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Hydrogenation of methanol to olefins over highly stable ruthenium oxide protonated fibrous ZSM5 catalyst

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Abstract. Olefins are known as a very decisive starting material for the production of particular polymer products. High demand of olefins as well as increasing of crude oil price make the production of olefins product became crucial issue. Catalytic methanol to olefins offered an alternative route in order to obtain olefins products. The protonated fibrous silica ZSM5 (HFZSM5) was synthesized by microwave assisted hydrothermal method and followed by impregnation of 0.5% ruthenium oxide (RuO₂) metal onto the HFZSM5 catalyst (RuO₂/HFZSM5). The catalysts were characterized using FESEM, TEM, nitrogen physisorption and pyridine adsorbed FTIR. FESEM and TEM results revealed the spherical morphology with dendrimeric silica fibers of HFZSM5 catalyst. Based on nitrogen physisorption result, slightly increase in surface area was observed after the addition of RuO₂ onto the HFZSM5 catalyst surface. Obviously, the introduction of ruthenium metal has increased both Lewis and Brønsted acidity significantly, as observed by pyridine FTIR results. The catalytic methanol to olefin reaction was conducted within 473-673K at atmospheric pressure using continuous fixed bed reactor. The RuO₂/HFZSM5 resulted in higher catalytic activity and performance which produced 93.92% olefin yields compared to HFZSM5 catalyst which obtained 88.60% olefin product.

1. Introduction

Energy crisis has recharged the interest for creating innovations to produce energy, fuels and synthetic concoctions from resources other than conventional petroleum derivatives (oil, coal, gas). Countless synthetic compounds are carbon-containing compounds, therefore elective sources for their production are extremely restricted. The significance of oil in worldwide economy nowadays is not underlined as significant due to the most part utilized as source of fuels in energy production plants, as a vitality source in local and mechanical uses and in transportation. Therefore, due to the high oil costs and restriction of resources, it is important to grow new procedures for the generation of intensifies that are customarily gotten from certain oil divisions.

Olefin was acknowledged as significant intermediate for the petrochemical and polymer industry product. One of the efficient ways to produce olefin products without using mainly fossil is methanol to olefin (MTO) process. The MTO process utilizing methanol as reactant material and considered to be economical method since the methanol can be produced from wide variety of materials. Methanol can be productively created from syngas acquired by gaseous petrol changing or carbon gasification, and it



may even give an ecologically carbon unbiased option to fossil carbon sources, whenever created by substance reusing of carbon dioxide through hydrogenation or from syngas gotten by biomass gasification [13].

Up to now, there is no study reported on the use of FZSM5 specifically in the MTO reaction. Nevertheless, another study involve the utilization of fibrous zeolite catalyst such as FBFA and FSMOR has proved that catalytic activity was enhanced significantly in the toluene alkylation with methanol and isomerization process respectively [18,19]. Most of the time, two dimensional (2D) of mesoporous silica nanoparticles as catalyst support like MCM-41, MSN and SBA-15 with cylindrical pore structure are commonly utilized in catalysis [14]. Nevertheless, because of the closed pack spherical that will result in poor availability of mass reactant to the dynamic site internal parts the pores. Along these lines, it will be constrain to their applications. Fibrous material was initially developed by Polshettiwar, *et al.* in 2010 [1]. The first fibrous material is a silica-based equipped with high surface area and better accessibility of active site. Development of zeolite-based fibrous material will significantly improve their catalytic activity, along with tuneable acidity and high surface area. Herein, the protonated fibrous silica ZSM5 (HFZSM5) catalyst and ruthenium oxide doped on HFZSM5 were synthesized as the dendrimer fiber increased the number of active sites and facilitates the transportation of reactant and product into and out of the catalyst pores. Ruthenium is an outstanding respectable metal catalyst frequently utilized industrially for homogeneous or heterogeneous synergist reaction such as CO₂ methanation [21]. Based on the literature, the metal regularly used in the MTO were zinc, manganese, iron and magnesium. There was no study reported on the uses of ruthenium metal in MTO. Therefore, zeolite-based fibrous material will have a great potential to be applied in petrochemical and polymer manufacturer.

2. Experimental

The experiment was isolated into three primary stages. The main stage was centred on the preparation of fibrous silica ZSM5 by microwave assisted hydrothermal method. The second stage was the synthesized protonated fibrous silica ZSM5 catalyst and the last stage was the preparation of ruthenium oxide doped on protonated fibrous silica ZSM5 by incipient wetness impregnation method. Afterward, the physicochemical properties of the protonated fibrous silica ZSM5 and ruthenium oxide doped on protonated fibrous silica ZSM5 were characterized.

2.1 Preparation of fibrous silica ZSM5 (FZSM5)

Fibrous silica ZSM5 catalyst was set up by microwave assisted hydrothermal method utilizing ZSM5 as seed. 1 mole of tetraethyl orthosilicate (TEOS) was put in a solution consist of 28 moles of toluene and 1.62 moles of butanol. A mixed solution of 0.9 moles of urea and 0.27 moles of cetyltrimethyl ammonium bromide (CTAB) was dissolved in distilled water. The mixture was stirred and mixed for 15 minutes at room temperature. The ZSM5 seed were then added to the solution pursued by mixing for an additional 30 minutes. The solution was then exposed to microwave radiation of 400W intermittently at 393K for 4 hours. The solid product that was get separation by the methods for centrifugation, were then washed with distilled water and acetone. Next, the solid product were dried in the oven at 383K overnight. The dried solid was then calcined in furnace at 823K for 6 hours. The sample was marked as FZSM5.

2.2 Preparation of protonated fibrous silica ZSM5 (HFZSM5)

Two fold ion exchange was performed on FZSM5 catalyst. The catalyst were put in a beaker equipped with magnetic stirrer. 1 M ammonium nitrate (NH₄NO₃) solution was poured in distilled water was added to the catalyst mixture. The mixture was stirred at 343K for 8 hours. These ion exchange steps were rehashed two times. The solution was separated utilizing vacuum pump, and afterward washed using distilled water, trailed by drying at 373K for overnight. Calcination of the solid product was performed at 823K for 3 hours. The catalyst was denoted as HFZSM5.

2.3 Preparation of ruthenium oxide doped on protonated fibrous silica ZSM5 ($RuO_2/HFZSM5$)

The sample evacuated and impregnated with ruthenium oxide metal. The $RuO_2/HFZSM5$ was prepared by incipient wetness impregnation of protonated HFZSM5 with the solution of Ruthenium (III) chloride monohydrate. Then, it followed by drying and calcination in air at 823K. The sample was labelled as $RuO_2/HFZSM5$.

2.4 Methanol to olefin catalytic reaction

Catalytic methanol to olefin reaction was carried out using continuous fixed bed reactor in the range of temperature 473K-673K. In this examination, 0.2g of catalyst required and set into a quartz tube with 8 mm distance across. At that point, the reactor was treated at 673K via air stream at 20mL/min for 1 hour and cooled down at 473K. Next, the reaction was conduct using methanol as reactant. The result from the chromatograph at each temperature was identified and evaluated. The equation 1-3 shows the formula for methanol conversion, product selectivity and olefin yield.

$$\text{Methanol conversion } (X_{\text{methanol}}) = \frac{\sum \text{all products}}{\sum \text{all products} + \text{methanol}} \times 100\% \quad (1)$$

$$\text{Product selectivity } (S_{\text{olefin}}) = \frac{\sum \text{olefin products}}{\sum \text{all products}} \times 100\% \quad (2)$$

$$\text{Yield} = \frac{S_{\text{olefin}}}{100} \times X_{\text{methanol}} \quad (3)$$

3. Results and Discussion

3.1 Morphological studies of catalysts

Figure 1 demonstrates the surface morphology HFZSM5 catalyst from FESEM analysis. HFZSM5 showed a uniform particle size and a dendrimeric silica fiber with round morphology. From TEM picture, the dendrimeric silica fiber of HFZSM5 appeared to develop radially outward, leaving the denser part at the center of HFZSM5 catalyst. HFZSM5 showed a very huge separation between dendrimers called interdendrimer distance which would enable quick diffusion and simple access to dynamic destinations which will prompt an expansion in their reactant execution. HFZSM5 morphology was almost comparable with KCC-1 from past report [1].

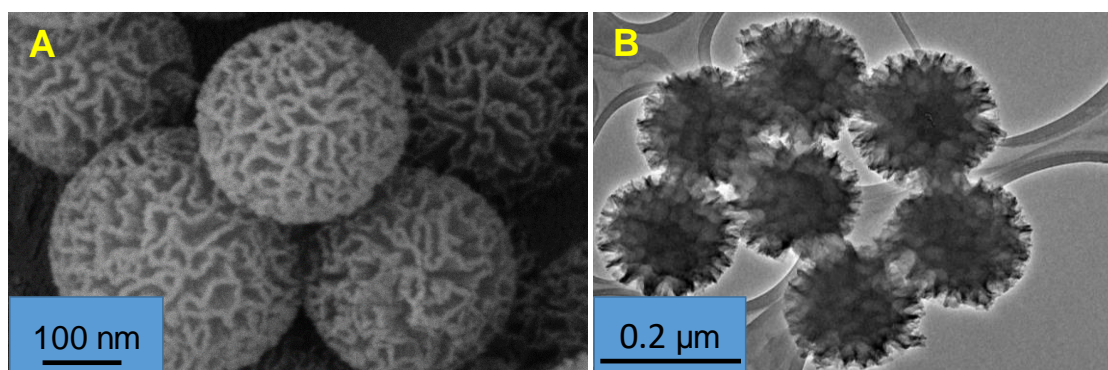


Figure 1. (A) FESEM images of HFZSM5 (B) TEM image for HFZSM5

3.2 Textural studies of catalysts

N_2 physisorption analysis is the well-known technique in order to identify the textural properties of catalysts. Figure 2 depicted the N_2 adsorption-desorption isotherms of HFZSM5 and $RuO_2/HFZSM5$. In Figure 2, it was found that higher nitrogen uptake was observed for HFZSM5 indicating the presence

of large amount of pores compared to RuO₂/HFZSM5. Subsequently, RuO₂/HFZSM5 and HFZSM5 catalyst exhibited type IV isotherms with H3 hysteresis loop that ascribed to the gas adsorbed was condensed as liquid in the catalyst pore. Plus, the presence of the hysteresis loop indicated the presence of mesopores 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 explained that the capillary condensation of nitrogen in the intraparticle void [17]. Meanwhile, the second step of capillary condensation observed at higher relative pressure of 0.9 suggesting to the existence of mesopores in the catalysts.

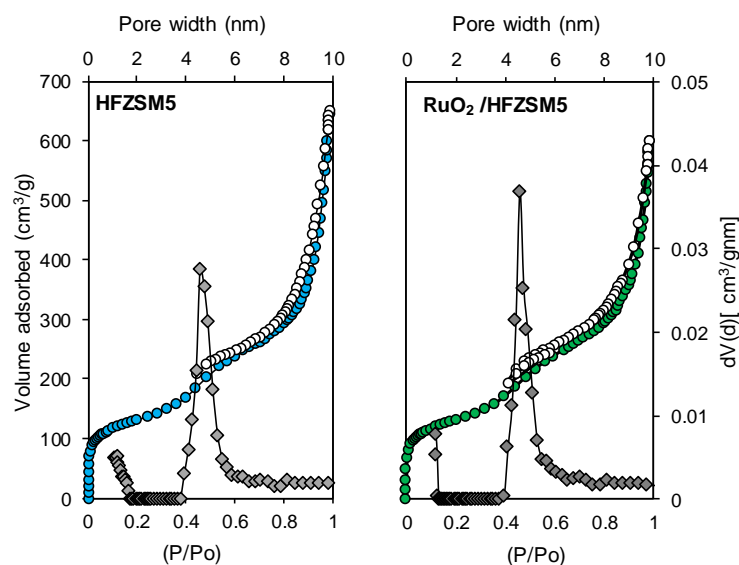


Figure 2. Nitrogen adsorption desorption isotherm and pore distribution of HFZSM5 and RuO₂/HFZSM5

The non-local density functional theory (NLDFT) method was applied to study the pore size distribution of both HFZSM5 and RuO₂/HFZSM5. As shown in Figure 2, a sharp and narrow peak of 4 to 5 nm was observed for both HFZSM5 and RuO₂/HFZSM5, indicating the presence of mesopores. The self-assembly of surfactant resulted in the existence of sharp and narrow peak. In addition, small and sharp peak was observed at 0.5 to 2 nm corresponding to the presence of micropores in the both catalyst. In contrast, pore size distribution RuO₂/HFZSM5 portrayed slightly higher of mesopores compared to HFZSM5 catalyst.

Table 1. Physicochemical properties of both catalysts

Catalyst	Surface area ^a (m ² /g)	Mesopore volume ^a (cm ³ /g)	Micropore volume ^a (cm ³ /g)	Total pore volume ^a (cm ³ /g)	Brønsted acid sites concentration ^b (μmol/g)	Lewis acid sites concentration ^b (μmol/g)
RuO ₂ /HFZSM5	569	1.30	0.04	1.34	15.57	8.49
HFZSM5	475	0.82	0.06	0.89	8.49	1.41

^aObtained from N₂ physisorption

^bObtained from Emeis equation in FTIR adsorbed pyridine based on adsorption peak at 423K

The overall analysis showed that the BET specific surface area of HFZSM5 and RuO₂/HFZSM5 were 569 and 474 m²/g, respectively as noted in Table 4.1. High surface area possessed by HFZSM5 and RuO₂/HFZSM5 might be attributed to the formation of dendrimeric silica fibers in the morphology.

Increasing in surface area was observed after the introduction of ruthenium oxide metal onto HFZSM5 catalyst surface. It is due to the well dispersion of ruthenium onto the catalyst surface, which will provides more accessible active sites and promotes the reaction to occur. 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 [2].

3.3 Acidic nature in catalysts

The changes in the IR spectra of hydroxyl spectra in the region of 3400-3800 cm^{-1} for both HFZSM5 and $\text{RuO}_2/\text{HFZSM5}$ catalysts are shown in Figure 3. Generally, spectra of both catalysts demonstrated the presence of five bands at 3740, 3700, 3660, 3610 and broad band at 3480 cm^{-1} . The terminal silanol groups which located at the zeolite surface, contributed to the appearance of the band at 3740 cm^{-1} . The interaction of RuO_2 with the framework of HFZSM5 can be observed in the changes of hydroxyl group region of the FTIR spectra for evacuated sample as depicted in Figure 3. It was observed that the addition of Ru has decreased the peak at 3740 cm^{-1} , which corresponded to the terminal silanol group (Si-O-H), suggesting a possible perturbation of the HFZSM5 framework upon the interaction with the RuO_2 [23]. Perturbation of OH through lattice defects or extra-lattice oxygen was detected due to the existence of the band at 3700 cm^{-1} . The presence of the band at 3660 cm^{-1} is attributed to the existence of hydroxyl group of extra framework aluminium species. The band at 3610 cm^{-1} can be assigned to the bridging hydroxyl group between Si and Al tetrahedral of ZSM5 framework [3, 5, 6]. Besides, the broad band at 3480 cm^{-1} for both catalysts were attributed to silanol group [15]. The presence of dendrimeric silica fiber increased the amount of terminal silanol group and lattice defect during their formation which was shown by the increase in the peak intensity at 3740 cm^{-1} and 3700 cm^{-1} HFZSM5 catalyst [4]. After doped with ruthenium oxide, the peak at 3740 cm^{-1} was observed decline significantly due to the hydroxyl group on the terminal silanol was replaced by the metal cation of ruthenium.

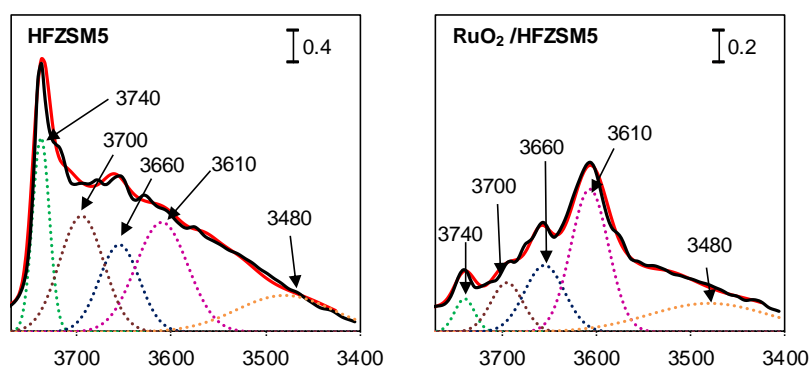


Figure 3 FTIR Evacuation of HFZSM5 and $\text{RuO}_2/\text{HFZSM5}$ catalyst at activated temperature 673K

Figure 4 depicted the FTIR spectra obtained via utilizing pyridine molecule as basic probe. Hughes and White (1967) claimed that the band at 1442 cm^{-1} was assigned to the pyridine adsorbed on Lewis acid site, the band at 1542 cm^{-1} indicated pyridine adsorbed on Brønsted acid sites [7]. Abundance of Lewis acid sites was observed in $\text{RuO}_2/\text{HFZSM5}$ compared to HFZSM5. Both catalysts exhibited a strong interaction between acidic sites and pyridine at all desorption temperature, as observed by no significant decreased in the peak intensity. Introduction of ruthenium oxide metal onto HFZSM5 catalyst has increased the Brønsted acid sites at 1542 cm^{-1} due to the hydroxyl group in the surface of ruthenium oxide which can act as Brønsted acid sites as claimed from previous study. Exactly speaking, the ruthenium oxide itself have their Brønsted acid sites which may contribute to the increment of Brønsted acid sites in $\text{RuO}_2/\text{HFZSM5}$ [22]. Inui *et al.*, (1997), the amount of Lewis and Brønsted acid sites were calculated using Emeis equation (Equation 4) which the integrated extinction coefficient (IMEC) of $\epsilon_{1442} \text{ cm}^{-1} = 2.22 \text{ cm}^2/\mu\text{mol}$ and $\epsilon_{1542} \text{ cm}^{-1} = 1.67 \text{ cm}^2/\mu\text{mol}$ respectively [8]. It was noticed that the

amount of acid sites (Lewis, Brønsted) for HFZSM5 catalyst were (1.41, 8.49) $\mu\text{mol/g}$, respectively whereas for $\text{RuO}_2/\text{HFZSM5}$ were (8.49, 15.57) $\mu\text{mol/g}$, respectively. In summary, the amount of Lewis acid sites for $\text{RuO}_2/\text{HFZSM5}$ has increased from 1.41 to 8.49 $\mu\text{mol/g}$, suggesting the promotion of acidity by the ruthenium metal.

$$\text{Emeis equation} = \frac{\text{Integrated intensity peak area} \times \text{pallet surface area}}{\text{IMEC} \times \text{pallet weight}} \quad (4)$$

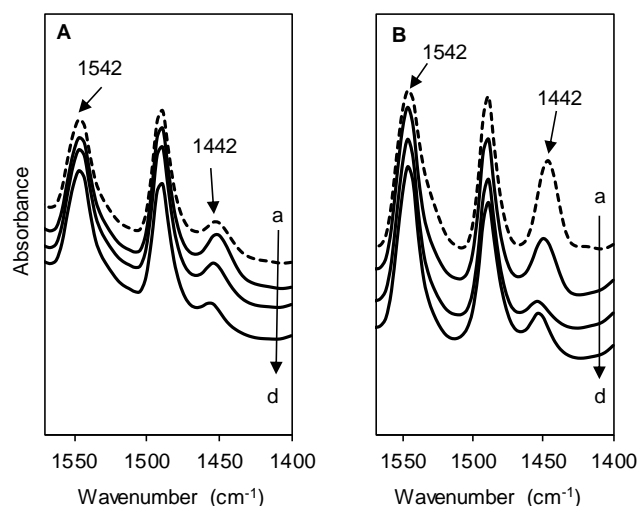


Figure 4. FTIR adsorbed pyridine at (a) 423K (dotted line) and desorbed (solid line) at (b) 423K, (c) 523K, (d) 623K of (A) HFZSM5 (B) $\text{RuO}_2/\text{HFZSM5}$ catalysts

3.4 Catalytic testing of methanol to olefin

Catalytic testing of methanol to olefin was performed using continuous fixed bed reactor in the temperature range 473-673K. Figure 5 portrayed the methanol conversion and olefin yield obtained over both catalysts. It was observed that conversion of methanol towards various products has increases gradually with increasing temperature. Figure 5A shows that higher methanol conversion was obtained over $\text{RuO}_2/\text{HFZSM5}$ catalyst. It might be due to the higher amount of Brønsted acid sites make the methanol molecule easily converted dimethyl ether and followed by the olefin formation as illustrated in Figure 4. Furthermore, fast diffusion of product molecule also one of the factor to the increment of methanol conversion. Moreover, methanol conversion of both HFZSM5 and $\text{RuO}_2/\text{HFZSM5}$ over MTO was achieved almost 88.60% and 95.14 % at 673K, respectively. This indicated that both catalysts were capable to convert methanol to its products due to the presence of abundance acid sites in the catalysts. Figure 5B depicts the olefin yield obtained from the methanol to olefin reaction. At 473K, no olefin product was obtained in $\text{RuO}_2/\text{HFZSM5}$ and small amount of olefin yield in HFZSM5 catalyst. It was due to the more paraffin product was favoured to form at lower temperature as described Table 2. As the temperature rising, the olefin product seems to increase until it reached 88.60% and 93.92% for HFZSM5 and $\text{RuO}_2/\text{HFZSM5}$, respectively. The paraffin product was consisted of light hydrocarbon such as $\text{C}_1\text{-C}_4$ product as well as dimethyl ether and the olefin product contain three product which are ethylene, propylene and butylene.

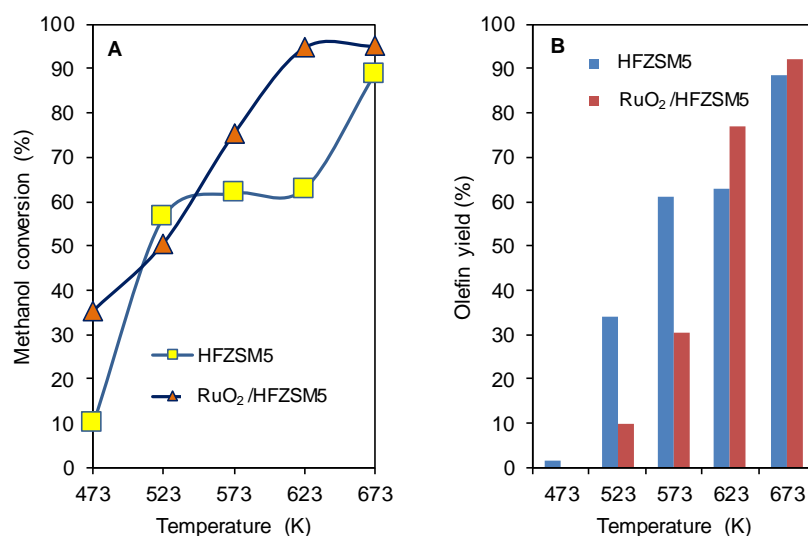


Figure 5. (A) Methanol conversion (B) olefin yield obtained over HFZSM5 and RuO₂/HFZSM5.

Table 2 represents the product distribution of both HFZSM5 and RuO₂/HFZSM5 catalysts. It was observed that at lower temperature, methanol was mainly converted to paraffin. The decreased in the selectivity of paraffin as temperature increased was observed in both catalysts indicated the formation of olefin product from the paraffin. It was observed that, at low temperature, methanol was mainly converted to DME. Decreases in the selectivity of DME as temperature increased was observed in both catalysts indicated that more DME was converted to olefins and paraffin. This can be explained by the mechanism of conversion of methanol to olefin, in which the methanol will first convert to DME, followed by conversion of DME to olefin via hydrocarbon pool mechanism [10]. Besides, it was clearly observed that the decreased of paraffin was accompanied by the increased in selectivity towards olefin. At 673K, the main products for both was consisted of olefins, suggesting both catalysts were selective towards olefins. Besides that, no selectivity towards aromatic was observed in HFZSM5 and RuO₂/HFZSM5 catalyst. It was reported that higher acidity in HFZSM5 type catalyst would prevent the suppression of hydrogen transfer reactions, which will passivate aromatic products [9].

The abundance of acid sites also plays vital role towards the selectivity of the products. In view of hydrocarbon pool mechanism, it is accounted for that methanol changes over to hydrocarbons and olefin on the acidic site [11-12]. Pyridine adsorbed FTIR results illustrated that the acid site density was much lower in HFZSM5 compared to RuO₂/HFZSM5. The acid sites in catalyst initiates the methanol reactivity and C-C bond arrangement just as coke development through the side reaction [9]. Therefore, in MTO reaction, HFZSM5 catalyst with low acidity was preferable as it can suppress the side reaction as well as increasing the catalyst lifetime. Similar observation was observed by previous studies where the reduction of acid site density was performed by impregnation of Ca to ZSM5 zeolite lead to a good selectivity for olefin compared to paraffin [16]. In other works, it was reported that incorporation of Fe onto ZSM5 framework also lead to the decrease in the amount of acid site as well as increasing the olefins selectivity [9]. High mesoporosity of HFZSM5 reduced the coke formation and prevent the deactivation of the catalyst. In contrast, the deactivation of HFZSM5 catalyst occurred faster compared to RuO₂/HFZSM5 as it was observed that the methanol conversions of almost 88.60% at 673K. The deactivation had always been the constraint for HFZSM5 catalyst due to the easily blocked microporous in the zeolite framework. Therefore, introduction of mesoporous into HFZSM5 parents certainly helps in improving the selectivity towards olefin products.

Table 2. Product distribution from methanol to olefin reaction

	Temperature (K)				
	473	523	573	623	673
HFZSM5					
Methanol conversion (%)	10.05	56.58	61.84	62.79	88.60
Selectivity products (%)					
<i>Paraffin</i>	85.64	39.90	1.42	0.00	0.00
<i>Olefin</i>	14.36	60.10	98.58	100	100
Yield products (%)					
<i>Paraffin</i>	8.61	22.58	0.88	0.00	0.00
<i>Olefin</i>	1.44	34.01	60.96	62.79	88.60
RuO₂/HFZSM5					
Methanol conversion (%)	35.32	50.60	75.29	94.70	95.14
Selectivity products (%)					
<i>Paraffin</i>	100.00	80.81	59.46	18.84	1.28
<i>Olefin</i>	0.00	19.19	40.54	81.16	98.72
Yield products (%)					
<i>Paraffin</i>	100	40.89	44.77	17.84	1.22
<i>Olefin</i>	0.00	9.71	30.52	76.86	93.92

Conclusion

The protonated fibrous silica ZSM5 (HFZSM5) catalyst was successfully prepared by microwave assisted hydrothermal method. Ion-exchange technique was used in order to prepare the HFZSM5 by protonation using ammonium nitrate. Then, the modified protonated fibrous silica ZSM5 was successfully synthesized by impregnation of ruthenium metal onto the HFZSM5 catalyst surface. As a result, the ruthenium supported on protonated fibrous silica ZSM5 (RuO₂/HFZSM5) possess lower surface area compared to HFZSM5. The pore volume of RuO₂/HFZSM5 was dominated by the mesopores. A significant changes of terminal silanol group was observed due to the decreasing of peak 3740 cm⁻¹ as observed in FTIR in evacuated system. Besides, Brønsted acid sites also plays a major role in conversion of olefins. Additionally, pyridine-adsorbed FTIR showed that the introduction of ruthenium oxide to the HFZSM5 has increased the Lewis acid sites as well as the Brønsted acid sites markedly. RuO₂/HFZSM5 possessed excellent catalytic activity and stability towards methanol to olefin reaction. The catalytic activity of Ru/HFZSM5 improved up to 95.14% compared with HFZSM5 88.60% at 673K. The yield of olefins products from RuO₂/HFZSM5 are higher than HFZSM5 which was 88.60% and 93.92%, respectively. The protonated HFZSM-5 was an excellent catalyst towards the production of olefins as it can reach higher conversion of methanol, which attributed to its wide distribution of acid sites as well as high surface area.

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