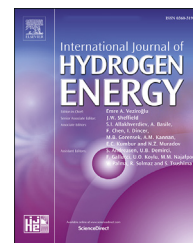


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Unique structure of fibrous ZSM-5 catalyst expedited prolonged hydrogen atom restoration for selective production of propylene from methanol

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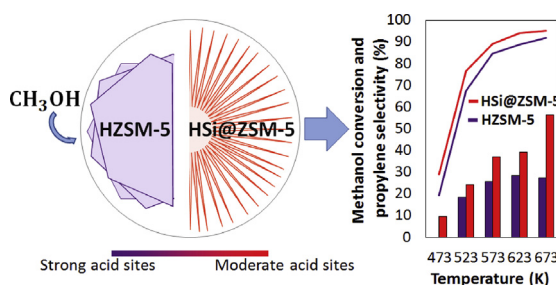
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HIGHLIGHTS

- Fibrous silica HSi@ZSM-5 was synthesized and explored in MTO process.
- Surface methoxy intermediates were generated for induced methylation.
- Methylation rates were faster in HSi@ZSM-5 than in commercial HZSM-5.
- HSi@ZSM-5 morphology suppressed aromatic hydrocarbons and coke formation.
- Alkene cycle reaction mechanism is responsible for enhanced propylene selectivity.

GRAPHICAL ABSTRACT



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ABSTRACT

A unique mesostructured fibrous silica@ZSM-5 (HSi@ZSM-5) catalyst was synthesized via microemulsion ZSM-5 zeolite seed assisted synthesis method and successfully applied in enhanced propylene formation in methanol to olefin (MTO) process. Characterization of the catalysts were carried out by FESEM, TEM, XRD, TGA, N₂ adsorption-desorption, NH₃ and KBr probed FTIR. Catalytic performance of as-synthesized catalyst was examined using a micro-pulse reactor and compared with the commercial HZSM-5. The reaction mechanism was elucidated by in-situ methanol FTIR spectroscopy. It was found that

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Fibrous HSi@ZSM-5

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Surface methoxy species

HSi@ZSM-5 produced higher propylene selectivity (56%) and was stable for long time on stream (80 h), nearly three-fold higher than that of commercial HZSM-5. In addition, HSi@ZSM-5 displayed higher rate of methanol dehydration, surface methoxy species generation and olefin methylation, indicating that alkene catalytic cycle is the dominant reaction mechanism. The higher selectivity towards propylene was correlated to the existence of moderate acidity which impeded the formation of paraffins and polymethylbenzene intermediates. These observations are further supported by KBr probed FTIR findings which revealed negligible paraffinic carbon species on HSi@ZSM-5. Thus, the unique fibrous silica@ZSM-5 retarded coke deposition due to suppression of undesired side reactions thereby signifying intensified propylene formation, which is highly desirable in commercial MTO processes.

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Introduction

The envisaged diminution of crude oil reserves and the markedly high demand for petrochemicals especially propylene, triggered unprecedented research on alternate feedstock processes [1,2]. Propylene is traditionally produced from steam cracking and fluid catalytic cracking processes. However, the global demand for propylene is anticipated to reach 135 million tons by the year 2025 when compared to 100 million tons in 2017 [3–5]. In view of this, methanol to olefins (MTO) has gained significance over the years, since methanol could easily be commercially produced from biomass, natural gas and coal [1,3]. The methanol transformation process has been studied over kinds of zeolite-based catalysts such as CHA [6], ZSM-11 [7], ZSM-22 [8] and ZSM-5 [9]. Peculiarly, ZSM-5 is among the most suitable catalyst to obtain considerable propylene selectivity due to its MFI structured morphology and strong acidic sites. However, carbon deposits generated during the MTO reaction, result in blockage of the pore openings and active sites which accelerates performance decay with time on stream [10]. Thus, concerted efforts have burgeoned in order to attenuate the severe deactivation and further enhance propylene selectivity.

Intrinsically, the MTO process involves cascade of reactions. The consensus is that the Brønsted acid sites are the most important active sites for the reaction [11]. So, interaction of methanol with the acid sites begins with dehydration to dimethyl ether (DME), which results in generation of intermediate complexes [12]. The intermediates formed play an integral role in the products spectrum. This phenomenon has been extensively examined from theoretical, experimental and computational viewpoint [13,14]. Notably, systematic investigation by Olsbye et al. reported that methoxy species are decisive intermediates in propylene products formation [15]. In a similar vein, infrared spectroscopy analysis by Yamazaki et al. asserted that methoxy species are active species, which form propylene products from carbon chain prolongation of olefins [16]. Also, Li et al. identified that methoxy groups led to generation of propylene as the primary product of MTO reaction [17]. More recently, Ma et al. reported that propylene is the major product formed from lower hydrocarbons via recurring methylations with methanol [18].

Basically, the mechanism leading to MTO products formation ranging from the desired (propylene) or undesired deactivation has been subject of continuous studies in industries and academia. The widely accepted mechanism for MTO reaction over MFI morphology catalyst is the dual cycle mechanism. According to the dual cycle mechanism, reaction products are formed via alkene and aromatic cycles, by concurrent methylation, cracking and dealkylation reactions. Yields for propylene and higher alkenes are controlled by the alkene cycle with surface methoxy species as intermediates, while aromatics and ethylene products are governed by the aromatic cycle with polymethylbenzene intermediates [19]. Therefore, intermediates and products formed during MTO reaction are decisive in unravelling the reaction mechanism.

The development of mesoporous zeolite materials has been conceived to hinder deactivation and improve propylene selectivity in MTO reaction. Integration of mesopores expedite mass transfer and escape of coke forming species, which in turn improve the catalytic performance [20]. It has been substantiated in numerous literatures that catalytic performance is influenced by mesoporous nature of the zeolite materials [10,21]. Besides mesoporosity, another vital issue relates to strength of the acid sites. Many findings attributed low performance of conventional ZSM-5 catalysts in MTO reaction as a consequence of its strong acidic properties [3,9,21].

Congruently, various synthesis routes have been explored to develop mesostructured zeolite materials. Abdurashied et al. developed core shell structured catalyst via in situ one-pot hydrothermal method [22]. Furthermore, introduction of seed material into template free synthesis batches has been reported to efficiently control topology and properties of the product zeolite. For instance, Yu et al. synthesized ZSM-5 via template-free ZSM-11 seeds assisted technique, which showed excellent performance in MTO reaction [23]. Likewise, Chen et al. developed modified ZSM-5 catalyst with nano crystals by seed induced technique in the presence of surfactant [24]. In addition, microemulsion technique was applied by Lee et al. to synthesize spherical structured zeolite [25]. Hussain et al. also utilized microemulsion synthesis method to develop fibrous nanostructured materials [26].

In this light, the microemulsion synthesis method seems ideal, since it is decisive in tailoring morphology and other

catalytic properties [27]. In recent times, novel core-shell fibrous silica mesoporous zeolites with high surface area have received attention because of their excellent performances in solid acid catalysed reactions such as isomerization [28], carbon dioxide methanation [29], and carbon dioxide reforming of methane [30,31]. To the best of our knowledge, research works have so far not been reported on fibrous silica mesoporous ZSM-5 catalyst synthesis for application in MTO reaction. Here in, role of the tailored morphology and other physicochemical properties of fibrous silica HSi@ZSM-5 catalyst towards improving catalytic performance and stability in MTO process were investigated. Next, reaction mechanism for enhanced propylene formation was elucidated with aid of in situ FTIR-spectroscopy, and combination of theoretical and catalytic performance experiment observations.

Experimental section

Catalyst preparation

Mesostructured core shell fibrous silica ZSM-5 was synthesized by microemulsion synthesis method coupled with zeolite seed crystallization technique. Commercial ZSM-5 (Zeolyst CBV 2314) was applied as seed crystal for the crystallization. Concisely, the mesostructured catalyst was synthesized by templating method using cetyltrimethylammonium bromide (CTAB) as a structure directing agent. The starting parameters are $H_2O/Si = 165.34$, $TEOS/Si = 1.0$, $toluene/Si = 28.00$ and $1-butanol/Si = 1.62$, $Si/Al = 23$, $CTAB/Si = 0.27$, and $urea/Si = 0.9$. Tetraethyl orthosilicate (TEOS, Merck) was dissolved in a solution of toluene (Bendosen) and 1-butanol (Qrec). Then, ZSM-5 crystal seed was added to the solution and stirred vigorously for 30 min. Thereafter, mixture of CTAB (Merck), Urea (Qrec) and distilled water (H_2O) were stirred to obtain a clear and homogeneous solution. The resulted mixture was subsequently microwaved (400 W) for 4 h. The solid product was obtained by centrifugation (4000 rpm) and was extensively washed severally with acetone and distilled water. Eventually, the obtained product was dried at 383 K overnight, and calcined at 823 K for 6 h to remove the structure directing agent.

Subsequently, the synthesized and commercial ZSM-5 catalysts were ion-exchanged three times with 1 M (NH_4NO_3) at 343 K for 8 h. Finally, the ion-exchanged catalysts were calcined at 823 K for 3 h. The resulted products are known as HSi@ZSM-5 and HZSM-5 respectively.

Characterization of catalyst

The catalysts under study were subjected to several characterization techniques. The field emission scanning electron microscopy (FESEM) (Zeiss Supra VP35) and transmission electron microscopy (TEM) (Philips, model EM 420) were used to analyse morphological properties of the catalysts. The crystalline structure of catalysts was confirmed with X-ray diffractometer (XRD) (Bruker Advance, model D8) under the condition of $Cu K\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation, scan range of $2\theta = 4\text{--}40^\circ$, scanning rate of 40 kV and step size of

40 mA. The specific surface area and pore volume were determined by nitrogen physisorption analysis (Beckman Coulter, model SA 3100). Prior to the analysis, the catalysts were outgassed at 573 K for 1 h. Thereafter, adsorption–desorption of nitrogen was carried out at 77 K. The surface area was determined by Brunauer–Emmett–Teller (BET) method while pore size distributions of the catalysts was identified through a non-local density functional theory (NLDFT) method. Other information, such as total pore volume, micropore volume and mesopores volume were obtained with t-plot method.

Ammonia probed IR spectroscopy was conducted to determine the acidity of the catalysts. The measurements were performed by in situ FTIR equipped with a high temperature stainless steel cell with CaF_2 windows. Prior to the analysis, the catalyst was activated at 673 K for 1 h and exposure of 10 Torr of ammonia at room temperature was conducted, followed by outgassing at 323 K. All samples. All spectra were recorded at room temperature. Furthermore, an in situ FTIR study was performed to observe the interaction of methanol and catalyst surface during the reaction by exposing the activated catalyst to 4 Torr of methanol at room temperature, followed by heating from 473 K to 673 K with 50 K increment. The spectra were recorded at room temperature after equilibrium conditions have been reached.

Thermogravimetric-differential thermal analysis (TGA) was conducted to determine coke deposits in the catalysts. For the analysis (Mettler Toledo TGA/SDTA851), 10 mg of catalyst was heated at temperature of 298 K, then at a stable increase of 10 K min^{-1} to 1073 K under flowing nitrogen (20 ml min^{-1}). Also, KBr-Infrared spectroscopy was performed to identify coke species in the catalysts. The catalysts were well grinded and compressed to form KBr powdered pellets using a ratio of approximately 1 mg catalyst/100 mg KBr. The IR spectra were obtained with the KBr pellet (Perkin Elmer GX FTIR spectrometer) over a range of wavenumbers ($4000\text{--}400 \text{ cm}^{-1}$).

Catalytic performance tests

The catalytic performance tests were carried out in a micro catalytic pulse reactor (internal diameter = 8 mm) at temperature range of 473–673 K. Prior to the experiment, 0.2 g of catalyst was activated in an air stream (100 ml min^{-1}) for 1 h at 723 K and cooled down to 473 K in a nitrogen stream (100 ml min^{-1}). The liquid methanol feedstock in a saturator was passed by nitrogen carrier gas stream into the reaction zone. The product stream was analysed by an online Gas Chromatograph (Agilent Technologies, 6090N) equipped with HP-5 capillary column and an FID/MS detector. Accordingly, methanol conversion and selectivity were computed by Eqs. (1) and (2), respectively.

$$X_{\text{methanol}}(\%) = \frac{\sum [C]_i}{\sum [C]_i + \sum [C]_{\text{residual methanol}}} \times 100\% \quad (1)$$

$$S_i(\%) = \frac{[C]_i}{\sum [C]_i} \times 100\% \quad (2)$$

where C_i referred to area of individual hydrocarbon product and $C_{\text{residual methanol}}$ represent area of residual methanol.

Results and discussion

Catalyst morphology

Fig. 1 reveals the FESEM images of HZSM-5 and H-Si@ZSM-5, particle size distribution and TEM image of H-Si@ZSM-5. The FESEM image of the commercial HZSM-5 (Fig. 1A) displayed coffin shape morphology, corresponding to MFI structure [26,32]. Remarkably, H-Si@ZSM-5 showed core shell dendrimeric morphology (Fig. 1B), with uniform particle size distribution around 600 nm (Fig. 1C) [28]. The TEM image (Fig. 1D) showed presence of dendrimers covering the core with large inter dendrimer distance. Though, the dendrimeric silica fiber of HSi@ZSM-5 catalyst appeared to grow radially outward, leaving the denser part at the centre of the catalyst. Cooperative interaction between the surfactant (Urea), oil phase (toluene), and aqueous phase (water) lead to the formation of dendrimeric fibrous silica ZSM-5. Several works reported in our laboratory has elaborated the mechanism involve in the formation of dendrimeric silica fiber during the synthesis process [26,28].

Fig. 2 displays XRD patterns of HSi@ZSM-5 and HZSM-5 catalysts. Reflections characteristic of the MFI topology are present in both catalyst, with diffraction peaks in the range of $2\theta = 7\text{--}10^\circ$ and $22\text{--}25^\circ$, which matched the referenced JCPDS data [33,34]. The intensity of the XRD pattern of HSi@ZSM-5 reduced as compared to HZSM-5. This may be attributed to presence of silica species added during the dendrimeric silica fiber formation. Moreover, the more intense peaks seen, demonstrated the highly crystalline structure of HZSM-5. The XRD patterns did not show presence of impurities or phases.

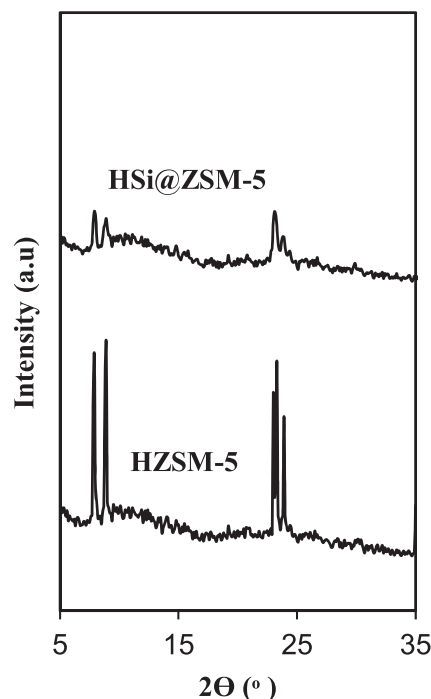


Fig. 2 – XRD patterns of HSi@ZSM-5 and HZSM-5.

Identification of textural properties

Fig. 3A shows the nitrogen adsorption-desorption isotherms of HZSM-5 and HSi@ZSM-5 catalysts. The isotherm of type 1 (according to the IUPAC classification), characteristic of the microporous structure, was recorded for HZSM-5 [35,36]. While, in case of HSi@ZSM-5, the adsorption-desorption isotherm is type IV with H3-type hysteresis loop,

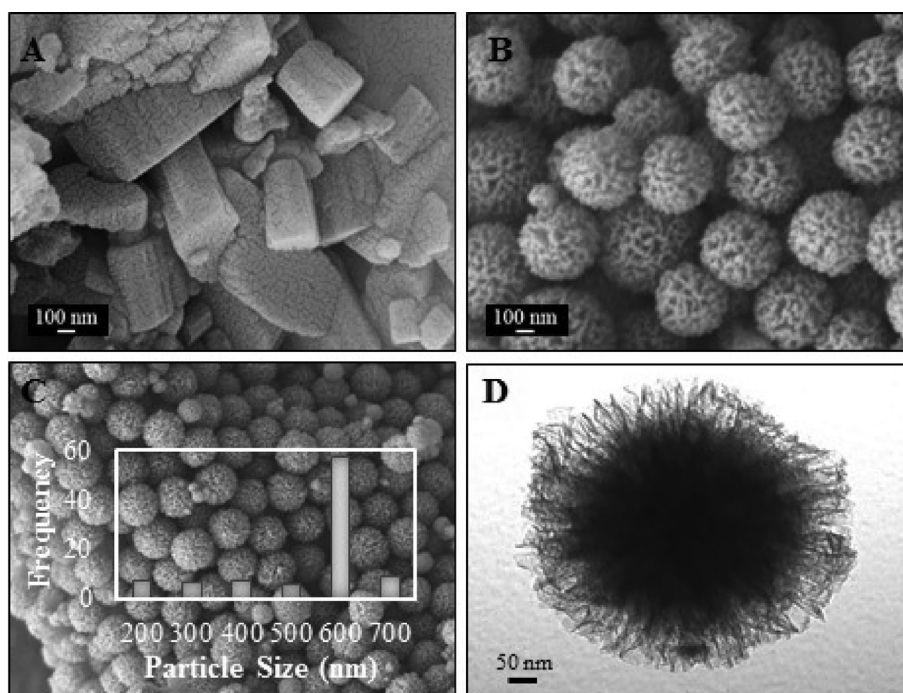


Fig. 1 – FESEM images of (A) HZSM-5 and (B) HSi@ZSM-5 (C) Particle size distribution and (D) TEM image of HSi@ZSM-5.

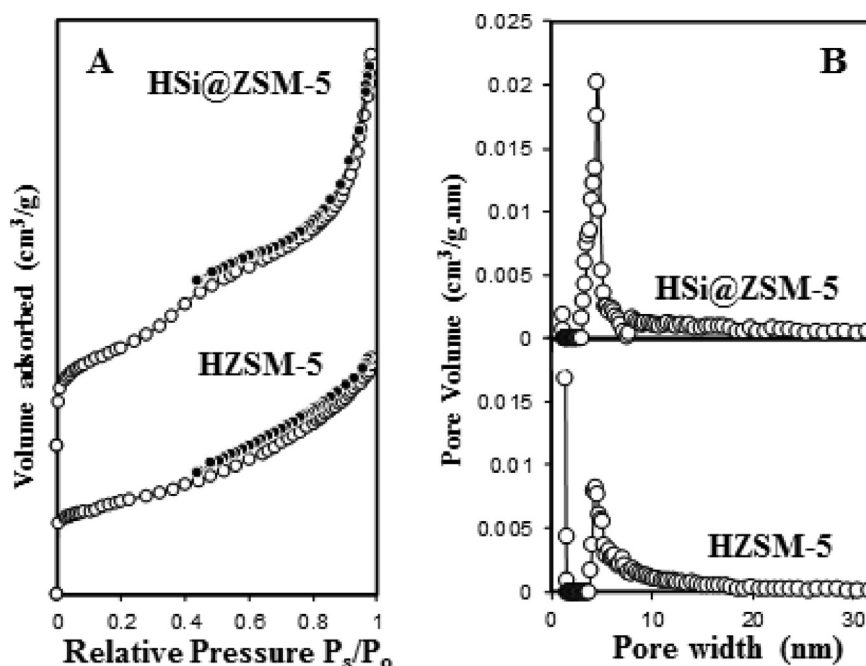


Fig. 3 – (A) Nitrogen adsorption-desorption isotherms and (B) NLDFT pore size distribution of HSi@ZSM-5 and HZSM-5.

characteristic for micro–mesoporous materials with narrow slit-shaped like pores. Besides, HSi@ZSM-5 exhibit higher nitrogen uptake compared to HZSM-5, indicating the presence of large pores [37]. Moreover, HSi@ZSM-5 showed two steps of capillary condensation at $P/P_0 = 0.3, 0.9$, which demonstrate the presence of intraparticle and interparticle voids. The nitrogen uptake at a lower relative pressure attest to the presence of micropores, while uptake at higher relative pressure confirm formation of mesopores. Jalil et al. reported similar pattern, portraying the existence of intra and inter particle porosity on mesoporous zeolite materials [28]. Recently, Feng et al. elaborated coexistence of micropores and mesopores on micro-sized synthesized ZSM-5 [38]. Obviously, the hysteresis loops obtained in case of the HSi@ZSM-5 proved the successful generation of mesopores. This feature may negate limited diffusion attributed to commercial HZSM-5 catalyst.

Fig. 3B displays the pore size distribution of both catalysts, obtained by a non-local density functional theory (NLDFT) method. HZSM-5 displayed narrow pore distribution in the range of 0.5–2 nm and 2–5 nm, which could be attributed to micropore and mesopore respectively. HSi@ZSM-5 showed similar pore size distribution with HZSM-5. However, formation of bigger pore size was signalled by broad and small peak found in the range of 5–20 nm which correspond to the presence of mesopores. Notably, the sharp peak is because of mesopores generated by self-assembly of surfactant, while the small peaks are consequence of the distance between the dendrimeric silica.

Table 1 summarizes the physiochemical properties of HZSM-5 and HSi@ZSM-5. The Brunauer-Emmett-Teller (BET) surface area of HZSM-5 and HSi@ZSM-5 are 325 m²/g and 534 m²/g respectively. Similarly, HSi@ZSM-5 showed mesopore volume of 0.596 cm³/g and HZSM-5 is 0.301 cm³/g. Interestingly, HSi@ZSM-5 was characterized by a significantly

higher surface area and volume of mesopores. These attributes might be due to the formation of dendrimeric silica fibres in the morphology, triggered by the cationic template (CTAB) during the synthesis. Substantiated findings have shown that catalytic performance is sturdily improved by existence of mesoporosity, which is desirable for commercial applications [21,38]. The analysis of textural properties of both catalysts led to the conclusion that the microemulsion seed assisted synthesis is efficient to engineer mesoporosity with concurrent microporosity preservation.

Assessment of acidic properties

Fourier-transform infrared (FTIR) spectroscopy is an efficient tool applied for the assessment of chemical species located on the surface of catalysts [39]. In order to examine the hydroxyl groups that describe their acidic properties, both catalysts were evacuated at 673 K for 1 h prior to FTIR analysis to remove the physisorbed water. Fig. 4A shows the FTIR spectra of both catalysts in the region of 3800–3200 cm^{−1}. The deconvolution using Gaussian curve fitting shows that they mainly consist of six main bands at 3738, 3707, 3663, 3609, 3520, and 3482 cm^{−1} which represent silanol groups located at external surface of the catalysts, vicinal silanol groups, hydroxyl group of extra framework Al–OH (EFAl) species, Bronsted OH band associated with bridging hydroxyl group between Si and Al tetrahedral framework, bridging hydroxyls which perturbed by H-bond interaction with the framework, and silanol nest, respectively [29,40]. For clarity, the intensities of those bands are presented in Fig. 4B. It was observed that the HSi@ZSM-5 was rich with almost all hydroxyl groups, revealing the formation of dendrimeric silica fibers as well as transformation of framework alumina into EFAl [41]. While, the HZSM-5 also possesses a band at

Table 1 – Physiochemical properties of HZSM-5 and HSi@ZSM-5.

Catalyst	BET surface area (m ² /g) ^a	Total pore volume (cm ³ /g) ^b	Micropore volume (cm ³ /g) ^b	Mesopore volume (cm ³ /g) ^b	Brønsted acid site (μmol/g) ^c	Lewis acid site (μmol/g) ^c
HZSM-5	325 (73)	0.361 (0.165)	0.060 (0.009)	0.301 (0.156)	107.98	29.76
HSi@ZSM-5	534 (377)	0.599 (0.452)	0.003 (0.002)	0.596 (0.449)	20.12	19.01

() is for spent catalyst.

^a Determined by Brunauer-Emmet-Teller method.

^b Determined by t-plot method.

^c Calculated using the integrated molar extinction coefficients for which $\epsilon_{1460} = 0.147 \text{ cm } \mu\text{mol}^{-1}$ for the Brønsted acid site and $\epsilon_{1622} = 0.022 \text{ cm } \mu\text{mol}^{-1}$ for Lewis acid site.

3760 cm⁻¹ which assigned to the Al–OH group linked to the framework and two additional bands at 3380 and 3295 cm⁻¹, attributed to the H-bonded acidic SiO(H)Al groups to the neighbouring oxygen atoms and H-bonded silanol groups located in the defective position [10,42]. The absence of those high acidic bands along with the lower intensity of bridging hydroxyls band at 3520 cm⁻¹ most probably will be a definite advantage to HSi@ZSM-5 as compared to HZSM-5 in the MTO reaction.

In fact, the catalytic performance of zeolite materials is governed by their inherent acidity, which is a vital parameter for attainment of valuable products from methanol. Hence, the acid properties of HZSM-5 and HSi@ZSM-5 were analysed by FTIR spectroscopy, using ammonia probe molecule. Fig. 5A shows the FTIR spectra of ammonia adsorbed in the region of 1700–1300 cm⁻¹ on both catalysts at room temperature. Two clear bands were seen at 1450 and 1620 cm⁻¹, which are ascribed to bounded ammonium ions on Brønsted acid sites (BAS) and Lewis acid sites (LAS), respectively [43]. The amount of both acid sites on HZSM-5 are higher than HSi@ZSM-5 particularly the BAS, which seemingly come from high acidity bridging hydroxyl groups and silanol nest (Fig. 4A).

In furtherance of the acidity assessment, the spectra of adsorbed ammonia were outgassed (323–573 K) and shown in

Fig. 5B and C for HZSM-5 and HSi@ZSM-5, respectively. The intensity of the broad peaks (1550–1350 cm⁻¹) appears to reduce slightly with the increase in desorption temperature. Hence, to get more insight on the peaks, deconvolution was conducted, and their integral areas were attained as depicted in Fig. S1. Three absorption peaks (1550, 1465, and 1430 cm⁻¹) ascribed to symmetric and antisymmetric bending vibration of NH₄⁺ ion were demonstrated [44]. Nonetheless, the peaks (1465 and 1430 cm⁻¹) remain unchanged with increasing outgas temperature, while the other peaks (1500 cm⁻¹) decrease rapidly as the outgassing temperature increased and eroded completely at 573 K.

Fig. 6 displays the variation of peak intensity changes in Fig. 5 with respect to outgassing temperature. The results (Fig. 6A and B) illustrated presence of strong interaction between ammonia molecules and acid sites (BAS and LAS) at 323 K. However, decrease in intensities was detected as the temperature increase, insinuating presence of BAS on both catalysts. It can be observed that concentration of acid sites for HZSM-5 was higher than HSi@ZSM-5. This connotes that the acidity of zeolite seed crystals was poisoned by synthesis conditions of as-synthesized fibrous silica catalyst. Accordingly, the amount of BAS and LAS were computed using the integrated molar extinction coefficients and presented in Table 1 [45]. The concentration of BAS and LAS were less on HSi@ZSM-5 in comparison to HZSM-5. The optimized concentration of acid sites (BAS and LAS) attained might be ascribed to passivation of external silanol hydroxyl groups by the fibrous silica morphology formed during HSi@ZSM-5 synthesis as portrayed in Fig. 1. Similar results were reported in literature [41,46].

Generally, moderating the strong acidity of conventional ZSM-5 catalyst is vital for MTO process. The strong acid sites increase the rate of undesired products formation (aromatics, alkanes) through side reactions such as aromatization and hydrogen transfer which cause deactivation [47]. However, the lower concentration of acid sites is enough for catalysing the C–C bond formation through methylation or alkylation reactions which result in generation of olefin products [13]. Also, lower strength of acid sites hinders side reactions and is adjudged to improve catalytic performance in MTO reaction [48]. Thus, optimized acidic feature of HSi@ZSM-5 with large amount of moderate and/or weak acid sites created by the synthesis condition is a promising characteristic for better catalytic performance in the MTO reaction.

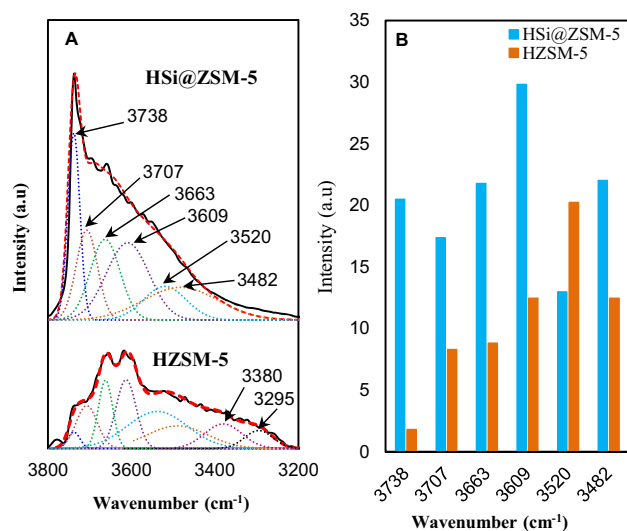


Fig. 4 – (A) FTIR spectra of activated HZSM-5 and HSi@ZSM-5 in the hydroxyl stretching region (B) Comparison of deconvoluted area of both catalysts in (A).

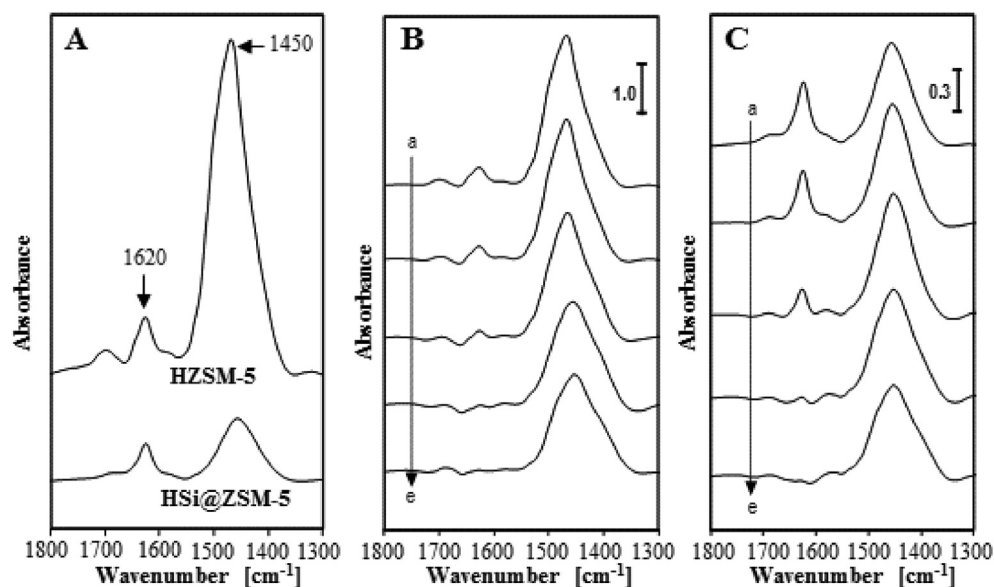


Fig. 5 – (A) FTIR spectra of ammonia adsorbed on HZSM-5 and HSi@ZSM-5 at room temperature. The ammonia adsorbed on (B) HZSM-5 and (C) HSi@ZSM-5 were outgassed at (a) 303K, (b) 323K, (c) 373K, (d) 473K, and (e) 573K.

Catalytic performance

The catalytic activities of commercial HZSM-5 and synthesized HSi@ZSM-5 catalysts were evaluated under MTO conditions at 473–673 K. Fig. 7 represents methanol conversion and products distribution. It was noticed from Fig. 7A that conversion increases gradually with increasing temperature, and almost 100% conversion was achieved

for both catalysts at temperature of 673 K. Similar findings in literature also reported high conversion in MTO reaction using ZSM-5 based zeolites [9,49]. Most notably, HSi@ZSM-5 showed higher trend of conversion. These might be attributed to the textural and acidic feature of HSi@ZSM-5, as evident in the nitrogen adsorption-desorption (Fig. 3), and ammonia probed IR spectroscopy (Fig. 5) results.

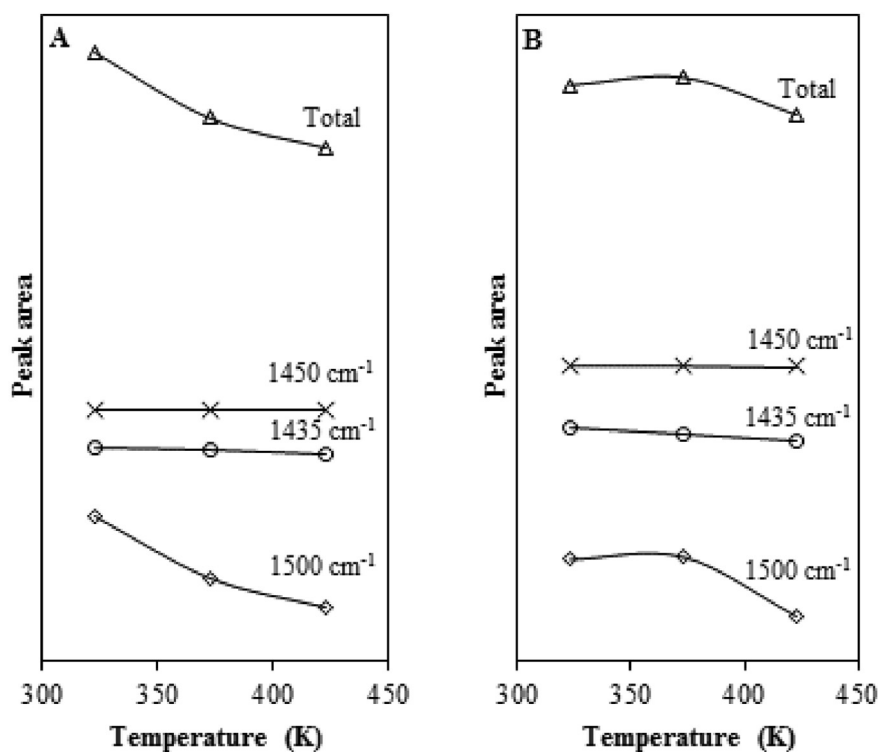


Fig. 6 – Peak area of adsorbed ammonia on (A) HZSM-5 and (B) HSi@ZSM-5 catalysts as the function of outgassing temperature.

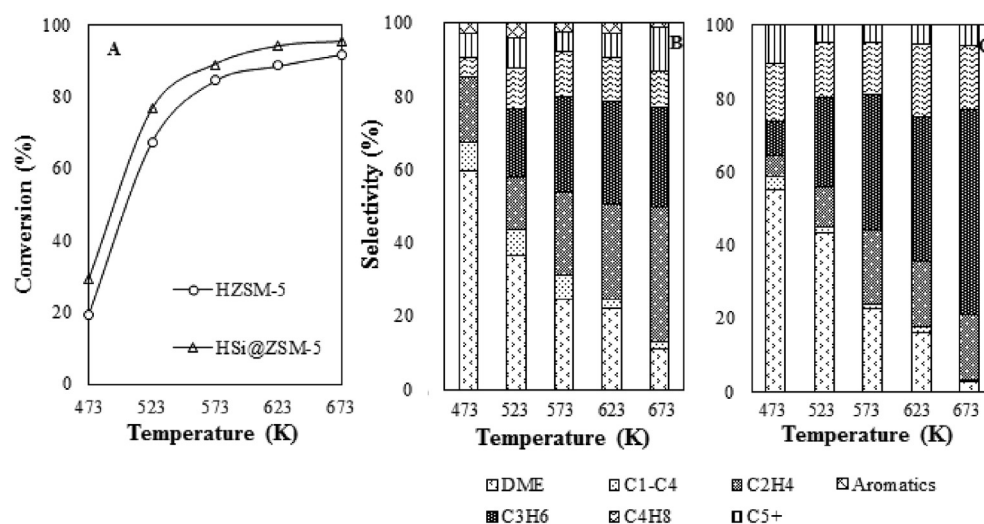


Fig. 7 – (A) Conversion for MTO in catalytic performance and product distribution as a function of reaction temperature (B) HZSM-5, and (C) HSi@ZSM-5.

The MTO reaction products distribution were depicted in Fig. 7B and C. For HZSM-5 (Fig. 7B), dimethyl ether (DME), ethylene, butylene, alkanes, higher alkenes and aromatic products were detected at 473 K. In the case of HSi@ZSM-5 (Fig. 7C), similar products were obtained. Though, propylene was among the products at this temperature. The selectivity towards light olefins showed an increasing trend with temperature, but DME decreased at higher temperature signalling that more of the DME were converted to hydrocarbons.

Contrastingly, propylene selectivity increased up to 56% for HSi@ZSM-5, and 27% on HZSM-5 at reaction temperature of 673 K. Similarly, higher fraction of propylene was observed in relation to ethylene for HSi@ZSM-5. It is worth noting that HSi@ZSM-5 showed high propylene selectivity. A plausible explanation can be the mesoporous nature of HSi@ZSM-5 symbolized by a higher concentration of lower acid sites developed during the microemulsion seed assisted synthesis, which prevent occurrence of secondary reactions leading to aromatics in the product spectrum. This agrees with findings in literature [21,38].

Furthermore, the conversion trend was observed for duration of 120 h on stream at temperature of 673 K for both catalysts to reveal the stability performance. As observed in Fig. 8, the initial 98% conversion on HZSM-5 dwindled to 70% after 30 h on stream, while the conversion was maintained on HSi@ZSM-5 till 80 h when it reduced to 90%. After observing the behaviour of both catalysts for 100 h on stream, they were subjected to oxidation treatment at 823 K to access their performance after regeneration. Increased conversion was recorded after regeneration, where HSi@ZSM-5 and HZSM-5 showed 98% and 80% conversion respectively.

Thus, the longer stability period observed for HSi@ZSM-5 indicates high resistance towards deactivation. This excellent performance could be attributed to its mesoporous structure and unrestricted diffusion. More so, the lower strength of acid sites of HSi@ZSM-5 limit propagation of side reactions, which have tendency towards forming coke species

[50]. A recent investigation by Yarulina et al. reported that mesoporous zeolites are more stable towards deactivation in MTO reaction due to enhanced mass transfer capabilities [9].

Properties of spent catalysts

The spent catalysts were applied for characterizations of TGA, nitrogen adsorption-desorption and KBr-Infrared spectroscopy, to elucidate the outstanding attributes of low coke deposits in the mesostructured HSi@ZSM-5 catalyst. The approximate amount of coke deposits on the spent catalysts were analysed by TGA. Fig. 9A represents the TGA analysis of the spent catalysts. The weight loss measured for HSi@ZSM-5 (3.3%) is significantly lower than for HZSM-5 (5.8%). Thus, HSi@ZSM-5 displayed lower coke deposition compared to HZSM-5.

Nitrogen adsorption-desorption analysis was also carried out to quantify the coke deposits on the surface and pores of the spent catalysts at temperature range of 323–1123 K as

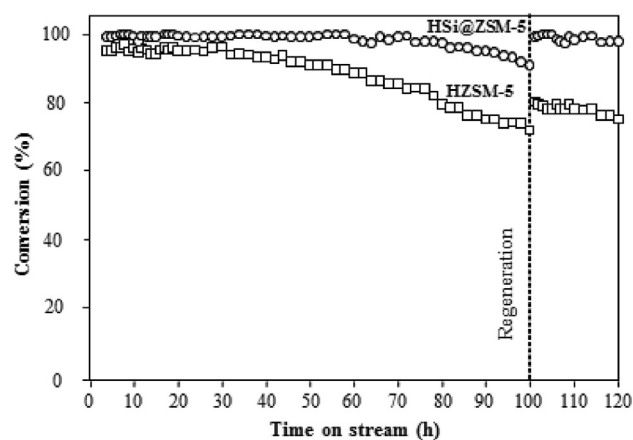


Fig. 8 – Time on stream dependence of methanol conversion.

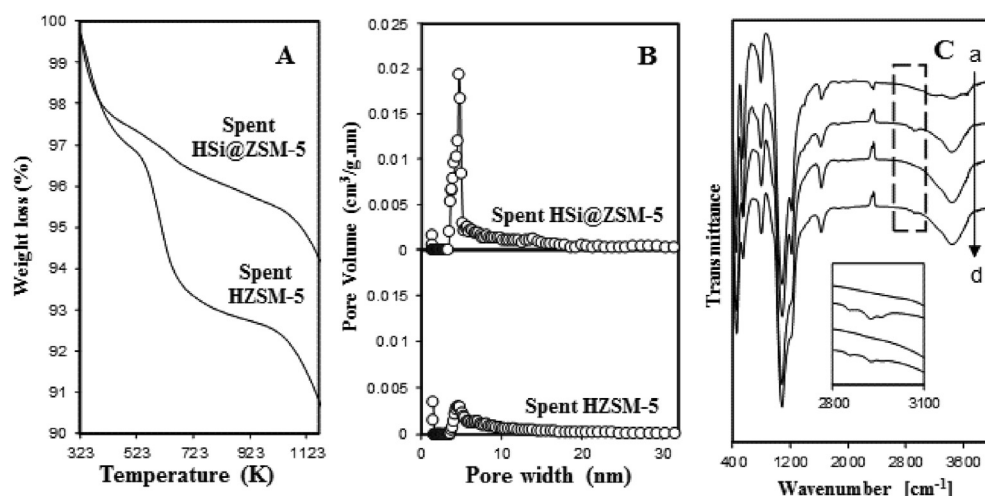


Fig. 9 – Properties of spent catalysts (A) TGA curves (B) Pore size distribution (C) IR-KBr spectra of (a) Fresh HZSM-5, (b) Spent HZSM-5, (c) Fresh HSi@ZSM-5 and (d) Spent HSi@ZSM-5 catalysts.

shown in Fig. 9B. Virtually both catalysts showed reduction in surface area (Table 1). The surface area of HZSM-5 reduced from 325 m²/g to 73 m²/g (reduction of 77%), while in the case of HSi@ZSM-5, the reduction was from 534 m²/g to 377 m²/g (reduction of 29%). The reduction in HSi@ZSM-5 is significantly lower in relation to HZSM-5. Besides, HZSM-5 performance was below the optimum after the regeneration (Fig. 8), signalling severe pore blockage by coke deposits. However, the mesoporous attribute of HSi@ZSM-5 results in transformation of larger amount of methanol before the commence of deactivation.

As presented in Table 1, the micropore volume of HZSM-5 reduced from 0.060 cm³/g to 0.009 cm³/g, while the mesopore volume was from 0.301 cm³/g to 0.156 cm³/g. The inherent diffusion constraints of ZSM-5 catalyst led to significant decrease in micropore volume as compared to mesopore [3,10]. This suggest that coke deposition occurred predominantly in the pore channels, due to accumulation of coke species blocking reacting molecule access to the active sites. On the contrary, the micropore and mesopore volume of HSi@ZSM-5 shows that coke deposition is more in the mesopores (24%) than in the micropores (15%). It is reported that coke deposition in mesopores led to insignificant deactivation during MTO reaction [10]. This is in accord with the low coke deposits detected on HSi@ZSM-5 during the TGA analysis (Fig. 9A). Interestingly, the inherent diffusion constraints of commercial ZSM-5 was alleviated by the introduction of secondary pore system during the synthesis of HSi@ZSM-5 [26,34]. This led to the relatively stable performance of HSi@ZSM-5 (Fig. 8). Thus, the outstanding diffusivity of fibrous silica ZSM-5 catalyst facilitates the removal of intermediate products that are prone to form coke species, thereby shifting the reaction equilibrium to formation of more propylene products [3,10].

Fig. 9C shows the KBr-Infrared spectroscopy spectra of fresh and spent HZSM-5 and HSi@ZSM-5. Both catalysts showed characteristics of paraffinic structured coke deposits in the region of 2800–3100 cm⁻¹ [51]. For the HZSM-5 catalyst, the intensity of the IR peaks corresponding to the longer

paraffinic carbon chain species are more obvious than that attained using the HSi@ZSM-5 catalyst. This result also agrees with the findings in the TGA analysis. From the spent catalysts characterization results, HSi@ZSM-5 displayed exceptional resistance to coke formation when compared to HZSM-5. Several literatures have examined the properties and contribution of high mesopore volume and reduced acidic sites of ZSM-5 catalyst in enhancement catalytic stability in MTO [9,13,38].

Most industrial conversion processes are operated at elevated conditions. As such, catalysts used require stable features in other to be functional over prolonged period. Coke deposits formed from intermediates or by products lead to the loss of activity by poisoning of the active sites. Hence, the rational design of catalysts is to limit deactivation. Interestingly, the synthesized core shell fibrous silica HSi@ZSM-5 displayed high stability and regenerability, which is anticipated to pave way for its application in commercial MTO plants.

Proposed reaction mechanism

An in situ FTIR spectroscopy of methanol adsorption on HZSM-5 and HSi@ZSM-5 were performed to gain insight into the dynamics and species transformation of surface adsorbed methanol and the result is depicted in Fig. 10. Fig. 10A and B illustrate the FTIR spectra of both catalysts in region of 3800–3500 cm⁻¹ which represents the hydroxyl groups stretching region. Both catalysts showed three adsorption bands attributed to interaction of adsorbed methanol with the silanol groups outside the zeolite channel (3748 cm⁻¹), vicinal silanol groups (3700 cm⁻¹) and acidic hydroxyl groups associated with framework aluminium within the catalyst channels (3637 cm⁻¹) [52].

The aforementioned peaks were less pronounced in the HSi@ZSM-5 compared to HZSM-5, feasibly due to low acidic characteristics of HSi@ZSM-5 as evident in Table 1. In the case of HZSM-5, the peaks intensity slightly decreased upon increasing adsorption temperature from 473 to 673 K,

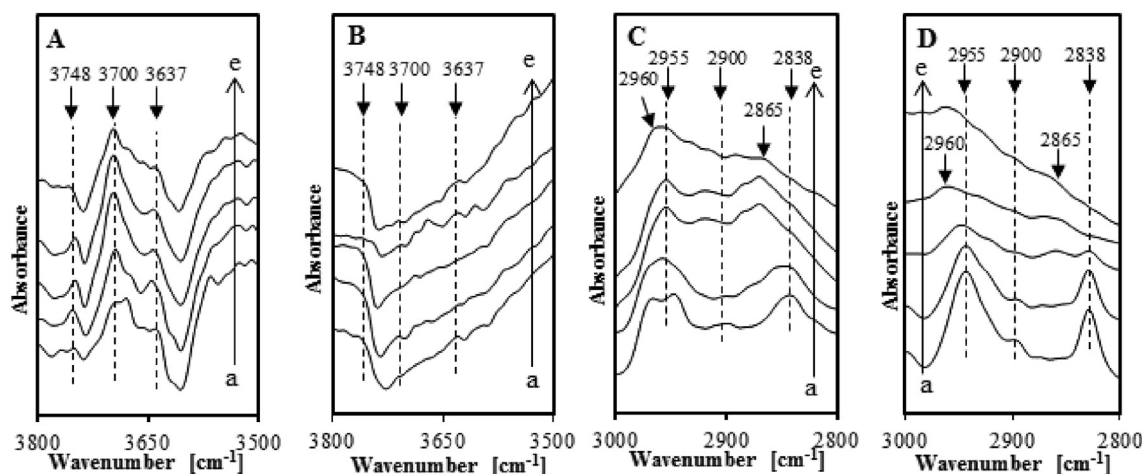


Fig. 10 – In-situ FTIR spectra of adsorbed methanol at O–H vibration region for (A) H-ZSM-5 and (B) H-Si@ZSM-5, and C–H vibration region for (C) H-ZSM-5 and (D) H-Si@ZSM-5. Adsorption temperature of (a) 473K (b) 523K (c) 573K (d) 623K and (e) 673K.

suggesting consumption of the hydroxyl groups by interaction with methanol molecules. On the other hand, these peaks show greater consumption of the hydroxyl groups on HSi@ZSM-5. At adsorption temperature of 523 K, the vicinal silanol and acidic hydroxyl peaks diminishes in intensity and reappeared at 623 K, signifying possible repeated methylation on the acidic sites.

Concurrently, FTIR spectra in region of 3000–2800 cm^{-1} were observed in Fig. 10C and D which correspond to the C–H stretching region. Peaks of surface methoxy groups emerged (2955 cm^{-1} , 2900 cm^{-1} and 2838 cm^{-1}) [53]. Nonetheless, two types of methoxy groups were detected. First are those (2955 cm^{-1} and 2900 cm^{-1}) associated with structural defects and/or external surface silanol groups, respectively whereas the second ones are those (2838 cm^{-1}) generated on the bridging acidic hydroxyl groups [15,54]. The methoxy peaks shifted gradually (2955 cm^{-1} to 2960 cm^{-1} and 2838 cm^{-1} to 2865 cm^{-1}) on both catalyst at elevated temperature. Nonetheless, Olsbye et al. observed similar spectral changes. Peculiarly, broader methoxy peaks observed on HSi@ZSM-5, gives a rough idea on the conspicuous surface methoxy species generated, signalling strong methylating capability [15]. The intensity of the methoxy peaks sharply decreased with increasing temperature, due to methylation reactions to form hydrocarbon products.

From the above findings, intermediate species were revealed, providing vital information from the interaction of reactant and active sites. The silanol and vicinal silanol hydroxyl groups participated more, due to their considerable consumption at lower temperature. Accordingly, surface methoxy species were produced via interaction of acidic hydroxyl groups with adsorbed methanol. Their susceptibility to polarization was obvious at higher temperatures, forming hydrocarbon products. Thus, HSi@ZSM-5 hinder occurrence of side reactions which might be attributed to absence of polymethylbenzene intermediates in the FTIR spectra. Several studies have shown that methoxy species play a vital role in formation of hydrocarbons [13,16]. It is worth pointing out the conclusive report by Olsbye et al. which outlined surface

methoxy species as active intermediate species capable of generating hydrocarbon products [15]. More recently, Meng et al. affirmed the production of hydrocarbons from fractions of surface methoxy intermediates [52].

The MTO reaction mechanism is summarized in Fig. 11. The incipient adsorption of methanol was heavily influenced by acid sites of the catalysts. The first stage begins with methanol dehydration to dimethyl ether (DME) and water. In agreement with this, the inclining trend of conversion with reaction temperature as shown in Fig. 7A, support the dehydration of methanol. Conspicuously, the FTIR spectra did not show peaks that can be assigned to DME or water, perhaps the initiation step is almost instantaneous. The dehydration product result in generation of surface methoxy species [12]. As can be seen in Fig. 10A and D, strong peaks of adsorbed methanol with acidic hydroxyls, accompanied by C–H deformation and stretch modes suggest conversion of methanol to surface methoxy species at 473 K.

In a later stage, the surface methoxy species undergo consecutive methylation, to form light olefins, which result in growth of hydrocarbons. A recent study by Ma et al. attested that higher alkenes are produced from propylene through repeated methylations with methanol [18]. Similarly, this agrees very well with the presence of propylene fragment in the products spectrum at temperature of 473 K as shown in Fig. 7. These attribute supports the notion that the onset lower olefin formed act as a co-catalyst to enhance hydrocarbons production, especially propylene [46]. Finally, the reaction progresses with further cracking of the higher olefins to produce hydrocarbon products.

In contrast, the rate of methanol dehydration is more rapid on HSi@ZSM-5 as compared to HZSM-5 ($R_{\text{HSi@ZSM-5}} > R_{\text{HZSM-5}}$). This interesting attribute can be supported by the higher conversion displayed in Fig. 7A. However, this can be correlated to the moderate or lower strength of HSi@ZSM-5 acid sites (Table 1), which seem to be enough for catalysing the reaction. Similar observations were reported in literature [13,48]. The other amazing attribute is the faster rate of methylation displayed by HSi@ZSM-5 as compared to HZSM-5

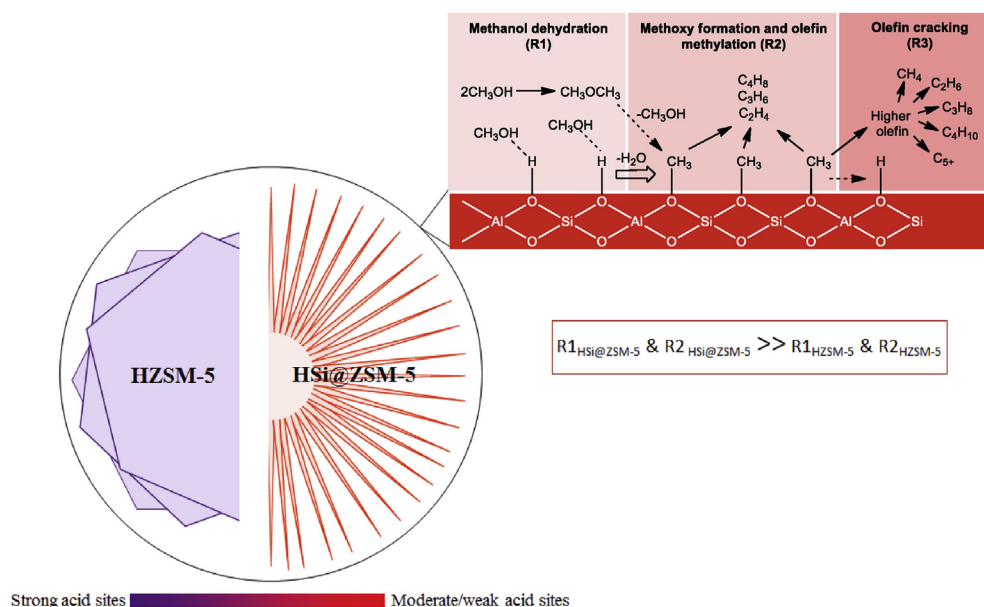


Fig. 11 – Proposed MTO reaction mechanism.

($\text{R2}_{\text{HSi@ZSM-5}} > \text{R2}_{\text{HZSM-5}}$). Besides, the prerequisite for this observation can be correlated to the topology of HSi@ZSM-5, since the category of the methoxy groups observed in the in situ FTIR are the ones associated with structural defects and/or external surface silanol groups. Similar findings by Lo et al. attested that the degree of methylation strongly depends on catalyst topology and porous structure [55]. Furthermore, the enhanced propylene selectivity in the product distribution (Fig. 7B), is the result of superior methylating capability of HSi@ZSM-5 and a growing contribution from the alkene route. Very recently, Jiao et al. reported that the formation of propylene products in MTO reaction, relates to facilitated methylation of olefins, which hinder side reactions [56]. A multitude of researches have resolved that the alkene cycle is highly selective to propylene products with surface methoxy species as active intermediates, while the aromatic cycle is the central pathway for aromatics and ethylene formation with polymethylbenzene as the active intermediates [18,57].

Unequivocally, the in situ FTIR and catalytic performance observations on the studied catalysts revealed that HSi@ZSM-5 catalyst favoured product formation via the alkene cycle. On the contrary, noticeable fractions of aromatics and alkanes observed in HZSM-5 product distribution (Fig. 7A), suggest the

occurrence of side reactions. Similarly, the catalyst stability (Fig. 9) findings discussed in the previous section, demonstrated that formation of less coke deposits on HSi@ZSM-5, signalling the aromatic cycle and other side reactions are conceivably not operational. Therefore, it seems reasonable to conclude that alkene cycle is the dominating reaction mechanism over fibrous silica HSi@ZSM-5. This finding is in accord with similar investigations [46,58,59].

In the quest for a more robust catalyst in transformation of methanol to olefin, a great number of MFI morphology-based catalysts have been developed. In Table 2, methanol conversion, propylene selectivity and stability period of synthesized HSi@ZSM-5 catalyst compared to commercial HZSM-5 and other archetypal ZSM-5 catalysts found in literature were presented. As-synthesized fibrous silica HSi@ZSM-5 catalyst demonstrated pronounced catalytic performance than the commercial ZSM-5 catalysts. However, nanostructured ZSM-5 synthesized by Kim et al. displayed 3.5% propylene selectivity higher than HSi@ZSM-5, which can be related to high Si/Al ratio (280) of the ZSM-5 seed used in fabrication of the nanostructured catalyst, as compared to ZSM-5 seed with Si/Al ratio of 23 applied in HSi@ZSM-5 synthesis [60]. Literatures [3,47,49] affirmed that zeolite with higher Si/Al ratio increases

Table 2 – Comparison of catalytic performance of MFI morphology-based catalysts in MTO reaction.

Catalyst	Reaction temperature (K)	Conversion (%)	Propylene selectivity (%)	Stability period (h)	Reference
Fibrous HSi@ZSM-5	673	100	56	80	This study
Commercial HZSM-5	673	100	27	30	This study
Synthesized HZSM-5	723	100	51	25	[13]
Nano-sized HZSM-5	623	98	36	42	[7]
Micro-sized HZSM-5	723	85	41	13	[38]
Nanostructured HZSM-5	773	98	58	30	[60]
Synthesized HZSM-5	673	95	28	24	[61]
Hierarchical HZSM-5	733	100	44	58	[62]
3%Mg-HZSM-5	723	100	46	8	[63]
10%Gd-HZSM-5	673	100	22	45	[64]

propylene selectivity. Nonetheless, HSi@ZSM-5 was more stable for nearly three-fold higher as compared to the nano-structured ZSM-5.

Thus, the tuned acidic strength of HSi@ZSM-5 was enough to induce greater interaction of adsorbed methanol with acidic hydroxyls, with formation of enormous surface methoxy intermediates as observed in the in situ FTIR studies. Also, the dendrimeric fibres and high surface area observed exposes more of the external surface to participate in the reaction, and hence, facilitates molecular diffusion. Strikingly, the unique topology, accessibility, unrestricted diffusion and optimized acidic nature of HSi@ZSM-5 played major role in tailoring the MTO reaction pathway towards the alkene cycle mechanism. These characteristics showed remarkable potentials in hindering deactivation and improving propylene selectivity.

Conclusion

Catalytic investigation on methanol transformation to olefin over as-synthesized fibrous silica HSi@ZSM-5 and commercial HZSM-5 catalysts were conducted. The reaction mechanism for enhanced propylene formation was elucidated, based on in situ FTIR studies on interaction of adsorbed methanol with acidic hydroxyls. Interestingly, rapid methanol dehydration, higher rate of surface methoxy intermediates generation and methylation reaction were observed on HSi@ZSM-5 relative to the commercial HZSM-5. Furthermore, catalytic performance results revealed that as-synthesized catalyst exhibited remarkable stability and improved propylene selectivity. Investigation into characteristics of spent catalysts showed less coke deposition on HSi@ZSM-5, which infers suppression of undesired side reactions. These findings led to the deduction that alkene cycle is the dominating reaction mechanism. Conspicuously, the high surface area, optimized acid sites and dendrimeric fibrous morphology of HSi@ZSM-5 were orchestrated by the microemulsion synthesis conditions resulting to its performance enhancement anticipated to pave way for practical application in commercial MTO plants.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ijhydene.2019.11.236>.

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