5 indirectly increased the percentage conversion of methanol to olefin from 88.60% to 95.14% and Ru/HFZSM-5 gave 93.93% yield of olefins.

Keywords: zeolite, physisorption, acidity, fibrous silica ZSM-5, physicochemical properties

1. INTRODUCTION

Olefins are unsaturated alkene compounds made up of hydrogen and carbon that contains of one or more pairs of carbon atoms bonded by a double bond and can be precursors for the improvement of industrial polymers and petrochemical products. Nowadays, natural gas has turned into a plenteous fuel and synthetic feedstock. As the innovation for methanol generation from flammable gas is generally utilized and entrenched, the transformation of methanol to olefins (MTO) has tendency to be a fascinating and promising method over methane to chemicals. At the presence, the polymer industry has become an important target in upholding the Malaysia's name in the eyes of the world. Light olefins such as ethylene, propylene and butylene are very significant starting materials to produce polyolefins in polymer industry. Nowadays, most of light olefins are mainly produced by thermal cracking of naphtha. Nevertheless, it requires high energy consumption and often low yield of light olefins is obtained. Plus, our country is now emphasized by the rapid development of economic and technological development from year to year. Therefore, it is imperative to introduce other alternatives to produce light olefins using non-oil feedstock.

Alternative routes to derive light olefins called methanol-to-olefins have been noted for many researchers as methanol is one of the most accessible chemicals available from any carbon source such as charcoal, biomass and natural gas. The methanol industry has been flourishing because of the shale gas transformation and the abundance of its shoddy feedstock and natural gas. The natural gas prices have dropped 30 percent over the decade whereas the crude oil prices have more than doubled. Two dimensional (2D) mesoporous silica nanoparticles such as MCM-41, MSN and SBA-15 with a cylindrical pore structure quite popular in catalysis as a catalyst support. Regrettably, due to closed-packed spherical empty cages, it results in poor accessibility of bulk reactant to the active site insides the pores. Thus, it limits their applications.

In this study, an analogue by the structure of fibrous mesoporous silica nanoparticles (KCC-1) which was developed by Polshettiwar, a protonated fibrous silica ZSM-5 (HFZSM-5) catalyst was synthesized since it has a higher surface area due to the presence of dendrimeric fiber as a silica source. The presence of dendrimeric fiber increases the number of active sites and facilitates transportation of reactants and products into and out of catalyst pores. Besides, it also has better accessibility of active sites as the dispersion of active sites is in their dendrimeric fiber instead of inside the catalyst pores. Recently, a lot of studies have used a metal loaded catalyst in the MTO reaction. Based on experimental results, it showed that the catalyst loaded by noble metals such as Pt, Rh and Ru exhibited high activity and selectivity even at low temperature and good stability towards coke deposition. In this study, it is expected that the combination of the ruthenium supported on protonated fibrous silica ZSM-5 (Ru/HFZSM-5) would enhance the catalytic activity of the MTO reaction.

2. EXPERIMENTAL

The experiment was divided into three main stages. The first stage focused on synthesis of fibrous silica ZSM-5 by ZSM-5 seed crystallization. The second stage was preparation protonated fibrous silica ZSM-5 catalysts and the last stage was preparation of ruthenium loaded on protonated fibrous silica ZSM-5 by impregnation method. Later, the physicochemical properties of the protonated fibrous silica ZSM-5 and ruthenium loaded on protonated fibrous silica ZSM-5 were investigated and the catalytic performance was tested in the MTO reaction.

2.1 Preparation of fibrous silica ZSM-5 (FZSM-5)

Fibrous silica ZSM-5 catalyst was prepared by the microwave assisted hydrothermal method using ZSM-5 as a catalyst seed. 1 mole of tetraethyl orthosilicate was dissolved in a solution of 28 moles of toluene and 1.62 moles of 1-butanol. A stirred solution of 0.9 moles of urea and 0.27 moles of cetyltrimethyl ammonium bromide in distilled water was also prepared. Both solutions were mixed and stirred for 15 minutes at room temperature. The ZSM-5 seed was then added to the mixture followed by stirring for another 30 minutes. The solution was then exposed to microwave radiation of 400W intermittently at 120 °C for 4 hours. The solid product that was obtained by isolation by means of centrifugation was then washed with distilled water and acetone. Next, the solid product was dried in the oven at 100 °C overnight. The dried solid was then calcined using a furnace at 550 °C for 6 hours. The sample was labelled as HFZSM-5.

2.2 Preparation of protonated fibrous silica ZSM-5 (HFZSM-5)

Two-fold proton ion-exchange was performed on FZSM-5 catalyst. The catalysts were then placed in a beaker equipped with a magnetic bar. 1 M NH_4NO_3 solution dissolved in distilled water was added to the catalysts. The beaker was placed on the magnetic stirrer, and the mixture was stirred at 70 °C for 8 hours. These proton ion-exchange steps were repeated twice. The solution was filtered using a vacuum pump, and then washed using distilled water, followed by drying at 100 °C for overnight. Calcination of the solid products was performed at 550 °C for 3 hours. The sample was labelled as HFZSM-5.

2.3 Preparation of ruthenium loaded on protonated fibrous silica ZSM-5 (Ru/HFZSM-5)

The sample evacuated and impregnated with ruthenium metal. The Ru/HFZSM-5 was prepared by impregnation of protonated HFZSM-5 with the solution of ruthenium (III) chloride hydrate. Then, it was followed by drying and calcination in air at 550 °C.

2.4 Catalytic testing of Methanol to Olefin

A micro catalytic reactor is firmly required to carry out the catalytic reaction methanol to olefin. In this study, 0.2 g of catalyst was needed and placed into a quartz tube with 8 mm diameter. Then, the reactor was treated by air stream at 20 ml/min for 1 hour. It was then heated to 200 ºC. Next, the flash evaporated into an online 6090 Agilent Gas Chromatography implemented with HP-5 capillary column and a flame ionization detector (FID). The interval between injections of methanol is 20 minutes. The evaluated temperature for this methanol to olefin reaction within 200-400 °C.

3. RESULTS AND DISCUSSION

3.1 Characterization of HFZSM-5 catalyst by Field Emission Scanning Electron Microscopy (FESEM)

The surface morphology of HFZSM-5 catalysts from FESEM analysis was shown as Figure 1. HFZSM-5 catalyst exhibited a dendrimeric silica fiber with spherical morphology. HFZSM-5 catalyst also exhibited a quite large distance between dendrimers (inter-dendrimer distance) which would allow fast diffusion and easy access to active sites which will lead to an increase in their catalytic performance. Similar morphology of protonated fibrous silica ZSM-5 with fibrous silica KCC-1 observed from previous report (Polshettiwar, *et al.*, 2010).

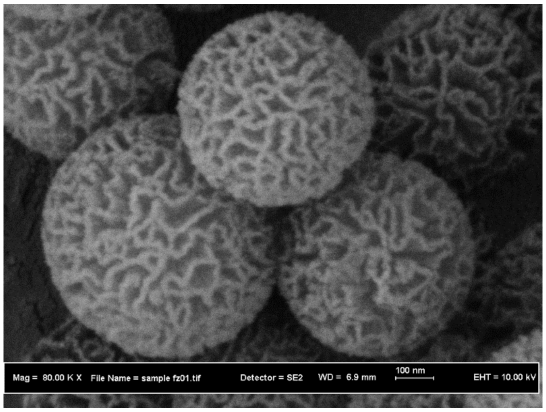


Figure 1 FESEM image of protonated fibrous silica ZSM-5 (HFZSM-5).

3.2 Characterization of HFZSM-5 and Ru/HFZSM-5 by N_2 physisorption analysis

The N_2 adsorption-desorption analysis is the most widely used technique to estimate textural properties of solid materials. Figure 2 represents the N_2 adsorption-desorption isotherms of HFZSM-5 and Ru/HFZSM-5 catalysts. According to the isotherms graph demonstrated in Figure 2, higher nitrogen uptake was observed for Ru/HFZSM-5 indicating the existence of large number of pores compared to HFZSM-5 catalyst. Subsequently, Ru/HFZSM-5 and HFZSM-5 catalyst exhibited Type IV isotherms with H3 hysteresis loop. The hysteresis loop occurs when the gas adsorbed was condensed as liquid in the catalyst pore. This phenomenon called as capillary condensation. Furthermore, the presence of the hysteresis loop indicated the presence of mesopore with non-uniform slit-shaped pores in the catalyst. Both isotherms showed the presence of two steps of capillary condensation. The first step was observed at lower relative pressure of 0.3 ascribed to the presence of micropore in the catalysts. Meanwhile, the second step of capillary condensation observed at higher relative pressure of 0.9 was attributed to the formation of mesopore in the catalysts.

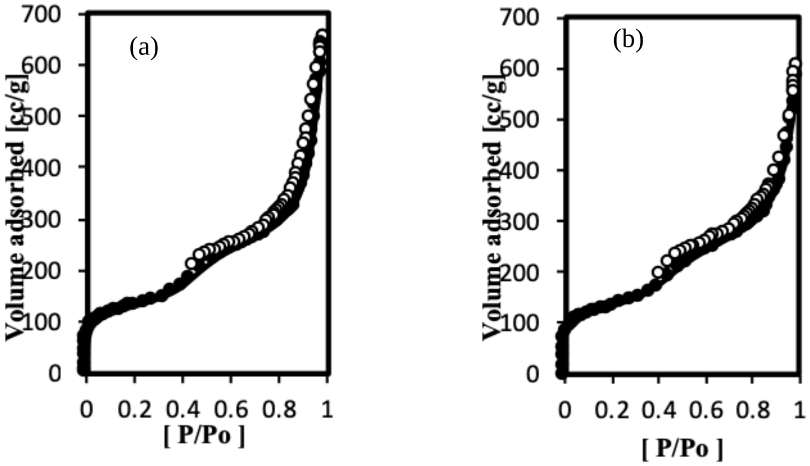


Figure 2 N2 adsorption-desorption of (a) HFZSM-5 and (b) Ru/HFZSM-5 catalysts.

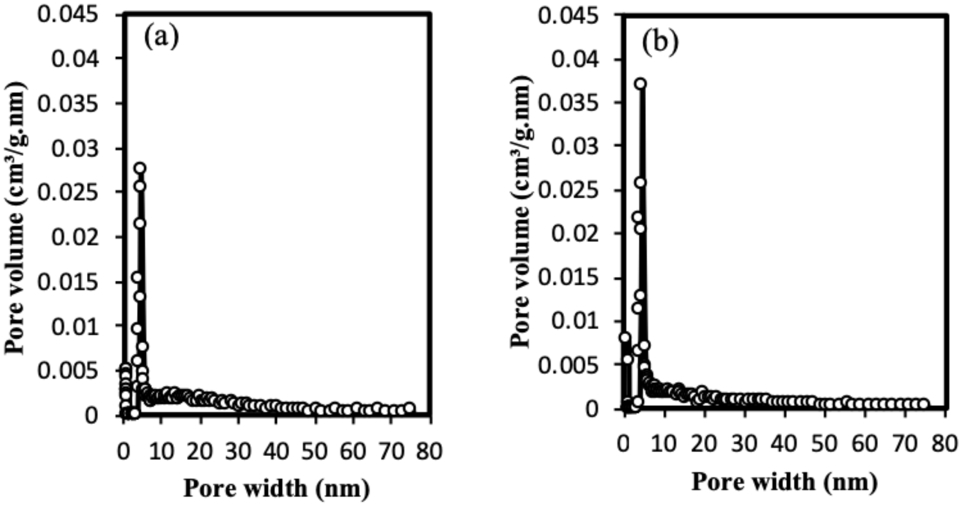


Figure 3 Pore distribution of HFZSM-5 and Ru/HFZSM-5 catalyst (a) HFZSM-5 and (b) Ru/HFZSM-5.

The non-local density functional theory (NLDFT) method was used to determine the pore size distribution of both HZSM-5 and Ru/HFZSM-5 as displayed in Figure 3. A sharp and narrow peak and a broad and small peak in the range of 5 to 8 nm as well as 10 to 20 nm, respectively were observed indicated the presence of mesopores in protonated HFZSM-5 catalyst. The existence of sharp and narrow peak was expected from the self-assembly of surfactant whereas the small peaks were from the distance between the dendrimeric silica. In addition, small and sharp peak was observed at 0.5 to 2 nm corresponding to the presence of micropores in the catalyst. In contrast, pore size distribution of Ru/HFZSM-5 displayed higher amount of micropores (0.5 to 2 nm) and mesopores (5 to 8 nm and 10-20 nm) compared to HFZSM-5 catalyst. The overall analysis showed that the BET specific surface area of HFZSM-5 and Ru/HFZSM-5 were 470.43 and 474.60 m^2/g, respectively. High surface area possessed by HFZSM-5 and Ru/HFZSM-5 might be attributed to the formation of dendrimeric silica fibers in the morphology. The surface area of the HFZSM-5 catalyst is slightly increased when doped with ruthenium. It is due to the well dispersion of ruthenium onto the catalyst surface, which will provide more accessible active sites and promotes the reaction to occur. The presence of Ru loaded on HFZSM-5 increase the microporosity volume (0.0572 cm^3/g) with simultaneous decrease in mesoporosity volume (0.8217 cm^3/g). The presence of mesopores in the morphology was expected to give positive impact towards the methanol to olefin reaction due to the low diffusion limitation and lead to enhance olefin selectivity.

3.3 Nature of acidity of the catalyst by Pyridine-FTIR

IR spectra of hydroxyl for both HZSM-5 and Ru/HFZSM-5 catalysts in the region of 3200-3800 cm^{-1} from 150-350 ^{o}C are shown in Figure 4. Generally, spectra of both catalysts demonstrated the presence of four bands at 3740, 3700, 3650 and 3610 cm^{-1}. At 3740 cm^{-1}, the band resembles to the terminal silanol groups which located at the zeolite surface. The band at 3700 cm^{-1} depicts that perturbation of hydroxyl through lattice defects or extra-lattice oxygen. The presence of band at 3650 cm^{-1} is attributed to the existence of hydroxyl group of extra framework aluminum species. Aziz *et al*,. (2014) claimed that the band at 3610 cm^{-1} is assigned to the bridging hydroxyl group between Si and Al tetrahedra of protonated HFZSM-5 framework.

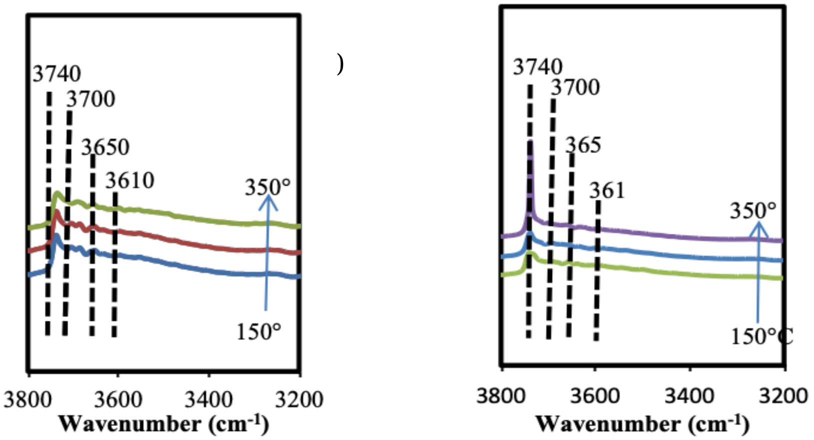


Figure 4 IR spectra in hydroxyl stretching of a) HFZSM-5 and b) Ru/HFZSM-5.

The increased in the amount of terminal silanol group and lattice defects were due to the formation of dendrimeric silica fiber which was shown by the increase in the peak intensity at 3740 cm^{-1} and 3700 cm^{-1} in protonated HFZSM-5 and Ru/HFZSM-5 catalysts. Furthermore, the upsurge in the peak intensity of band at 3740 cm^{-1} was due to the existence of ruthenium on the catalyst. Meanwhile, HFZSM-5 exhibited same intensity of the band at 3650 cm^{-1} with the Ru/HFZSM-5 due to the presence of the same amount of silica.

Figure 5 illustrates the FTIR spectra of Lewis and Brønsted acid sites for HFZSM-5 and Ru/HFZSM-5 between temperature ranges of 150-350 ºC. Figure 6 are summarized based on peak intensity of both Lewis and Brønsted acid sites. Hughes and White (1967) claimed that the band at 1454 cm^{-1} is due to the pyridine adsorbed on Lewis acid site, the band at 1545 cm^{-1} indicated pyridine adsorbed on Brønsted acid sites. Both catalysts exhibited a strong interaction between acidic sites and pyridine at 150 ºC, which were significantly retained in the outgassing at and below 250 ºC. At higher outgassing temperature, the intensity of Lewis acid sites of HZSM-5 slightly decreased, showing the presence of a large number of medium and strong acid sites. However, the distribution of Lewis acid sites for Ru/HFZSM-5 with HFZSM-5 was similar but a moderate change was observed at and above 350 ºC. However, introduction of Ru onto HFZSM-5 catalyst decrease the Brønsted acid sites at 1545 cm^{-1}. This occurs when the Ru cation substitute the protons of hydroxyl groups that results in decrease of number of Brønsted acid sites and increase the number of Lewis acid sites. It is due to the existence of extra framework Ru bonded with hydroxyl group on the surface of HFZSM-5 catalyst.

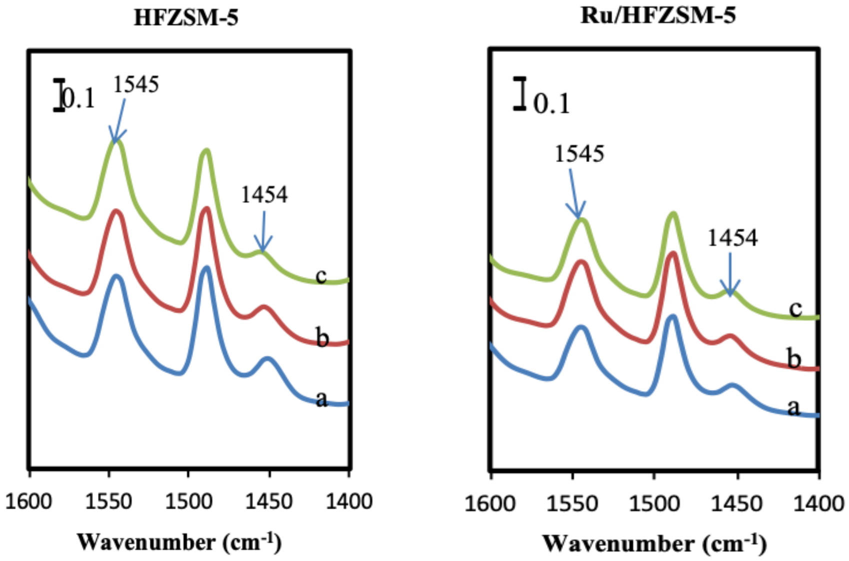


Figure 5 Spectral changes of pyridine adsorbed on HFZSM-5 (left) and Ru/HFZSM (right) at 150°C, b) 250°C, and c) 350°C.

According to the Inui *et al*., (1997), the amount of Lewis and Brønsted acid sites were calculated using the integrated extinction coefficient of ε1454 cm^{-1} = 2.22 cm^2/µmol and ε1545 cm^{-1} = 1.67 cm^2/µmol respectively. It was noticed that the amount of Lewis acid sites and Brønsted acid sites for HFZSM-5 catalyst were 0.8491 and 10.1598 µmol/g, respectively whereas the Lewis acid and Brønsted acid sites for Ru/HFZSM-5 were 1.1322 and 7.9021 µmol/g, respectively. In a glance, the amount of Lewis acid sites for Ru loaded on HFZSM-5 increased from 0.8491 to 1.1322 µmol/g was suggested due to ability of Ru to promote the acidity of catalyst.

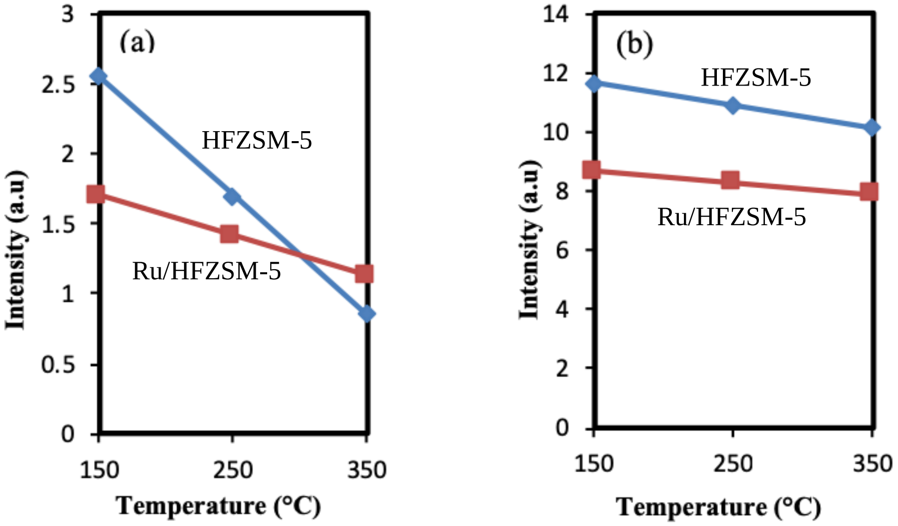


Figure 6 Acid sites for the HFZSM-5 and Ru/HFZSM-5 catalyst of a) Lewis acid sites b) Brønsted acid site.

3.4 Methanol to Olefin reaction

Catalytic testing of methanol-to-olefin reaction was carried out using continuous fixed bed reactor at reaction temperature in the range of 200 - 400 °C. The graph conversion of methanol against reaction temperature is shown in Figure 7. It was observed that conversion of methanol towards various product increases gradually with increasing temperature. In addition, methanol conversion was slightly enhanced for Ru/HFZSM-5 compared to HFZSM-5. The improvement in methanol conversion might be due to enhancement in diffusion of the methanol associated to the formation of dendrimeric silica fiber and the acidity effect from the presence of ruthenium. In addition, the formation of dendrimeric silica fiber seems to help the diffusion of methanol into the active sites in the catalyst. Moreover, methanol conversion of both HFZSM-5 and Ru/HFZSM-5 over MTO achieved almost 88.60 % and 95.14 % at 400°C respectively. This indicated that both catalysts were capable to convert methanol to its products due to the presence of more acid sites in the catalysts.

Figure 8 and Figure 9 represents the hydrocarbon selectivity in MTO reaction for both catalysts. It was demonstrated that the methanol was converted to paraffin (C1-C4), light olefins (ethylene and propylene) as well as butylene. It was observed that, at low temperature, methanol was mainly converted to paraffin. Decreases in the selectivity of paraffin as temperature increased was observed in both catalysts indicated that more paraffin was converted to olefins. This can be observed by the mechanism of conversion of methanol to olefin, in which the methanol will first convert to paraffin, followed by conversion of paraffin to olefin via hydrocarbon pool mechanism. Therefore, it can be clearly observed that the decrease of paraffin was accompanied by increase in selectivity towards olefin. At 400 °C, both catalysts gave main products of olefins and these indicate that both HFZSM-5 and Ru/HFZSM-5 are selective towards olefins. Regrettably, because of the presence of high mesopore volume in HFZSM-5, butylene selectivity increased up to 100 % for HFZSM-5 and 96.89 % for Ru/HFZSM-5. In addition, the propylene selectivity increased up to 1.82 % by using Ru/HFZSM-5 catalyst, while no selectivity toward propylene for HFZSM-5. The enhancement in olefin selectivity may be associated to the availability of more mesopore for HFZSM-5. Controlling the porosity of EU-1 zeolite with basic and acidic treatment to create more mesopore indeed lead to the increment of production of olefins. Besides that, lower selectivity of product towards aromatic was observed in HFZSM-5 and Ru/HFZSM- catalyst. It was reported that weak acidity in HFZSM-5 type catalyst will suppress the hydrogen transfer reactions which will produce aromatic as the main products.

Besides the presence of mesopore, the concentration of acid site also plays an important role towards the selectivity of the products. Based on hydrocarbon pool mechanism, it is reported that methanol converts to hydrocarbons and olefin on the acid site. From pyridine adsorbed FTIR, it was illustrated that the acid site density was much lower in HFZSM-5 compared to Ru/HFZSM-5. The strong acid sites in HZSM-5 initiate methanol reactivity and C-C bond formation as well as coke formation through the side reaction. Therefore, in the MTO reaction, HFZSM-5 type catalyst with low acidity are more desirable as we are able to suppress the side reaction as well as increasing the catalyst lifetime. Similar observation was observed by Li where the reduction of acid site density was performed by impregnation of Ca to ZSM-5 zeolite lead to a good selectivity for olefin compared to paraffin. In other works, it was reported that incorporation of Fe onto ZSM-5 framework also lead to the decrease in the amount of acid site as well as increasing the olefins selectivity. Introduction of mesopore via desilication caused the Brønsted acid site to be reduced and enhancement to olefins selectivity. High mesoporosity of HFZSM-5 reduced the coke formation in the catalyst that leads to deactivation of the catalyst. In contrast, the deactivation of HFZSM-5 occurred faster compared to Ru/HFZSM-5 as it was observed that the methanol conversions of almost 88.60 % at 400 °C. The deactivation had always been the limitation for HFZSM-5 catalyst due to the easily blocked microporous in the zeolite framework. Therefore, introduction of mesoporous into HZSM-5 parents certainly helps in improving the selectivity towards olefin products.

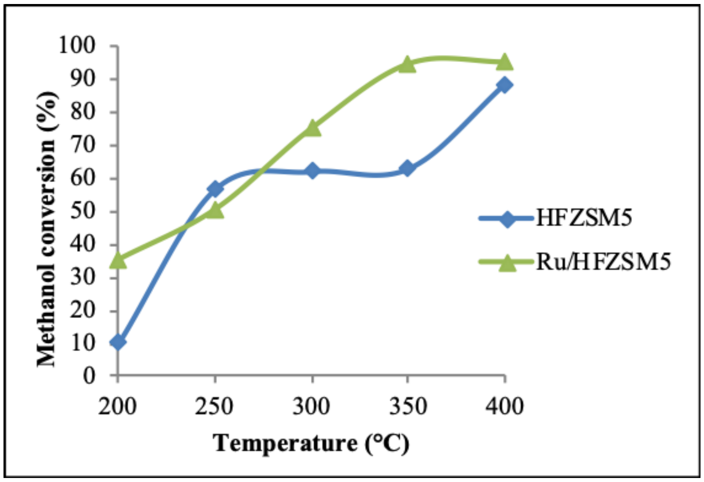


Figure 7 Methanol conversions by HFZSM-5 and Ru/HFZSM-5 catalyst.

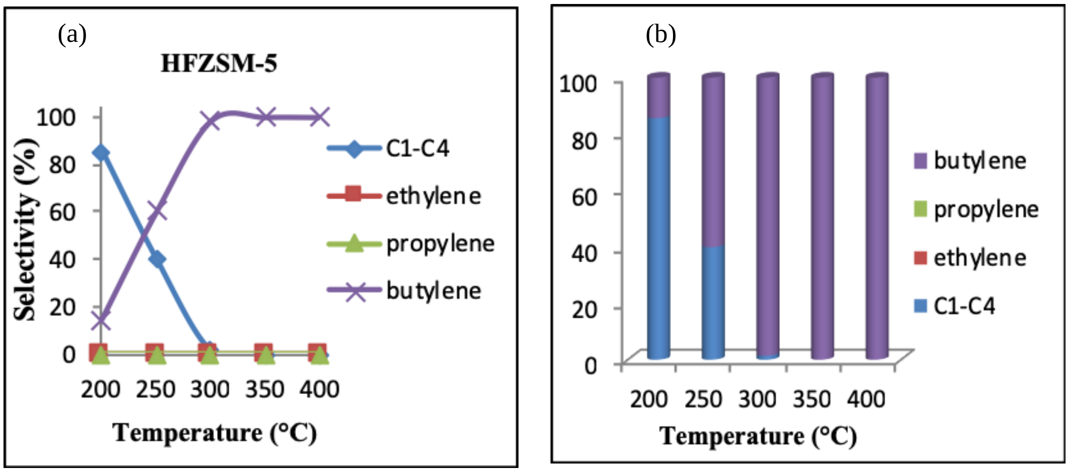


Figure 8 Selectivity of the HFZSM-5 catalyst toward olefins (a) line graph and (b) product distribution graph.

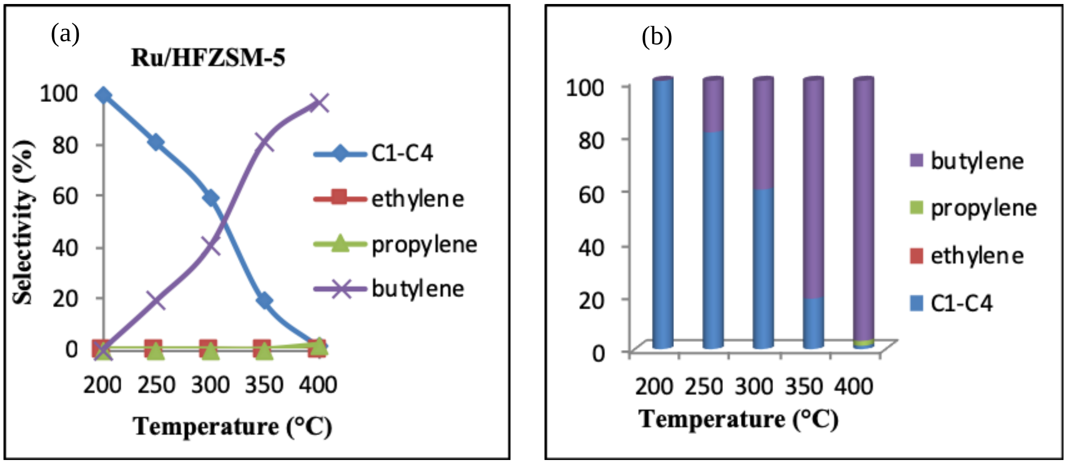


Figure 9 Selectivity of the Ru/HFZSM-5 catalyst towards olefins (a) line graph and (b) product distribution graph.

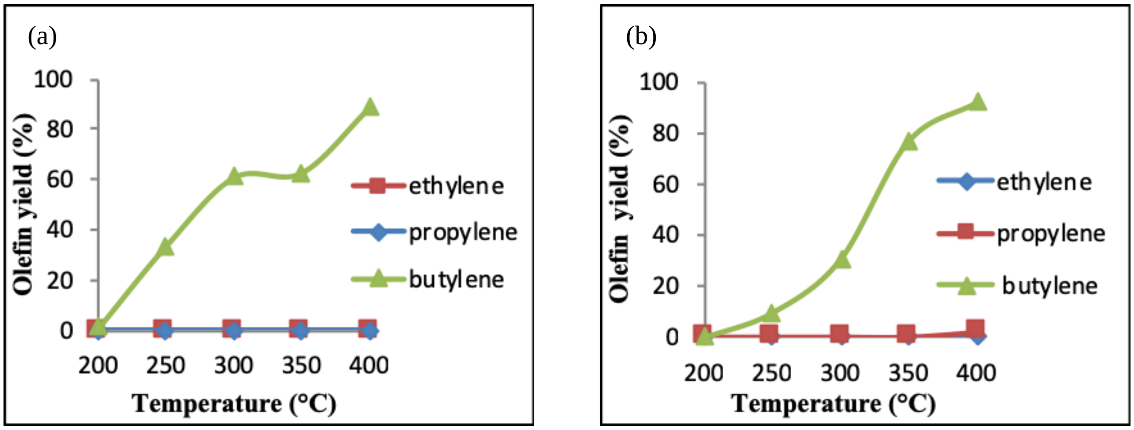


Figure 10 The olefin yield based on respective catalyst a) HFZSM-5 b) Ru/HFZSM-5.

3.5 Proposed mechanism for production of HFZSM-5

The protonated fibrous Silica ZSM-5 (HFZSM-5) has been successfully synthesized by the hydrothermal method supplied by the microwave. It is then calcined at 550 °C. The catalyst product of HFZSM-5 resembles a white color in powder form. The formation of the HFZSM-5 type catalyst incorporates crystalline crystals with a microemulsion as a template. The ZSM-5 seed acts as nucleation site of an early nucleus formed on the surface of the seed and the nucleus then flung from the surface of the seed. The crystallization process may occur in the small part of the ZSM-5 seed. Desilication is required when distributing part of the ZSM-5 seed. The desilication process is triggered by a basic presence like urea. Desilication has led to a partial encounter and this phenomenon has affected the increasing of perturbation of hydroxyl groups and alumina extra framework alumina HFZSM-5.

Surfactants such as cetyltrimethylammonium bromide (CTAB) have led to the formation of fibrous morphology through a bicontious micro emulsion process. The head of cationic surfactant of CTAB could bind with the nucleus of ZSM-5 by interaction between negatively charged of ZSM-5 framework with the positive charge of surfactant hydrophilic head. This phenomenon could be observed in silicate-surfactant interaction. Increment in water-oil interface and encase by surfactant created a shut structure micelle from the bicontinous micro emulsions. This procedure happened at the same time with permeation of the micelle circles which prompted the development of dendrimeric layout (Moon and Lee 2012) as shown in Figure 11. These micelle totals were interconnected by their water layer and ZSM-5 cores would experience crystallization on these water layers. In the long run, the zeolite with center shell structure was shaped where the center parts were developed from ZSM-5 seeds and dendrimeric silica fiber as the shell parts which developed from the hydrolyzed tetraethyl orthosilicate (TEOS).

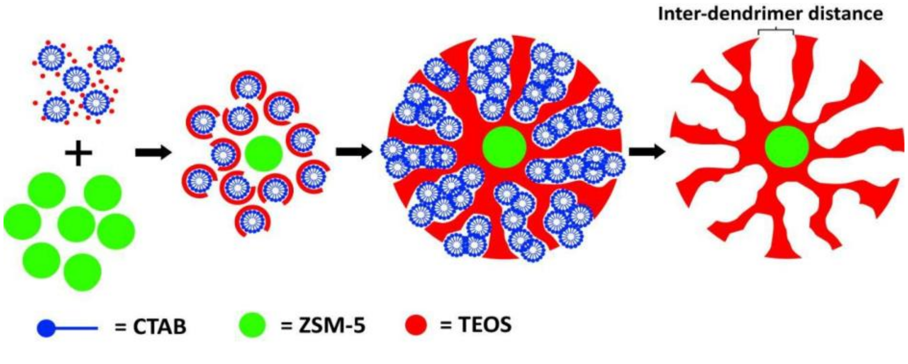


Figure 11 Proposed mechanism of HFZSM-5 formation.

4. CONCLUSION

The protonated fibrous silica ZSM5 (HFZSM-5) catalyst was successfully prepared by microemulsion of CTAB, toluene, and water coupled with zeolite crystal-seed crystallization. The ion-exchange technique was used to prepare the HFZSM-5 by protonation using ammonium nitrate. Then, the modified protonated fibrous silica ZSM-5 was successfully synthesized by impregnation of ruthenium metal onto the HFZSM-5 catalyst surface. As a result, the ruthenium supported on protonated fibrous silica ZSM-5 (Ru/HFZSM-5) possess a higher surface area as compared to HFZSM-5's. The higher surface area of catalyst gave a higher conversion of methanol to olefin. The pore size distribution result of Ru/HFZSM-5 showed two major distributions at 3-5 nm and 10-20 nm. These pores were attributed to the pore from self-assembly surfactant molecules and the inter-dendrimer distance of HFZSM-5 and Ru/HFZSM-5 respectively. A significant change in the hydroxyl group was observed due to the formation of dendrimeric silica fiber by FTIR spectroscopy. Besides, Lewis and Brønsted acid sites also plays a major role in conversion of olefins. The pyridine-adsorbed FTIR spectrum showed that the introduction of Ru to HFZSM-5 increased the Lewis acid sites and decreased Brønsted acid sites markedly. Ru/HFZSM-5 possessed excellent catalytic activity and stability towards methanol to olefin reaction. The catalytic activity of Ru/HFZSM-5 improved up to 95.14 % compared with HFZSM-5 88.60 % at 400 °C. Ru/HFZSM-5 demonstrated high selectivity towards olefins as it reaches until 98.71 %. The yield of olefin products from the Ru/HFZSM-5 catalyst are higher than that of HFZSM-5 catalyst which was 88.60 % and 93.93 %, respectively. The protonated HFZSM-5 catalyst was an excellent catalyst towards the production of olefins as it can reach higher conversion of methanol.

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