



Contents lists available at ScienceDirect

Chemical Engineering Research and Design

journal homepage: [www.elsevier.com/locate/cherd](http://www.elsevier.com/locate/cherd)

IChemE



# Dehydration of methanol to light olefins upon zeolite/alumina catalysts: Effect of reaction conditions, catalyst support and zeolite modification

Saeed Hajimirzaee<sup>a</sup>, Mohammed Ainte<sup>a</sup>, Behdad Soltani<sup>a</sup>,  
Reza Mosayyebi Behbahani<sup>b</sup>, Gary A. Leeke<sup>a</sup>, Joseph Wood<sup>a,\*</sup>

<sup>a</sup> School of Chemical Engineering, University of Birmingham, Birmingham B15 2TT, UK

<sup>b</sup> Gas Engineering Department, Petroleum University of Technology, Ahwaz, Iran

## ABSTRACT

The reaction of methanol to propene was studied in a fixed bed reactor using a pelleted zeolite in alumina matrix support catalyst. The effect of reaction conditions (temperature, pressure, space velocity, feed composition), as well as the effect of support to ZSM-5 zeolite ratio on the conversion of methanol to light olefins ( $C_2^=$ – $C_4^=$ ) was studied. The best catalyst and optimum reaction conditions leading to a maximum yield of  $C_2^=$ – $C_4^=$  were determined. Use of  $\gamma$ -alumina as support improved the catalyst selectivity to propene and light olefins. Zeolite/alumina catalyst with 25 wt.% ZSM-5 dispersed in a matrix containing 75% alumina led to highest selectivity to propene and light olefins. ZSM-5 zeolite was modified with phosphorus, Cs, Ca and Fe. The effect of their impregnation on the conversion of methanol and selectivity to light olefins was studied. Modification in all cases increased the shape-selectivity to light olefins. ZSM-5 zeolite ion exchanged by Cs led to highest selectivity to light olefins and particularly propene by changing the acid sites distribution.

© 2014 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.

**Keywords:** Methanol to propene; MTP; ZSM-5; Modification; Wet impregnation; Support

## 1. Introduction

The formation of hydrocarbons from methanol over zeolite catalysts enables petrochemical and gasoline based products to be obtained from raw materials other than conventional oil based substances. This development is therefore of great importance, as the dependence on resources which are depleting is reduced significantly. Methanol is a key ingredient in the synthesis of many organic molecules. World methanol production has increased from 32 million metric tons annually (MTA) in 2006 to 62 MTA in 2012 and is expected to increase to 94 MTA in 2016. Each day more than 100,000 tons of methanol is used as a chemical feedstock or as a transportation fuel. Also, it can be economically converted to ethylene and propene, two

of the largest volume petrochemical feed stocks. Using zeolite as catalyst for methanol to olefins (MTO) process has been studied widely while the products are generally the mixed  $C_2^=$ – $C_4^=$  olefins (Keil, 1999; Mei et al., 2008; Stocker, 1999). Extensive research has been devoted to improve the process development and selectivity to light olefins. High selectivity to ethylene was achieved over Ni-SAPO-34 catalyst (Inui and Kang, 1997) while better selectivity to propene was observed over high silica ZSM-5 zeolite modified by phosphoric acid (Liu et al., 2009) or zirconium oxide (Zhao et al., 2006). More than 20 mechanisms have been proposed for this reaction (Stocker, 1999), but it has been established that the reaction mechanism for the formation of hydrocarbons from methanol over acidic zeolites can be illustrated by the hydrocarbon pool

\* Corresponding author. Tel.: +44 (0) 121 414 5295; fax: +44 (0) 121 414 5324.

E-mail addresses: [J.Wood@bham.ac.uk](mailto:J.Wood@bham.ac.uk), [joe\\_wood99@hotmail.com](mailto:joe_wood99@hotmail.com) (J. Wood).

Received 13 November 2013; Received in revised form 18 April 2014; Accepted 9 May 2014

Available online 19 May 2014

<http://dx.doi.org/10.1016/j.cherd.2014.05.011>

0263-8762/© 2014 The Institution of Chemical Engineers. Published by Elsevier B.V. All rights reserved.



**Scheme 1 – Reaction path for dehydration of methanol to light and heavy hydrocarbons (Li et al., 2011).**

mechanism (Bjørger et al., 2007). This involves the formation of dimethylether (DME), as an intermediate product, via a dehydration process which reaches equilibrium as shown in Scheme 1. This precursor is then converted into light olefins via cracking. It has been shown, once a small number of light olefins are produced, an autocatalytic reaction starts to occur (Patcas, 2005). Subsequently, heavy organic compounds are formed via the formation of cyclic compounds and polyalkylation.

Unfortunately, zeolite catalysts may suffer from rapid deactivation during the reaction due to the deposition of carbonaceous residues in the catalyst pores which block the reactants from accessing the active acid sites (Bibby et al., 1992). Although ZSM-5 zeolite shows much higher resistance to coke formation compared to SAPO-34 or other zeolites in MTO reaction, structural factors of zeolite that can affect coke deposition and catalyst deactivation should be investigated to further decrease coking and thus improve the cost effectiveness of the process. In the MTO reaction, besides the production of the desired light olefins, undesired polyolefins, aromatic compounds and carbon deposits are also formed which may lead to catalyst deactivation (Mores et al., 2011). Much effort has been made to increase the shape selectivity of zeolite by modifying its acid sites distribution using alkali metals (Mei et al., 2008), alkaline earth metals (Goto et al., 2010), transition metals (Dubois et al., 2003), organic acids such as oxalic acid (Lücke et al., 1999) or inorganic acids such as phosphoric acid (Liu et al., 2009). It has been shown that, in conversion of methanol to propene, iron from transition metals (Inaba et al., 2007), calcium from alkaline earth metals (Zhang et al., 2010) and caesium from alkali metals as well as treatment with phosphoric acid can improve the propene selectivity significantly.

In this work, firstly, the effect of reaction conditions on the dehydration of methanol to other hydrocarbons over ZSM-5 zeolite with no support was studied and the effects of a number of reaction parameters upon methanol conversion and product selectivity were investigated. Fresh and selected used catalysts were characterised using Temperature Programmed Desorption (TPD) or Thermogravimetric Analysis (TGA). Secondly, the effect of using different ratios of alumina as a support to zeolite was studied. The conversion to propene over these catalysts was studied with respect to their characteristics such as acidity, pore volume and BET surface area. Subsequently, product distribution over ZSM-5 zeolites modified by iron, calcium caesium, and phosphoric acid were studied in order to investigate the best promoter. Catalyst properties such as the crystal size, surface area and pore geometry of different samples were reported.

## 2. Experimental

### 2.1. Chemicals

Methanol (99.99%), ethanol (HPLC grade) and orthophosphoric acid (85 wt.%) were purchased from Fisher Scientific. ZSM-5 catalyst (CBV 8014,  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 80$ ) was purchased from Zeolyst International in the ammonium form. Boehmite (Pseudoboehmite, Pural SB1) was supplied by Condea Chemie

GmbH. Caesium nitrate (99%), calcium nitrate- $4\text{H}_2\text{O}$  (99%) were supplied by Sigma–Aldrich. Iron nitrate- $9\text{H}_2\text{O}$  (99%) was procured from Honeywell Riedel-de Haen. All chemicals were used as purchased without further purification.

### 2.2. Catalyst preparation

To convert the ammonium form of ZSM-5 zeolite to hydrogen form, the sample was calcined in flowing air at  $773\text{ K}$  for 5 h with a heating rate of  $10\text{ K min}^{-1}$ . In order to determine the effect of ZSM-5 to  $\gamma$ -alumina ratio, powder samples were converted into pellets. Before mixing, ZSM-5 and boehmite were sieved to  $100\text{ }\mu\text{m}$ . A desired amount of ZSM-5 and boehmite were mixed to make the required amounts of supported ZSM-5 (25, 50, 75 and 85 wt.% ZSM-5) with the corresponding finished catalysts named ZSM-5 (25), ZSM-5 (50), ZSM-5 (75) and ZSM-5 (85), respectively. Then 10 ml of distilled water and 0.1 g of nitric acid were added to make it into a paste. The paste was extruded into rods with 3 mm diameters and 5 mm in length using an Instron 4467 Universal Testing Machine with 30 kN uniaxial loading. The samples were dried in an oven at  $80\text{ }^\circ\text{C}$  for 1 h and calcined at  $500\text{ }^\circ\text{C}$  with heating rate of  $10\text{ K min}^{-1}$  for 5 h. The commercial ZSM-5 zeolite named ZSM-5 (100) was used as reference in powder form with no support.

Modification of zeolite was carried out by the wet impregnation method using phosphoric acid and nitrates of Cs, Ca and Fe. For each sample, the desired amount of ion-exchanging component (2.4 g orthophosphoric acid, 1.5 g  $\text{CsNO}_3$ , 7.7 g  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ , 11.9 g  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) was dissolved in 25 ml of solvent (ethanol or distilled water), separately. Subsequently, 10 g of ZSM-5 powder, sieved to  $100\text{ }\mu\text{m}$ , was added to the solution and stirred using a magnetic stirrer at room temperature for 2 h. The treated zeolite was filtered and washed with ethanol (or distilled water) and dried in an oven at  $80\text{ }^\circ\text{C}$  for 1 h followed by calcination at  $500\text{ }^\circ\text{C}$  for 5 h. All the samples were crushed and sieved to  $100\text{ }\mu\text{m}$  (140 mesh) particles before they were loaded into the reactor.

### 2.3. Catalytic test

The effect of reaction conditions on the methanol conversion and product selectivity in the reaction was carried out in a fixed bed reactor (i.d. 15 mm, length 550 mm) charged with 2 g of ZSM-5 (100) catalyst. Glass beads were used above the catalyst bed to ensure a well distributed inlet gas/vapour stream. For a typical run, the feed containing 50 wt.% methanol in distilled water was introduced to the top of reactor using a HPLC pump at constant volume flow rate of  $1.25\text{ ml min}^{-1}$ . The feed was preheated to reaction temperature before entering the reactor. The reactor was purged with nitrogen before and after each reaction. To make sure non-catalytic methanol decomposition occurs in the reactor, a blank run was carried out at  $400\text{ }^\circ\text{C}$  and 1 bar with lowest tested residence time. Fig. 1 shows the schematic diagram of the rig. A thermocouple and back pressure regulator ensured that the process operated within these parameters, with an accuracy of  $\pm 2\text{ }^\circ\text{C}$  and  $\pm 1\text{ bar}$  respectively. The following reaction conditions were investigated in the fixed bed reactor: temperature  $340\text{--}460\text{ }^\circ\text{C}$ , pressure 1–20 bar, Weight Hourly Space Velocity

(WHSV) 7–53 h<sup>-1</sup>, feed composition of methanol 25–75 wt.% in water and time on stream (TOS) 4 h.

The gas and liquid products were collected from the gas–liquid separator after cooling from the reaction temperature to 20 °C. The gas samples were withdrawn from the system using Wheaton® glass serum bottles and analysed off-line by using an Agilent 7890A GC equipped with HayeSepQ 80/100 (0.5 m), HayeSepQ 80/100 (6 ft), Molsieve5A 60/80 (6 ft), HayeSepQ 80/100 (3 ft), Molsieve5A 60/80 (8 ft), DB-1 (2 m × 0.32 mm × 5 µm), HP-AL/S (25 m × 0.32 mm × 8 µm) and 3 detectors including an FID and two TCD detectors. FID connected to DB-1 and HP-AL/S columns were used for hydrocarbon detection with the following conditions: helium as carrier gas flowing at 3.3 ml min<sup>-1</sup> in constant flow mode (12.7 psi at 60 °C), split ratio 1:60, with a 25 µl loop. One TCD connected to HayeSepQ 80/100 (0.5 m), HayeSepQ 80/100 (6 ft) and Molsieve5A 60/80 (6 ft) was used to detect permanent gases with following conditions: helium as carrier gas flowing at 25 ml min<sup>-1</sup> in constant flow mode (36 psi at 60 °C), with a 500 µl loop. Another TCD connected to HayeSepQ 80/100 (3 ft) and Molsieve5A 60/80 (8 ft) was used to detect hydrogen with following conditions: nitrogen as carrier gas flowing at 24 ml min<sup>-1</sup> in constant flow mode (26 psi at 60 °C), with a 500 µl loop.

The column oven temperature program was as follows: hold at 60 °C for 5 min, ramp to 200 °C at 5 K min<sup>-1</sup> then hold for 15 min. Liquid products were identified and analysed by using a Trace GC Ultra Gas Chromatograph equipped with a FID detector and HP-5 column (30 m × 0.32 mm × 0.25 µm). The analytical conditions were as follows: column oven temperature program had an initial temperature of 40 °C, held for 2 min, heating up to 240 °C at a rate of 10 K min<sup>-1</sup>, injection temperature and detector temperature of 250 °C, carrier flow rate (N<sub>2</sub>) of 2 ml min<sup>-1</sup>, split ratio of 50 and injection volume of 0.1 µl. Further analysis was performed by GC–MS to provide verification of the GC results.

## 2.4. Catalyst characterisation

X-ray powder diffraction (XRD) patterns were recorded on an Equinox 3000 diffractometer with CuKα<sub>1</sub> radiation source ( $\lambda = 1.5406 \text{ \AA}$ ) in order to determine crystallite dimensions. The specific surface areas and pore diameters were measured using adsorption–desorption of nitrogen at 77 K using a Micromeritics ASAP 2010 instrument. The acidity of both the modified and parent catalysts was measured using Temperature Programmed Desorption of t-butylamine (t-BA) using a Micromeritics AutoChem 2920 machine. 100 mg of the catalyst sample was placed inside the U-shaped sample tube and exposed to helium at 120 °C for 1 h to remove the moisture, then the temperature of the sample was decreased to 40 °C. Subsequently, pulses of t-butylamine were injected from a loop (0.54 cm<sup>3</sup>) into the sample until it became saturated. Once again, the sample was exposed to helium and its temperature was increased to 150 °C, where it was kept constant for 1 h. This was done to ensure that the physisorbed t-butylamine was completely removed from the sample. A TPD profile was then obtained from 120 °C to 500 °C by heating the sample at a rate of 10 K min<sup>-1</sup>. The amount of t-butylamine desorbed during the process was quantified with a TCD detector. The areas under the peaks were integrated using GRAMS/32 software to determine the amount of t-butylamine desorbed during TPD. The total amount of coked material on the catalyst after reaction was analysed by a NETZSCH TG 209 thermogravimetric analyzer. Typically, 20 mg of the sample was placed in an alumina crucible and heated in a flow of air (20 ml min<sup>-1</sup>) from room temperature to 120 °C at a heating rate of 10 K min<sup>-1</sup> and then held for 30 min to remove all the moisture, subsequently, the temperature was increased further to 700 °C using the same heating rate and it was kept constant for 1 h. The change in weight of sample corresponds to the amount of coke on the catalyst which can be quantified to compare the performance of each catalyst, excluding the weight change during

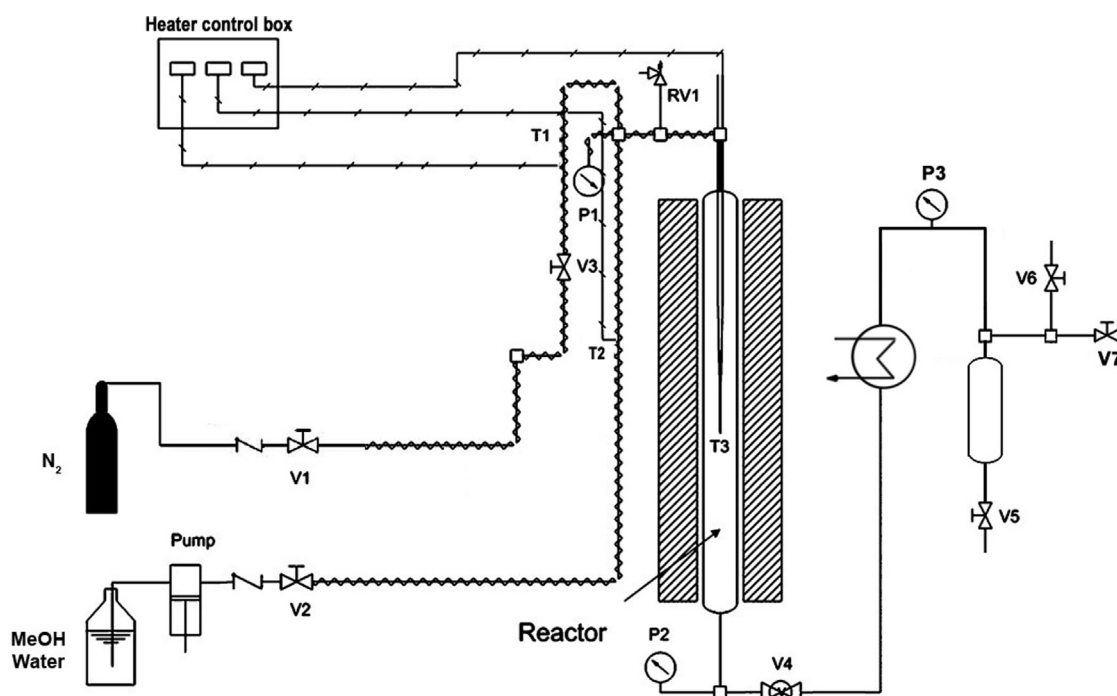
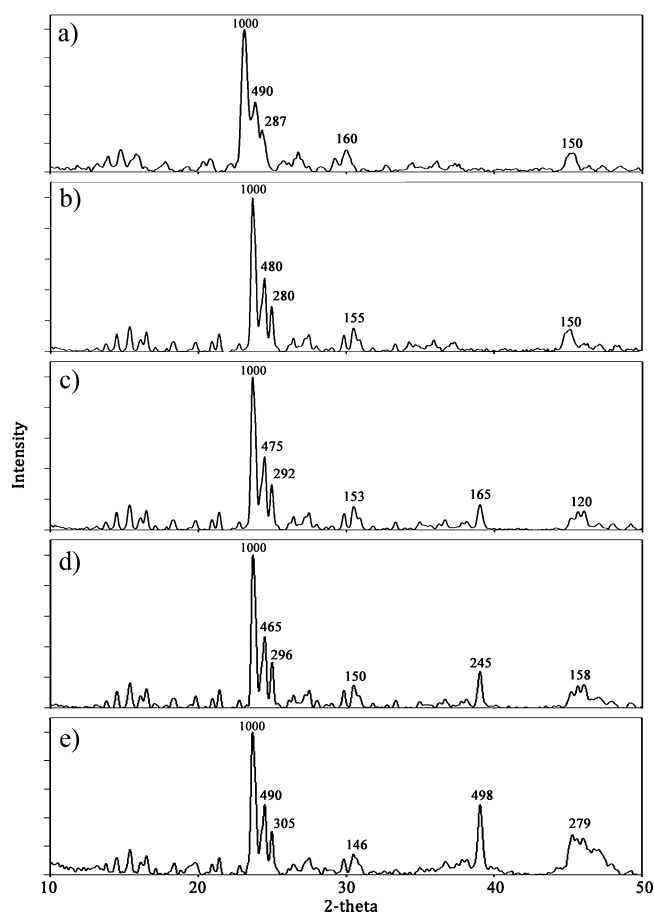


Fig. 1 – Schematic diagram of the experimental apparatus; pump: HPLC pump for feed mixture. V1, V2, V3, V5, V6 and V7: needle valves. V4: back pressure regulators. T1, T2, and T3: thermocouples. P1, P2 and P3: pressure gauges, and RV1 and RV2: safety pressure relief valves.



**Fig. 2 – XRD patterns for the different amount of ZSM-5 on support: (a) ZSM-5 (100), (b) ZSM-5 (85), (c) ZSM-5 (75), (d) ZSM-5 (50), and (e) ZSM-5 (25).**

increasing the temperature up to 120 °C which is related to weight of moisture on the zeolite.

### 3. Results and discussion

#### 3.1. Characterisation of the catalyst

##### 3.1.1. X-ray diffraction (XRD)

In this section, the characterisation of catalysts is presented in terms of XRD analysis, acidity strength and distribution, and nitrogen adsorption–desorption measurements.

Fig. 2 shows the XRD patterns of catalysts with different amounts of ZSM-5 zeolite on the support. All samples exhibit the typical pattern of calcined ZSM-5 zeolite. By increasing the amount of support, a new peak appears at 39 2 $\theta$  which confirms the presence of gamma alumina in the catalyst structure. All peaks are sharp within the range of 10–40 2 $\theta$  which indicates that the zeolite sample possesses a high degree of crystallinity, however by increasing the amount of alumina support, peak broadening occurs at 46 2 $\theta$ . Peak broadening in XRD patterns of zeolites can occur for a variety of reasons such as small crystal size (below 0.2  $\mu\text{m}$ ), disorder, absorption, and inconsistent sample packing density (ASTM, 2004).

The XRD patterns of zeolite modified by metals are not shown in this figure as similar patterns to pure ZSM-5 were observed in all cases. The similar patterns confirm that modification has not destroyed the crystalline structure of the zeolite. Moreover, an undetectable crystalline phase of metal ions implies that they are finely dispersed at the cation sites

of the zeolite. The average crystallite size of samples were calculated by applying Scherrer equation on (1000), (490) and (287) XRD reflections. The relative crystallinity of the sample was determined according to the ASTM D5758 measuring the intensity of the reflection peak at 24.3 2 $\theta$  and comparing the intensities with that of the reference sample. The results confirm that all the samples had a high degree of crystallinity. Crystal size and relative crystallinity are listed in Table 1.

##### 3.1.2. Acidity measurement

Temperature-programmed desorption (TPD) of tert-butylamine (t-BA) was carried out in the temperature range of 50–500 °C to compare the acid properties of the catalysts. Use of tert-butylamine for measuring the acid strength of microporous catalysts is recommended as its high vapour pressure and its molecular structure does not have diffusional limitation in the microporous zeolites (Aguayo et al., 1994). During the desorption of t-BA, three peaks were observed in the range of 150–300 °C, 300–400 °C and 400–500 °C which correspond to weak, medium and strong type acid sites, respectively. Bibby et al. (1992) stated that the intensity of the peak in the range of 150–400 °C corresponds to the total Brønsted acid site population calculated from the aluminium content of the zeolite, while the next peak at higher temperature (400–500 °C) was attributed to ammonia desorption from very strong Brønsted or Lewis sites. The results of TPD for ZSM-5 zeolite with no support, catalyst samples with different ZSM-5 zeolite to support ratios, alumina as support and metal doped zeolite are listed in Table 2.

The ZSM-5 zeolite contains mainly weak acid sites (77%) and very few strong acidic centres (4%), while the support ( $\gamma$ -alumina) contains more strong acid sites (15%). It is possible to change the acid distribution by changing the Si/Al ratio of catalysts by changing the zeolite to support ratio. For instance, by decreasing the amount of zeolite in the catalyst, the Si/Al is decreased and as a result weak acid sites are decreased, but strong acidic centres as well as total acidity is increased. Studies on the effect of Si/Al ratio on the acidity of ZSM-5 zeolite show that as Si/Al ratio decreases, the Brønsted/Lewis sites ratio (weak/strong acid sites ratio) is decreased, while total acidity as well as acidic site density is increased (Benito et al., 1996; Gayubo et al., 1996). It is well known that the presence of strong acid sites promotes the polymerisation of olefins and increases the rate of coke formation (Bibby et al., 1992; Xu et al., 1997). As observed from the TPD measurements in Table 2, modification of ZSM-5 zeolite by iron and calcium seems to have no noticeable effect on catalyst acidity. Machado et al. (2006) have studied production of hydrocarbons from ethanol over iron incorporated ZSM-5 zeolite. They observed that the total acidity of the samples with different amount of iron does not change significantly. Lersch and Bandermann (1991) impregnated the ZSM-5 zeolite with alkaline earth metals such as Ca, Mg and Ba. They observed that the peak corresponding to weak acidic sites in the TPD spectra is almost same for all the catalysts, but a new third peak at higher temperature in which represents strong Lewis acid sites appeared in the case of impregnation with Mg and Ca.

Modification of zeolite with Cs and phosphoric acid increased the weak acidic and decreased the strong acidic centres (Table 2). Haag (1994) reported that caesium can selectively poison the strongest acid sites of ZSM-5 zeolite first and demonstrated that modification of zeolite with Cs-ions leads to a dramatic decrease of catalyst activity. Lercher and Rumplmayr (1986) reported that modification of ZSM-5 zeolite

**Table 1 – Properties of various catalyst samples.**

Catalyst name	Zeolite/metal in the sample (wt.%)	BET surface area (m <sup>2</sup> /g)	Crystal size (nm)	Relative crystallinity (%)	Micropore volume (cm <sup>3</sup> /g)	Micropore area (m <sup>2</sup> /g)
ZSM-5 (100)	100	413	16	100	0.10	245
ZSM-5 (85)	85	386	16	98	0.18	240
ZSM-5 (75)	75	370	18	102	0.21	185
ZSM-5 (50)	50	328	19	103	0.30	150
ZSM-5 (25)	25	270	22	106	0.43	70
$\gamma$ -Alumina	–	218	28	100	0.50	14
Fe-ZSM-5	1.1	423	15	100	0.12	268
Ca-ZSM-5	1.4	395	14	101	0.11	236
Cs-ZSM-5	1.7	394	15	99	0.13	296
P-ZSM-5	1.2	322	15	101	0.10	212

**Table 2 – TPD results of various catalyst samples.**

Catalyst name	Acidity (mmol t-BA/g)/distribution			
	Weak (150–300 °C)	Medium (300–400 °C)	Strong (400–500 °C)	Total
ZSM-5 (100)	0.52 (77%)	0.13 (19%)	0.03 (4%)	0.68
ZSM-5 (85)	0.30 (65%)	0.12 (27%)	0.04 (8%)	0.46
ZSM-5 (75)	0.35 (68%)	0.12 (24%)	0.04 (8%)	0.51
ZSM-5 (50)	0.43 (67%)	0.15 (24%)	0.06 (9%)	0.64
ZSM-5 (25)	0.47 (60%)	0.22 (28%)	0.09 (11%)	0.78
$\gamma$ -Alumina	0.44 (58%)	0.21 (28%)	0.11 (15%)	0.76
Fe-ZSM-5	0.52 (76%)	0.13 (19%)	0.04 (5%)	0.69
Ca-ZSM-5	0.53 (78%)	0.11 (16%)	0.04 (6%)	0.68
Cs-ZSM-5	0.59 (84%)	0.10 (14%)	0.01 (1%)	0.70
P-ZSM-5	0.72 (85%)	0.11 (13%)	0.02 (3%)	0.85

with H<sub>3</sub>PO<sub>4</sub> could convert the strong Brønsted acid sites to weak Brønsted acid sites without changing the overall acidic properties of the sample.

### 3.1.3. Nitrogen adsorption–desorption isotherms

Nitrogen adsorption–desorption at 77 K was used to determine the BET surface area, pore volume and micropore area. Fig. 3a illustrates the nitrogen adsorption–desorption isotherms of samples with different amounts of zeolite on the support. All the isotherms are typical reversible Type IV adsorption isotherms as defined by IUPAC (Sing et al., 1985). The hysteresis loops are due to capillary condensation of nitrogen in mesopores. The hysteresis loop for pure ZSM-5 zeolite and samples with 85% or 75% ZSM-5 is very similar to the H4 type adsorption isotherm which is associated with narrow slit-like pores. In samples with lower amounts of zeolite (e.g. ZSM-5 (50%) or ZSM-5 (25%)) the loop is similar to H1 type, which is often associated with porous materials consisting of either agglomerates or compacts of approximately uniform spheres in a fairly regular array, and hence narrow distributions of pore size. The isotherms for zeolite modified by metals are shown in Fig. 3b. All the isotherms exhibit the general pattern of ZSM-5 (100) sample. Modification in all cases except Fe has decreased the liquid nitrogen uptake due to blockage of pore channels by metal ions. It is well known that during the wet impregnation of ZSM-5 zeolite, metallic compounds can penetrate into the pores of ZSM-5 and block them, thereby greatly reducing the surface area (Berndt et al., 1996; Qian and Yan, 2001).

Table 1 lists the physical properties of the parent ZSM-5 zeolite, samples with different zeolite to support ratio and zeolite ion exchanged by metals and phosphorous. In case of catalyst samples with different amount of zeolite on support, by increasing the amount of  $\gamma$ -alumina in the sample, both BET surface area and micropore area are decreased, while the average pore volume are increased.

## 3.2. Dehydration of methanol to light olefins

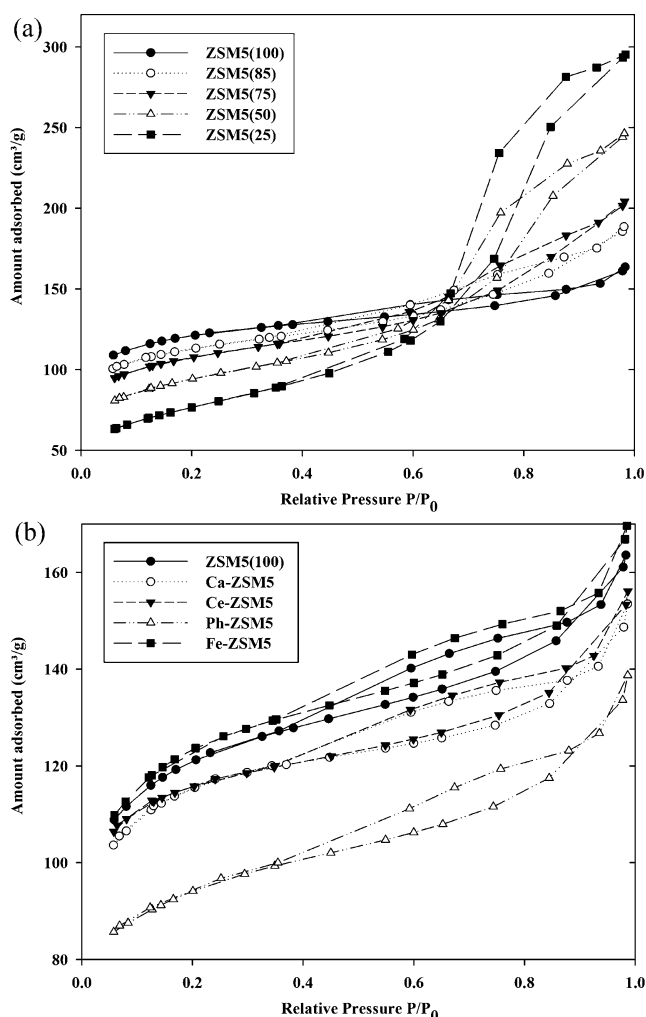
### 3.2.1. Product selectivity

The results are reported in terms of light olefins consist of ethylene (C<sub>2</sub><sup>+</sup>), propene (C<sub>3</sub><sup>+</sup>) and butene (C<sub>4</sub><sup>+</sup>), propane/propene ratio (C<sub>3</sub>/C<sub>3</sub><sup>+</sup>), light alkanes consisting of methane to butane (C<sub>1</sub>–C<sub>4</sub>), and heavier hydrocarbons (C<sub>5</sub><sup>+</sup>) including aromatic and aliphatic compounds. Due to a low amount of aromatics in this reaction (less than 5%), the aromatics were lumped as C<sub>5</sub><sup>+</sup>. The production of small amounts of aromatics in the same reaction has been reported in the literature, illustrating that aromatics are only a minor product of the methanol dehydration (Al-Jarallah et al., 1997; Kaarsholm et al., 2007; Stocker, 1999).

### 3.2.2. Effect of time on stream

The effect of time on stream (TOS) on the methanol conversion and olefins distribution over ZSM-5 (100) up to 21 h are shown in Fig. 4a. Over the duration of the experiment, the conversion of methanol decreased gradually from 96% to 78%. Similarly, the selectivity to propene and butene decreased from 38% to 32% and 13% to 8%, respectively, whilst the selectivity to ethene increased in the same time, from 23% to 32%. The C<sub>3</sub>/C<sub>3</sub><sup>+</sup> ratio was used in presenting the results as an indicator for hydride transfer reaction which facilitates the production of paraffins and aromatics. After 21 h, the C<sub>3</sub>/C<sub>3</sub><sup>+</sup> ratio decreased from 0.18 to 0.13 which implies the suppression of hydride transfer reaction during the reaction time on stream due to faster deactivation of strong acid sites (Liu et al., 2009).

Fig. 4b shows the distribution of paraffinic products (C<sub>1</sub>–C<sub>4</sub>) and lumped C<sub>5</sub><sup>+</sup> containing olefinic, paraffinic and aromatics compounds with five or more carbons. The selectivity to methane increased from 2% to 7%, simultaneously, C<sub>5</sub><sup>+</sup> increased from 6% to 12%. Ethane selectivity is almost constant and less than 1%. Propane decreased from 7% to 14%

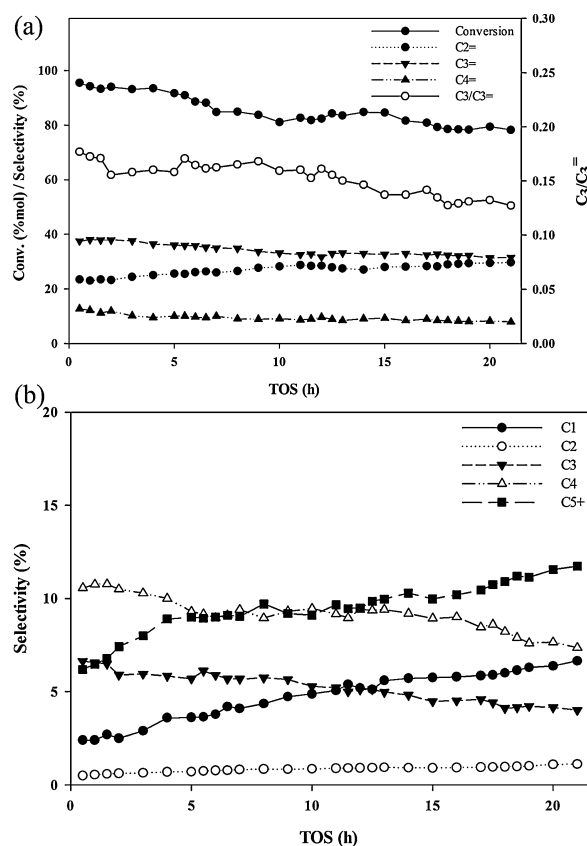


**Fig. 3 – (a) Nitrogen adsorption–desorption isotherms of samples with different amounts of zeolite and (b) nitrogen adsorption–desorption isotherms of modified zeolite.**

while butane increased slightly from 11% to 13% after 12 h and then decreased gradually.

The decrease in the propene to ethene ratio and increase in the selectivity to  $C_5^+$  products can be related to the deactivation of the acid sites via coke formation. Ivanova et al. (2009) explain such observations that coke formation limits the transformation of methanol to DME and favours the formation of higher olefins. The observed increase in the formation of methane is another result of coke formation. Chen et al. (1986) found that the yield of methane is related to the extent of coking. They conclude that the coke deposition on the acid sites of the catalyst enhances the secondary cracking reactions through non-ionic mechanism, led to increase in methane and the  $C_5^+$  fraction.

Deactivation of ZSM-5 zeolite in the conversion of methanol to hydrocarbons, first occurs on the outside surface of the catalyst and then in the pore structure. Firstly, polyalkylation and the formation of cyclic compounds occur on the acidic centres located on the outer surface of the catalyst and block the access to the inner channels leading to slower coke formation in the second stage inside the zeolite channels (de Lucas et al., 1997a; Guisnet and Magnoux, 1989). This effect was confirmed by the analysis of acid sites distribution of ZSM-5 zeolite before and after reaction. Table 3 shows the TPD results for both fresh and used catalyst after 4 h and 21 h time on stream, respectively. The results show



**Fig. 4 – Effect of time on stream on (a) methanol conversion and olefins distribution and (b) paraffins distribution over ZSM-5 (100) catalyst under typical reaction conditions: temperature: 400 °C, pressure: 1 bar, WHSV: 34 h<sup>-1</sup> methanol/water ratio: 1 w/w, TOS: 21 h.**

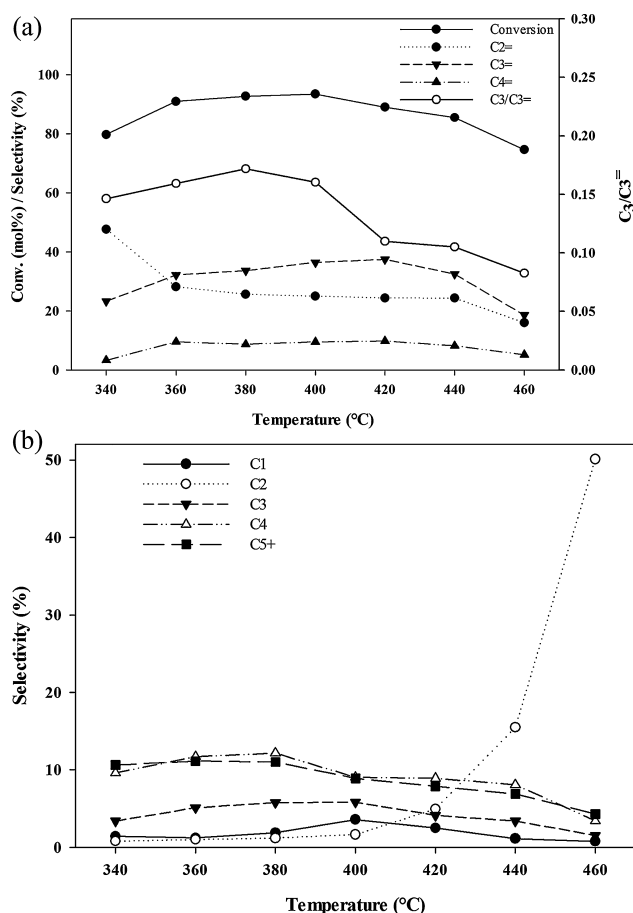
that during the first few hours of the reaction (e.g. 4 h), all acid sites become deactivated evenly and the catalyst still has a uniform acid site distribution, but after longer reaction, most of the medium acid sites become deactivated, which suggests this type of acid site is more involved in the formation of coke precursors. Due to the stability of the catalyst during the first 4 h, and no fluctuation in product selectivity, the TOS of 4 h was chosen for further analysis of reaction conditions effect on catalyst activity and selectivity.

### 3.2.3. Effect of temperature

The effect of temperature on the conversion of methanol to hydrocarbons over ZSM-5 (100) catalyst was investigated over the range 340–460 °C. Fig. 5a shows the methanol conversion and selectivity to olefins at the different temperatures. Methanol conversion increased from 80% to 94% by increasing the temperature from 340 °C to 400 °C. However, at higher temperatures, the conversion then decreased from 94% to 75%. This suggests faster deactivation of catalyst after 4 h at such temperatures. The selectivity to propene increased from 23% to 36% by increasing the temperature from 340 °C to 420 °C, however it decreased to 19% once the temperature was raised further to 460 °C. Similarly, the selectivity to butene jumped from 3% to 10% by increasing the temperature from 340 °C to 360 °C, and then remained almost constant at this value in the range of 340–420 °C, but when the temperature was raised to 460 °C, it decreased to 5%. The selectivity to ethene significantly decreased from 48% to 26% once the temperature had changed from 340 °C to 360 °C but it remained almost constant up until a temperature of 440 °C. When the

**Table 3 – TPD results of fresh and used catalyst (TOS = 4 and 21 h).**

Catalyst name	TOS (h)	Acidity (mmol t-BA/g)/distribution			
		Weak (150–300 °C)	Medium (300–400 °C)	Strong (400–500 °C)	Total
Fresh ZSM-5 (100)	0	0.52 (77%)	0.13 (19%)	0.03 (4%)	0.68
Used ZSM-5 (100)	4	0.45 (76%)	0.12 (20%)	0.02 (4%)	0.59
Used ZSM-5 (100)	21	0.25 (86%)	0.03 (10%)	0.01 (4%)	0.29



**Fig. 5 – Effect of temperature on (a) methanol conversion and olefins distribution and (b) paraffins and C<sub>5</sub><sup>+</sup> distribution over ZSM-5 (100). Reaction conditions; pressure: 1 bar, WHSV: 34 h<sup>−1</sup>, methanol/water ratio: 1 w/w, TOS: 4 h.**

temperature was further increased to 460 °C it decreased to 16%. Dehertog and Froment (1991) observed that the yield of ethene decreases with increasing temperature, in contrast to the yields of propene and butene. They also observed strong temperature dependency of the olefin yield and distribution at high temperatures. They indicate that whereas the ethene is most abundant at low temperature, butene and especially propene become more important at higher temperature. It is believed that high temperature favours alkene formation at the expense of the aromatisation reactions and as a result, the yield of ethene decreases with increasing temperature, in contrast to the yields of propene and butene (Chang et al., 1984; Dehertog and Froment, 1991). However, a greater increase in the temperature leads to decomposition of methanol and produces other basic components, such as methane, H<sub>2</sub>, and CO (Al-Jarallah et al., 1997; Chen and Reagan, 1979). Increasing CO<sub>x</sub> (not shown) from 0.1% at 420 °C to 0.4% at 460 °C could be evidence for this claim. The C<sub>3</sub>/C<sub>3</sub><sup>+</sup> ratio increased from 0.15 to 0.17 by increasing the temperature from 340 to 380 °C

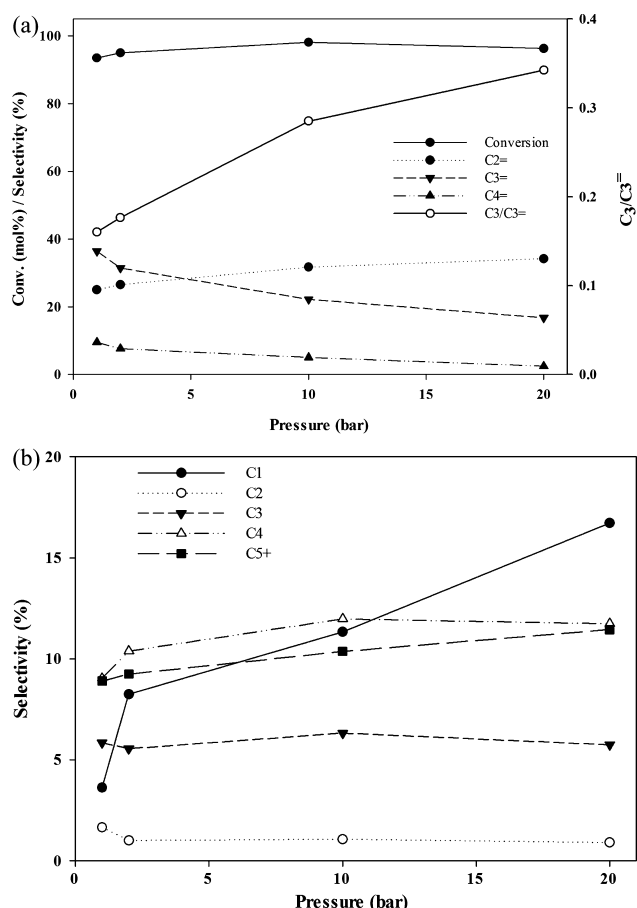
indicates increasing temperature in this region promotes the hydride transfer reaction to produce more paraffins or aromatics as undesired products, however by further increasing the temperature to 420 °C, this ratio dropped significantly to 0.10.

Fig. 5b shows the selectivity to light alkanes and C<sub>5</sub><sup>+</sup> compounds. By increasing the temperature from 340 °C to 400 °C, the methane content in the gas product increased slightly from 1% to 4%. Simultaneously, increasing temperature up to 380 °C, increased ethane and propane production by providing required activation energy at elevated temperatures, however increasing temperature more than 380 °C, led to a decrease in butane and propane content. The rapid increase in ethane with temperature is due to increasing secondary reaction rates favoured at high temperatures. Anthony and Singh (1980) studied the kinetics of methanol conversion to olefins over ZSM-5 zeolite. They concluded that propylene, methane, and propane are produced by primary reactions and do not participate in any secondary reactions, whereas dimethylether, carbon monoxide, and ethane are produced through secondary reactions.

Lastly, regarding the selectivity towards C<sub>5</sub><sup>+</sup>, only a negligible change was observed over 340–380 °C, with the composition with respect to this product around 11% over that temperature range. Once the temperature was increased from 380 °C to 460 °C, the selectivity to C<sub>5</sub><sup>+</sup> molecules decreased to 4%. At elevated reaction temperatures cracking of heavier hydrocarbons are induced over HZSM-5 (Bibby et al., 1992, 1986; Mores et al., 2011). Hence, a low number of acidic centres and enough high temperature provide appropriate conditions for obtaining optimum olefin selectivity whilst hindering the formation of heavy hydrocarbons. Based on these results, 400 °C was determined to be the optimum temperature for propene production.

### 3.2.4. Effect of pressure

Since the optimum reaction temperature for the highest conversion and selectivity of propene was found at 400 °C, the effect of pressure was studied from 1 to 20 bar at this temperature. As shown in Fig. 6a and b, by increasing the pressure from 1 bar to 10 bar conversion of methanol was increased from 93% to 98% and declined slightly to 96% at 20 bar after 4 h TOS. The selectivity to propene decreased significantly from 36% to half of this value, whereas the selectivity to ethene increased from 24% to 37%. Also, butene selectivity decreased from 10% to 3%. Increasing the selectivity to ethene while the selectivity to propene decreased in higher pressure can be concluded as a faster catalyst coking over the time due to increasing influence of the hydrogen transfer reaction (Gubisch and Bandermann, 1989). However, the C<sub>3</sub>/C<sub>3</sub><sup>+</sup> ratio doubled from 0.16 to 0.34 in this range of pressure which confirms the strong influence of pressure to enhance the hydride transfer reaction. At higher pressure a sharp increase in methane formation is indicative of catalyst deactivation. In this case, the reaction between coke and methanol is carried out through methylation and



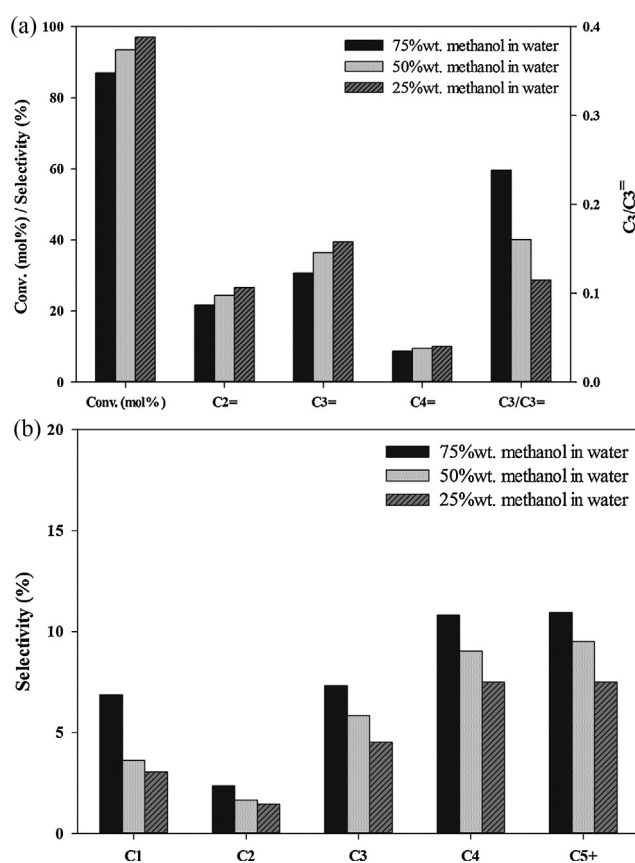
**Fig. 6 – Effect of pressure on (a) methanol conversion and olefins distribution and (b) paraffins and C<sub>5</sub><sup>+</sup> distribution over ZSM-5 (100). Reaction conditions; temperature: 400 °C, WHSV: 34 h<sup>-1</sup>, methanol/water ratio: 1 w/w, TOS: 4 h.**

dehydrogenation (Schulz, 2010). An increase in C<sub>5</sub><sup>+</sup> compounds is another explanation for faster deactivation of catalyst at higher pressures. A similar result was observed by Chang et al. (1979) on the ZSM-5 at 370 °C in the range of 0.04–50 bar. To provide further evidence to confirm this claim, the TGA result of used catalyst is reported in Table 4. As it can be seen, higher pressure favours faster coking.

As highest selectivity of propene was obtained at 1 bar, this pressure was chosen as the optimum pressure. The choice of a low operating pressure also offers advantages for industrial operation in terms of lower cost of equipment and pumping, compared with high pressure processes.

### 3.2.5. Effect of feed composition

The effects of different compositions of water/methanol mixtures upon conversion and product distribution were investigated by changing the methanol content in the feed from 25 to 75 wt.%. The results are shown in Fig. 7a and b. By decreasing the amount of methanol in feed the conversion was increased from 87% to 97%. The lower conversion at



**Fig. 7 – Effect of feed composition on (a) methanol conversion and olefins distribution and (b) paraffins and C<sub>5</sub><sup>+</sup> distribution over ZSM-5 (100). Reaction conditions; temperature: 400 °C, pressure: 1 bar, WHSV: 34 h<sup>-1</sup>, TOS: 4 h.**

higher concentration of methanol in the feed could be due to the faster coking of zeolite after 4 h and/or dealumination by steam (Gayubo et al., 2004). This is confirmed by the TGA result of used catalyst which is shown in Table 5. The amount of coke on the used catalysts after 4 h TOS is higher when the feed contains more methanol. Decreasing the concentration of methanol in the feed from 75% to 25% increased the selectivity to light olefins, and at the same time production of light alkanes and heavy hydrocarbons diminished. Ethene and propene increased from 22 and 31% to 27 and 40%, respectively. Froment et al. (1992) have discussed that water molecules seem to weaken the acid sites responsible for the hydrogen-transfer reactions and as a result, decreasing the conversion of olefins to paraffins. A noticeable increase in C<sub>3</sub>/C<sub>3=</sub> ratio and methane production at 75 wt.% methanol in water, implies that faster coking occurs with more concentrated feed at 4 h TOS. As discussed by Schulz (2010), one of the issues in the dehydration of methanol to olefins over HZSM-5 zeolite in fixed bed reactors is that undesirable reactions proceed in the front- and tail-zones of the catalytic bed (e.g. formation of paraffins and aromatics from olefins in the front zone and formation of further coke and methane

**Table 4 – TGA result of used ZSM-5 (100) catalyst at different pressures.**

Pressure	Coke (wt.%)
1	3.4
2	3.8
10	4.5
20	6.8

**Table 5 – TGA result of catalyst after reaction with different feed composition.**

Methanol in feed (wt.%)	Coke (wt.%)
75	4.4
50	3.4
25	2.1

**Table 6** – TPD result of catalyst after reaction with different feed composition.

Methanol in feed (wt.%)	Acidity (mmol t-BA/g)/distribution			
	Weak (150–300 °C)	Medium (300–400 °C)	Strong (400–500 °C)	Total
25	0.47	0.13	0.02	0.62
50	0.45	0.12	0.02	0.59
75	0.35	0.05	0.01	0.41

by reaction of methanol with coke in the tail-zone) which are more pronounced at higher feed concentrations.

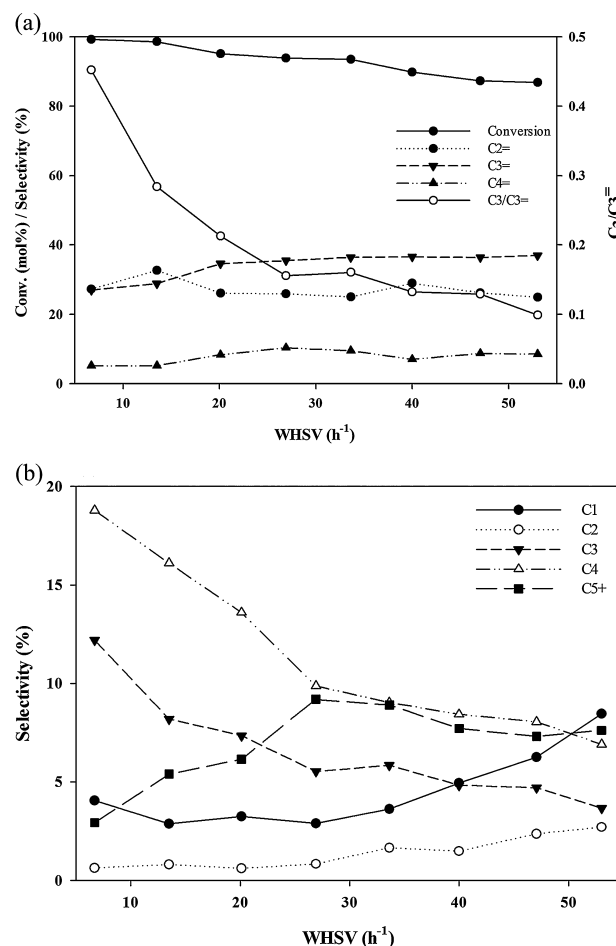
Gayubo et al. (2004) investigated the role of water on the acidity deterioration and coking of ZSM-5 zeolite in MTO process. They found that at 400 °C there is less coking (65%) on the ZSM-5 when 50 wt.% methanol in water was used in comparison to pure methanol whereas no acidity deterioration was observed even after reaction regeneration cycles. They also report severe dealumination of zeolite at higher temperature (500 °C) by the water produced during the reaction. The loss of strong acid sites is more pronounced with pure methanol than methanol diluted with water.

To better understand the effect of adding water to the feed on the weakening of the medium or strong acid centres of the zeolite, the TPD results of catalysts after reaction with different feed composition are summarised in Table 6. In a very diluted feed (25 wt.%), the number of medium and strong sites were not changed significantly after reaction but the number of weak acidic sites were decreased slightly, while using feed with a higher amount of methanol (75 wt.%) led to a noticeable decrease in all acid sites.

The addition of water to the reaction system is necessary to remove the reaction heat and to enhance light olefin selectivity and for this purpose, diluted methanol (55–65 wt.% water) as feed is recommended (Liu et al., 2000). However, the problem of irreversible deactivation arises as the reaction temperature is increased, which is due to dealumination of the HZSM-5 zeolite at elevated temperatures (Aguayo et al., 2002; de Lucas et al., 1997b). To overcome this problem, use of an inert gas was proposed by Schulz and Bandermann (1994). They reported that high water concentrations in the ethanol feed has the same effect on product distribution as dilution by inert gas. In both cases lower methanol partial pressures lead to higher yields of light olefins in the product stream.

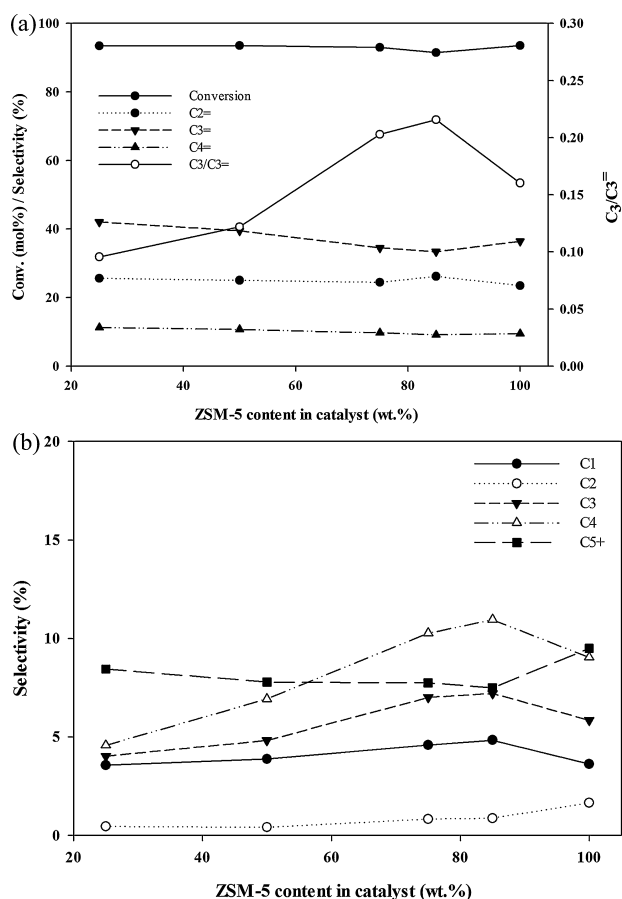
### 3.2.6. Effect of WHSV

The effect of varying the Weight Hourly Space Velocity (WHSV) from 7 h<sup>-1</sup> to 53 h<sup>-1</sup> on product distribution and conversion was investigated. To make sure that there is no internal diffusion resistance, samples with four different pellet sizes (e.g. 5, 3, 1 and 0.5) mm were loaded in the reactor under same reaction conditions. No significant change in the methanol conversion was observed. Therefore, under the test conditions used, the internal mass transfer resistance was negligible. As shown in Fig. 8a, methanol conversion was decreased from 99% to 86% by increasing the WHSV from 7 h<sup>-1</sup> to 53 h<sup>-1</sup>. The selectivity to propene increased from 28% to 36% by increasing the WHSV from 7 h<sup>-1</sup> to 53 h<sup>-1</sup>. The selectivity to ethene decreased slightly from 27% to 25% in this range. The selectivity to butene increased from 6% to 11% by increasing the WHSV from 7 h<sup>-1</sup> to 27 h<sup>-1</sup>. This figure then decreased slightly to 10%. The remarkable decline of C<sub>3</sub>/C<sub>3</sub><sup>=</sup> ratio from 0.45 to 0.1 suggests that olefins are the dominant products at higher WHSV (corresponding to lower contact time). As shown in Fig. 8b, by increasing the WHSV from 7 h<sup>-1</sup> to 53 h<sup>-1</sup>, methane and



**Fig. 8** – Effect of WHSV on (a) methanol conversion olefin distribution and (b) paraffins and C<sub>5</sub><sup>+</sup> distribution over ZSM-5 (100). Reaction conditions; temperature: 400 °C, pressure: 1 bar, methanol/water ratio: 1 w/w, TOS: 4 h.

ethane increased from 4% to 8% and 0.6% to 3%, respectively. In contrast, propane and butane decreased from 12% to 4% and 19% to 7%, respectively. Such an observation suggests that increasing WHSV only increases the formation of light paraffins (e.g. C<sub>1</sub> and C<sub>2</sub>) while heavier paraffins undergo different reaction pathways. With respect to the C<sub>5</sub><sup>+</sup> product distribution, the selectivity increased from 3% to 9% by increasing the WHSV from 7 h<sup>-1</sup> to 27 h<sup>-1</sup>. By further increasing WHSV up to 53 h<sup>-1</sup>, the selectivity decreased slightly to 8%. At low WHSV (high contact time), formation of saturated paraffins are more favoured while by increasing WHSV, light olefins are more favoured. In other words, at high WHSV (low residence time), there is not enough time for ethene, propene or other low molecular olefin compounds to form paraffins and aromatics in a consecutive reaction and as a result the reaction sequence is hence shortened at the intermediate species resulting in product mixtures containing more proportions of olefins. This observation confirms the proposed hydrocarbon pool mechanism for dehydration of methanol to hydrocarbons



**Fig. 9 – Effect of ZSM-5 content in catalyst on (a) methanol conversion and olefins distribution and (b) paraffins and  $C_5^+$  distribution.** Reaction conditions; temperature: 400 °C, WHSV: 34 h<sup>-1</sup>, pressure: 1 bar, methanol/water ratio: 1 w/w, TOS: 4 h.

(Scheme 1). This is in close agreement with result of Chang and Silvestri (1977) and Al-Jarallah et al. (1997). It is shown that increasing WHSV is led to formation of coke due to growing influence of non-shape selective hydrogen transfer reactions. Based on these results, 34 h<sup>-1</sup> was therefore chosen, as the point at which optimum propene selectivity was obtained.

### 3.3. Effect of catalyst to support ratio

Fig. 9a and b respectively shows the methanol conversion and product selectivity over catalyst with different amounts of ZSM-5 to  $\gamma$ -alumina support ratio. It was explained in Section 2.2, ZSM-5 (100) was used as reference in powder form while other samples were prepared as pellets. It can be seen that the conversion was not influenced significantly by this ratio, however by increasing the amount of zeolite in the catalyst from 25% to 85%, selectivity to propene decreased from 42% to 33%. Increasing the  $C_3/C_3^=$  ratio from 0.09 to 0.21 suggests that the higher amount of zeolite in the catalyst matrix can promote the hydride transfer reaction to some extent. In other words, although selectivity to saturated paraffins increased to due to higher amount of zeolite in catalyst, selectivity to heavy hydrocarbons ( $C_5^+$ ) decreased. Since  $\gamma$ -alumina has higher amount of strong and medium acid sites (Table 2) its addition as a binder can be used to tune the acidity of the catalyst to produce one compound more selectively than the others. However, use of zeolite on alumina led to a decrease in micropore area and BET surface area, compared to

the pure ZSM-5 (Table 1). It was shown that using alumina as a binder with ZSM-5 zeolite can improve the production of DME from methanol (Kim et al., 2006). DME is the most important medium to produce light olefins through three steps: (a) the dehydration of methanol to DME, (b) the dehydration of DME to olefins, and (c) the transformation of olefins to aromatics and alkanes. It should be noted that the initial dehydration step is rapid and reversible with close approach to equilibrium (Chang et al., 1979; Jiang et al., 2004; Liu et al., 2000). Though  $Al_2O_3$  has high activity for production of DME, it tends to adsorb water on its surface and thereby loses its activity in the presence of water because of its hydrophilic nature. In this case, water blocks the active sites for methanol consumption through competitive adsorption with methanol on the catalyst surface (Jun et al., 2003). Kim et al. (2006) investigated the effect of using  $\gamma$ -alumina as a binder with ZSM-5 zeolite on the production of DME. They reported that zeolite modified by sodium and containing 70 wt.% alumina has a high stability against coke formation and water for 15 days at 270 °C, with ca. 80% of DME yield. Although, ZSM-5 with the medium pore size showed a superior selectivity towards propene, at the same time boehmite gave a high strength and proper shape to the catalyst. Comparing the result of the catalyst with no binder (ZSM-5 (100)) and catalyst with 25% zeolite on alumina (ZSM-5 (25)), it can be concluded that the catalyst with binder can improve the selectivity to light olefins (e.g. ethene or propene) while less by-products (e.g. paraffins or heavy hydrocarbons) were produced.

### 3.4. Effect of modified ZSM-5 zeolite

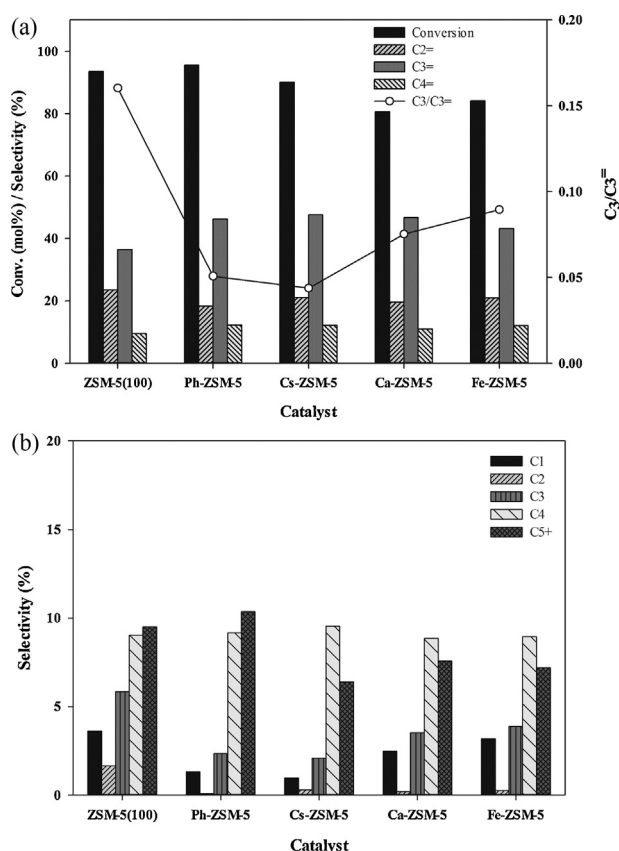
The ZSM-5 (100) zeolite was ion exchanged using phosphorous, caesium, calcium and iron. Fig. 10a and b illustrates the effect of modification on product distribution and conversion. Modification of zeolite with phosphoric acid (P-ZSM-5) improved the propene selectivity from 36% to 45%, whilst the selectivity to ethene was decreased slightly to from 24% to 18% compared to the parent zeolite. The conversion of 96% was the highest amongst all the catalysts implying high activity and prolonged catalyst lifetime. However, the highest selectivity to  $C_5^+$  molecules of 11% was also obtained. The addition of phosphoric acid therefore added to the total acidity of the catalyst by increasing the number of weak acid sites possibly on the outer surface of the zeolite and increased it from 0.52 to 0.72 mmol t-BA/g (Table 2). A decrease in the  $C_3/C_3^=$  ratio from 0.16 to 0.05 from one side and decrease in selectivity to paraffins from other sides imply on suppressed hydride transfer reaction to form more saturated hydrocarbons, however a slight increase on  $C_5^+$  from 9 to 10.5% is still observed.

Vu et al. (2010) treated ZSM-5 zeolite with  $H_3PO_4$  solutions of various concentrations. They observed that the selectivity to olefins was significantly improved. They reported that higher phosphorus content in P-HZSM-5 significantly decreased the selectivity to ethene and aromatics due to lower acidity of the H-ZSM-5's strong acid sites caused by dealumination. Dehertog and Froment (1991) modified zeolite by trimethylphosphite to make P-HZSM-5. They reported that this modification resulted in a significant decrease in activity but the yield of light olefins increased.

The conversion of 90% was obtained for the zeolite modified by caesium (Cs-ZSM-5). Propene selectivity of 48% was highest among the all samples. The selectivity to ethene was 21% and that of the butene selectivity was 12%. Similar to the P-ZSM-5 catalyst, selectivity to paraffins decreased after

**Table 7 – TGA results of different catalyst samples under typical reaction conditions (temperature: 400 °C, WHSV: 34 h<sup>-1</sup>, pressure: 1 bar, methanol/water ratio: 1 w/w, TOS: 4 h).**

Catalyst name	ZSM-5 (100)	ZSM-5 (85)	ZSM-5 (75)	ZSM-5 (50)	ZSM-5 (25)	P-ZSM-5	Cs-ZSM-5	Ca-ZSM-5	Fe-ZSM-5
Coke (wt.%)	3.4	2.2	2.5	2.8	2.9	4.1	2.1	2.2	3.2

**Fig. 10 – Effect of modification of ZSM-5 on (a) methanol conversion and olefins distribution and (b) paraffins and C<sub>5</sub><sup>+</sup> distribution. Reaction conditions; temperature: 400 °C, WHSV: 34 h<sup>-1</sup>, pressure: 1 bar, methanol/water ratio: 1 w/w, TOS: 4 h.**

modification Cs. In this case, selectivity to C<sub>5</sub><sup>+</sup> dropped to 6%. Caesium is an alkali metal and therefore it can reduce the acid sites zeolite after ion-exchanging. It is very important to use proper amount of alkali metals during the modification of zeolite as using high concentration of caesium cause the deactivation of medium and strong acid sites. From Table 2 it can be seen that the addition of caesium increased the total acidity of the catalyst, although the number of medium and strong sites is diminished.

The lowest conversion of 81% amongst all the catalysts was obtained on the catalyst ion exchanged by calcium (Ca-ZSM-5). After modification, the selectivity to ethene was decreased from 24% to 20% but propene selectivity increased from 37% to 47%. The C<sub>3</sub>/C<sub>3</sub><sup>+</sup> ratio was reduced from 0.16 to 0.07. Similarly, the selectivity to C<sub>5</sub><sup>+</sup> slightly decreased from 10% to 8%. As mentioned before, the weak acid sites are responsible for the production of light olefins. Addition of an alkali metals such as calcium reduces the acidity of the catalyst by forming an acid-base centre (Blaszkowski and van Santen, 1996) leading to better selectivity to light olefins. The total acidity of Ca-ZSM-5 sample remains constant to 0.68 mmol t-BA/g after modification but more strong acid sites are generated.

The iron modified catalyst (Fe-ZSM-5) gave methanol conversion of 84%. The propene selectivity increased to 43%, whilst the ethene selectivity was decreased slightly to 21%. The selectivity to butene was increased to 12%. The C<sub>3</sub>/C<sub>3</sub><sup>+</sup> ratio decreased from 0.16 to 0.09 and selectivity to C<sub>5</sub><sup>+</sup> components was decreased to 7%. ZSM-5 zeolite containing Fe can inhibit the formation of aromatics and suppress the olefins hydrogenation by reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub>, resulting in a higher olefins/alkanes ratio (Inaba et al., 2007; Lücke et al., 1999).

### 3.5. Coke measurement by thermogravimetric analysis (TGA)

The amount of coke deposited on the catalysts was measured by TGA. Table 7 shows the TGA result of used catalyst under typical reaction conditions. The mass loss of the catalyst samples under air flow at temperature 120–700 °C was taken as being due to coke deposits upon the catalyst samples. In case of zeolite bound with different amount of  $\gamma$ -alumina, a higher amount of alumina led to an increase in coke weight from 2.2 to 2.9 wt.%, possibly due to an increase in strong acid sites (Table 2).

ZSM-5 zeolite samples with relatively high aluminium content (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio <70) display a remarkably high activity in the steps of olefin aromatisation (Luk'yanov, 1992; Mores et al., 2011). The trend of changing coke amount on catalyst samples is very similar to changing in C<sub>5</sub><sup>+</sup> components including aromatics. Modification by Ca and Cs decreased the amount of coke by reducing the strong and medium acid centres, while zeolite treatment by P led to faster coking due to higher amount of total acidity. The amount of coke on Fe-ZSM-5 zeolite samples is very similar to the parent ZSM-5. It was expected as both samples exhibit similar acid site distribution.

## 4. Conclusion

The effect of reaction temperature, pressure, space velocity and feed composition on the conversion of methanol to light olefins was studied. Temperature as high as 400 °C is essential to produce light olefins more selectively, although elevated temperatures led to faster deactivation, more selectivity to alkanes and lower selectivity to light olefins. Pressure higher than 1 bar led to production of heavier hydrocarbons (C<sub>5</sub><sup>+</sup>) and lower selectivity to light olefins. It was shown that high water concentrations in the feed led to higher yields of light olefins. High space velocity is required to produce more light olefins, although methanol conversion is decreased, a WHSV higher than 34 h<sup>-1</sup> however led to faster deactivation with no improvement in selectivity to propene or other light olefins. Use of  $\gamma$ -alumina as support improved the catalyst selectivity to propene and light olefins. Zeolite catalyst with 25 wt.% ZSM-5 in the catalyst sample led to highest selectivity to propene and light olefins, but faster deactivation was observed on this catalyst. ZSM-5 zeolite was modified with P, Cs, Ca and Fe. Modification in all cases increased the shape-selectivity to propene. ZSM-5 zeolite ion exchanged by Cs led to highest

selectivity to propene by changing the acid site distribution. The lowest selectivity to  $C_5^+$  compounds and least amount of coking was observed on this catalyst.

## Acknowledgments

Financial support for this project by the Dr. R.M. Behbahani, Centre for Oil and Gas Research in Ahwaz Petroleum University of Technology, Iran is gratefully acknowledged. The TGA and XRF used in this research were respectively obtained through Birmingham Science City: Hydrogen and Science City: Innovative Uses for Advanced Materials in the Modern World with support from Advantage West Midlands (AWM) and part funded by the European Regional Development Fund (ERDF).

## References

- Aguayo, A.T., Gayubo, A.G., Ereña, J., Olazar, M., Arandes, J.M., Bilbao, J., 1994. Isotherms of chemical adsorption of bases on solid catalysts for acidity measurement. *J. Chem. Technol. Biotechnol.* 60, 141–146.
- Aguayo, A.T., Gayubo, A.G., Tarrío, A.M., Atutxa, A., Bilbao, J., 2002. Study of operating variables in the transformation of aqueous ethanol into hydrocarbons on an HZSM-5 zeolite. *J. Chem. Technol. Biotechnol.* 77, 211–216.
- Al-Jarallah, A.M., El-Nafaty, U.A., Abdillahi, M.M., 1997. Effects of metal impregnation on the activity, selectivity and deactivation of a high silica MFI zeolite when converting methanol to light alkenes. *Appl. Catal. A: Gen.* 154, 117–127.
- Anthony, R.G., Singh, B.B., 1980. Kinetic analysis of complex-reaction systems – methanol conversion to low-molecular weight olefins. *Chem. Eng. Commun.* 6, 215–224.
- ASTM, 2004. Test Methods for Rating Motor, Diesel, and Aviation Fuels; Catalysts; Manufactured Carbon and Graphite Products, D5758: Test Method for Determination of Relative Crystallinity of Zeolite ZSM-5 by X-Ray Diffraction. ASTM, PA 19428-2959, United States, pp. 4.
- Benito, P.L., Gayubo, A.G., Aguayo, A.T., Olazar, M., Bilbao, J., 1996. Effect of Si/Al ratio and of acidity of H-ZSM5 zeolites on the primary products of methanol to gasoline conversion. *J. Chem. Technol. Biotechnol.* 66, 183–191.
- Berndt, H., Lietz, G., Lücke, B., Völter, J., 1996. Zinc promoted H-ZSM-5 catalysts for conversion of propane to aromatics. I. Acidity and activity. *Appl. Catal. A: Gen.* 146, 351–363.
- Bibby, D.M., Howe, R.F., McLellan, G.D., 1992. Coke formation in high-silica zeolites. *Appl. Catal. A: Gen.* 93, 1–34.
- Bibby, D.M., Milestone, N.B., Patterson, J.E., Aldridge, L.P., 1986. Coke formation in zeolite ZSM-5. *J. Catal.* 97, 493–502.
- Björger, M., Svelle, S., Joensen, F., Nerlov, J., Kolboe, S., Bonino, F., Palumbo, L., Bordiga, S., Olsbye, U., 2007. Conversion of methanol to hydrocarbons over zeolite H-ZSM-5: on the origin of the olefinic species. *J. Catal.* 249, 195–207.
- Blaszkowski, S.R., van Santen, R.A., 1996. The mechanism of dimethyl ether formation from methanol catalyzed by zeolitic protons. *J. Am. Chem. Soc.* 118, 5152–5153.
- Chang, C.D., Chu, C.T.W., Socha, R.F., 1984. Methanol conversion to olefins over ZSM-5: I. Effect of temperature and zeolite  $SiO_2Al_2O_3$ . *J. Catal.* 86, 289–296.
- Chang, C.D., Lang, W.H., Smith, R.L., 1979. The conversion of methanol and other O-compounds to hydrocarbons over zeolite catalysts: II. Pressure effects. *J. Catal.* 56, 169–173.
- Chang, C.D., Silvestri, A.J., 1977. The conversion of methanol and other O-compounds to hydrocarbons over zeolite catalysts. *J. Catal.* 47, 249–259.
- Chen, G., Liang, J., Wang, Q., Cai, G., Zhao, S., Ying, M., 1986. *New Developments in Zeolite Science and Technology*. Elsevier.
- Chen, N.Y., Reagan, W.J., 1979. Evidence of autocatalysis in methanol to hydrocarbon reactions over zeolite catalysts. *J. Catal.* 59, 123–129.
- de Lucas, A., Canizares, P., Durán, A., Carrero, A., 1997a. Coke formation, location, nature and regeneration on dealuminated HZSM-5 type zeolites. *Appl. Catal. A: Gen.* 156, 299–317.
- de Lucas, A., Canizares, P., Durán, A., Carrero, A., 1997b. Dealumination of HZSM-5 zeolites: effect of steaming on acidity and aromatization activity. *Appl. Catal. A: Gen.* 154, 221–240.
- Dehertog, W.J.H., Froment, G.F., 1991. Production of light alkenes from methanol on ZSM-5 catalysts. *Appl. Catal.* 71, 153–165.
- Dubois, D.R., Obrzut, D.L., Liu, J., Thundimadathil, J., Adekanattu, P.M., Guin, J.A., Punnoose, A., Seehra, M.S., 2003. Conversion of methanol to olefins over cobalt-, manganese- and nickel-incorporated SAPO-34 molecular sieves. *Fuel Process. Technol.* 83, 203–218.
- Froment, G.F., Dehertog, W.J.H., Marchi, A.J., 1992. Zeolite catalysis in the conversion of methanol into olefins. In: Spivey, J.J. (Ed.), *Catalysis*, vol. 9. The Royal Society of Chemistry, pp. 1–64.
- Gayubo, A.G., Aguayo, A.T., Atutxa, A., Prieto, R., Bilbao, J., 2004. Role of reaction-medium water on the acidity deterioration of a HZSM-5 zeolite. *Ind. Eng. Chem. Res.* 43, 5042–5048.
- Gayubo, A.G., Benito, P.L., Aguayo, A.T., Olazar, M., Bilbao, J., 1996. Relationship between surface acidity and activity of catalysts in the transformation of methanol into hydrocarbons. *J. Chem. Technol. Biotechnol.* 65, 186–192.
- Goto, D., Harada, Y., Furumoto, Y., Takahashi, A., Fujitani, T., Oumi, Y., Sadakane, M., Sano, T., 2010. Conversion of ethanol to propylene over HZSM-5 type zeolites containing alkaline earth metals. *Appl. Catal. A: Gen.* 383, 89–95.
- Gubisch, D., Bandermaun, F., 1989. Conversion of methanol to light olefins over zeolite H-T. *Chem. Eng. Technol.* 12, 155–161.
- Guisnet, M., Magnoux, P., 1989. Coking and deactivation of zeolites: influence of the pore structure. *Appl. Catal.* 54, 1–27.
- Haag, W.O., 1994. Catalysis by zeolites – science and technology. In: Weitkamp, J., Hölderich, H.G.K.H.P.W. (Eds.), *Studies in Surface Science and Catalysis*. Elsevier, pp. 1375–1394.
- Inaba, M., Murata, K., Saito, M., Takahara, I., 2007. Production of olefins from ethanol by Fe-supported zeolite catalysts. *Green Chem.* 9, 638–646.
- Inui, T., Kang, M., 1997. Reliable procedure for the synthesis of Ni-SAPO-34 as a highly selective catalyst for methanol to ethylene conversion. *Appl. Catal. A: Gen.* 164, 211–223.
- Ivanova, S., Lebrun, C., Vanhaecke, E., Pham-Huu, C., Louis, B., 2009. Influence of the zeolite synthesis route on its catalytic properties in the methanol to olefin reaction. *J. Catal.* 265, 1–7.
- Jiang, S., Hwang, J., Jin, T., Cai, T., Cho, W., Baek, Y., Park, S., 2004. Dehydration of methanol to dimethyl ether over ZSM-5 zeolite. *Bull. Korean Chem. Soc.* 25, 185–189.
- Jun, K.W., Lee, H.S., Roh, H.S., Park, S.E., 2003. Highly water-enhanced H-ZSM-5 catalysts for dehydration of methanol to dimethyl ether. *Bull. Korean Chem. Soc.* 24, 106–108.
- Kaarsholm, M., Joensen, F., Nerlov, J., Cenni, R., Chaouki, J., Patience, G.S., 2007. Phosphorous modified ZSM-5: deactivation and product distribution for MTO. *Chem. Eng. Sci.* 62, 5527–5532.
- Keil, F.J., 1999. Methanol-to-hydrocarbons: process technology. *Microporous Mesoporous Mater.* 29, 49–66.
- Kim, S.D., Baek, S.C., Lee, Y.J., Jun, K.W., Kim, M.J., Yoo, I.S., 2006. Effect of gamma-alumina content on catalytic performance of modified ZSM-5 for dehydration of crude methanol to dimethyl ether. *Appl. Catal. A: Gen.* 309, 139–143.
- Lercher, J.A., Rumpelmayr, G., 1986. Controlled decrease of acid strength by orthophosphoric acid on ZSM5. *Appl. Catal.* 25, 215–222.
- Lersch, P., Bandermaun, F., 1991. Conversion of chloromethane over metal-exchanged ZSM-5 to higher hydrocarbons. *Appl. Catal.* 75, 133–152.
- Li, J., Wei, Y., Liu, G., Qi, Y., Tian, P., Li, B., He, Y., Liu, Z., 2011. Comparative study of MTO conversion over SAPO-34, H-ZSM-5 and H-ZSM-22: correlating catalytic performance and reaction mechanism to zeolite topology. *Catal. Today* 171, 221–228.
- Liu, J., Zhang, C.X., Shen, Z.H., Hua, W.M., Tang, Y., Shen, W., Yue, Y.H., Xu, H.L., 2009. Methanol to propylene: effect of

- phosphorus on a high silica HZSM-5 catalyst. *Catal. Commun.* 10, 1506–1509.
- Liu, Z.M., Sun, C.L., Wang, G.W., Wang, Q.X., Cai, G.Y., 2000. New progress in R&D of lower olefin synthesis. *Fuel Process. Technol.* 62, 161–172.
- Lücke, B., Martin, A., Günschel, H., Nowak, S., 1999. CMHC: coupled methanol hydrocarbon cracking: formation of lower olefins from methanol and hydrocarbons over modified zeolites. *Microporous Mesoporous Mater.* 29, 145–157.
- Luk'yanov, D.B., 1992. Effect of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio on the activity of HZSM-5 zeolites in the different steps of methanol conversion to hydrocarbons. *Zeolites* 12, 287–291.
- Machado, N.R.C.F., Calsavara, V., Astrath, N.G.C., Neto, A.M., Baesso, M.L., 2006. Hydrocarbons from ethanol using [Fe,Al]ZSM-5 zeolites obtained by direct synthesis. *Appl. Catal. A: Gen.* 311, 193–198.
- Mei, C., Wen, P., Liu, Z., Liu, H., Wang, Y., Yang, W., Xie, Z., Hua, W., Gao, Z., 2008. Selective production of propylene from methanol: mesoporosity development in high silica HZSM-5. *J. Catal.* 258, 243–249.
- Mores, D., Kornatowski, J., Olsbye, U., Weckhuysen, B.M., 2011. Coke formation during the methanol-to-olefin conversion: in situ microspectroscopy on individual H-ZSM-5 crystals with different Brønsted acidity. *Chem. Eur. J.* 17, 2874–2884.
- Patcas, F.C., 2005. The methanol-to-olefins conversion over zeolite-coated ceramic foams. *J. Catal.* 231, 194–200.
- Qian, L., Yan, Z.F., 2001. Micropore modification of zeolites with transition-metal oxides. *Colloids Surf., A* 180, 311–316.
- Schulz, H., 2010. Coking of zeolites during methanol conversion: basic reactions of the MTO-, MTP- and MTG processes. *Catal. Today* 154, 183–194.
- Schulz, J., Bandermann, F., 1994. Conversion of ethanol over zeolite H-ZSM-5. *Chem. Eng. Technol.* 17, 179–186.
- Sing, K.S.W., Everett, D.H., Haul, R.A.W., Moscou, L., 1985. Reporting physisorption data for gas/solid systems with special reference to the determination of surface area and porosity. *Pure Appl. Chem.*, 603–619.
- Stocker, M., 1999. Methanol-to-hydrocarbons: catalytic materials and their behavior. *Microporous Mesoporous Mater.* 29, 3–48.
- Vu, D.V., Hirota, Y., Nishiyama, N., Egashira, Y., Ueyama, K., 2010. High propylene selectivity in methanol-to-olefin reaction over H-ZSM-5 catalyst treated with phosphoric acid. *J. Jpn. Petrol. Inst.* 53, 232–238.
- Xu, M., Lunsford, J.H., Goodman, D.W., Bhattacharyya, A., 1997. Synthesis of dimethyl ether (DME) from methanol over solid-acid catalysts. *Appl. Catal. A: Gen.* 149, 289–301.
- Zhang, S., Zhang, B., Gao, Z., Han, Y., 2010. Ca modified ZSM-5 for high propylene selectivity from methanol. *React. Kinet. Mech. Catal.* 99, 447–453.
- Zhao, T.-S., Takemoto, T., Tsubaki, N., 2006. Direct synthesis of propylene and light olefins from dimethyl ether catalyzed by modified H-ZSM-5. *Catal. Commun.* 7, 647–650.