

INTERNATIONAL JOURNAL OF CHEMICAL  
REACTOR ENGINEERING

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*Volume 8*

2010

*Article A164*

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ISSN 1542-6580

# HZSM-5 and H-Ferrierite Acidity Modification by Silylation and Their Activities in n-Butene Isomerisation\*

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## Abstract

H-ZSM5 and H-Ferrierite acidities were modified by chemical liquid deposition using tetraethylorthosilicate (TEOS), silicontetrachloride ( $\text{SiCl}_4$ ) and triaminopropyltriethoxysilane (3-APTES). All depositions were carried out at room temperature for deposition times of 0.5 and 1 h. Reaction tests were performed in a tubular quartz fixed bed reactor at  $375^\circ\text{C}$  for weight hour space velocities of 22 h<sup>-1</sup>. Surface area and pore volume of the catalysts were decreased upon modifications. The least modification of acidity was achieved by TEOS. However,  $\text{SiCl}_4$  and 3-APTES deposition modification strongly decreased the number of Bronsted and Lewis acid sites. As the effect of the modification increased, total acidity of the  $\text{SiCl}_4$  modified catalyst decreased. The catalysts were tested in isomerization of n-butene. Modification decreased the activity of the catalysts, but improvement in selectivity was observed with TEOS deposition. TEOS deposition increased the selectivity of the catalysts; for synthesized H-ZSM5 from 57.95 to 63.74 percent, for commercial H-ZSM5-C from 26.78 to 32.52 percent, and for H-FER from 63.06 to 81.23 percent. However, modification with  $\text{SiCl}_4$  and 3-APTES decreased both conversion and selectivity of the parent catalysts.

**KEYWORDS:** isobutene, isomerization, HZSM-5, Ferrierite, modification, chemical liquid deposition, silylation

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\*The financial support from Turkish State Planning Organization (2002K120390) and Izmir Institute of Technology Research Funds (2008?YTE07) are gratefully acknowledged.

## 1. INTRODUCTION

Over the past few decades the applications of isobutene has increased. Methyltertbutylether (MTBE), which is an octane booster and important additive of unleaded gasoline, is produced from the reaction of methanol and isobutene. Isobutene is also used in ethyltertbutylether and polyisobutene manufacture and other various applications (Young et al., 1993). Therefore isobutene demand has also increased (Houzvicka et al., 1997a). However, current isobutene supplies do not compensate this demand (Asensi et al., 1997). Thus, skeletal isomerization of n-butene to isobutene reaction has attracted much attention on all of the world. Many researchers have studied on this reaction and tried different catalysts to obtain high isobutene selectivity (Houzvicka et al., 1997b).

Isomerization of n-butene takes place on acidic catalysts. Zeolite catalysts with 10 membered rings (E.g., H-ZSM-5 and H-Ferrierite) have been shown to have high selectivity toward isobutene (Bygginsbacka et al., 1997, Seo et al., 1996, Houzvicka et al., 1999). Their catalytic behaviors are highly dependent on the pore topology, acid strength, acid density and the location of the acid sites. Moderate Bronsted acid sites in the catalyst are considered to be the active sites required for skeletal isomerization, while the pore structure of the catalyst is another key factor with respect to the isobutene selectivity and the stability (Seo et al., 1996). Strong acidic catalysts cause cracking and oligomerization, on the other hand weak acidic catalysts cause double bond isomerization. Pore size determines the shape selectivity of the catalysts. So that catalyst must be at the optimum acid strength and its acidity must be suitable for isobutene formation (Canizares et al., 2000). Modification of H-ZSM5 and H-FER acidities could be an alternative way to increase their selectivity (Houzvicka et al., 1998).

Acidity and pore size of zeolites can be modified by different methods. Tetraethoxysilane (TEOS), silicon tetrachloride ( $\text{SiCl}_4$ ) and 3-aminopropyltriethoxy silane (3-APTES) treatment are among these methods. The use of deposition of TEOS by chemical vapour deposition (CVD) and chemical liquid deposition (CLD) to cover the external surface of zeolites with silicon alkoxides, whereby a silica layer is deposited around the crystals, has been investigated (Weber et al., 1998, Yue et al., 1996, Chudasama et al., 2005, Niwa et al., 1986, Niwa et al., 1988, Shang et al., 2008, Mainstein et al., 2002, Zheng et al., 2002, Zheng et al., 2003). The aim of these types of modifications, especially in the case of H-ZSM5 and H-FER is to improve the shape selectivity by rendering the easily accessible, non-selective acid sites found on the external surface inactive. In addition, catalyst lifetime may be improved.

Weber et al. (1998) found that CLD of TEOS narrowed pore size and decreased external surface acidity of H-ZSM5 up to about 70 %. Niwa et al. (1986, 1988) reported on deposition of  $\text{Si}(\text{OCH}_3)_4$  (critical diameter of 8.9 Å) on

H-ZSM5. Silicon alkoxides were not expected to enter the channels of the zeolite. Their findings showed that the zeolite adsorption capacity was conserved, but the channel openings were narrowed upon deposition of silicon alkoxide. This modification was found to increase shape selectivity and was ascribed mainly to narrowing of the channel openings rather than to the inertisation of the channel surface sites themselves. Cañizares et al. (2000) reported that the isomerization properties of Ferrierite zeolite could be improved by chemical vapour deposition (CVD) of  $\text{SiCl}_4$ . They supposed that the inactivation of non-shape selective acid sites (strong Brønsted acid sites) and the reduction in the void volume of the zeolite lead to a significant improvement in the isobutene selectivity and yield. It was reported that this small molecular agent can be deposited on the outer surface and inside the pores of ferrierite, thus it could decrease the acidity amounts of the zeolites considerably.

Shang et al. (2008) silylated MCM-22 with TEOS,  $\text{SiCl}_4$  and 8-hydroxyquinoline via a CVD process, and investigated them as catalysts for the skeletal isomerization of n-butene. The catalytic performance, especially the selectivity to isobutene, was considerably improved by controlled CVD treatment. This was attributed to silylation which diminished the Bronsted acid sites located on the external surface of zeolites. Their results showed that the Bronsted acid sites on the internal surface of the zeolites should be the main active centers for the selective skeletal isomerization of n-butene to isobutene.

The aim of this work is to improve the catalytic performance H-ZSM-5 and H-Ferrierite in n-butene isomerization by chemical liquid deposition method. Herein, tetraethoxysilane (TEOS), silicon tetrachloride ( $\text{SiCl}_4$ ) and 3-APTES were used as deposition agents to modify the surface acidic properties of the zeolites by a chemical liquid deposition process. The structure, texture and the acidic properties of parent and the modified samples were characterized and their performance in n-butene isomerization was investigated.

## 2. EXPERIMENTAL

### 2.1. Preparation of H-ZSM5

Na-ZSM5 catalyst was synthesized with a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  molar ratio of 77 following a method given in literature (Nicolaides et al., 1999). Three different solutions named, A, B and C, were prepared. For solution A, 20.10 g fumed silica was added to 162.50 ml deionised water. For solution B, 4.48 g NaOH and 1.48 g  $\text{Al}(\text{OH})_3$  was dissolved in 18.75 ml deionised water. The solution B was added to the solution A and mixed for 15 min in order to obtain a homogeneous solution. For solution C, 7.43 g of tetra-propyl-ammonium bromide (TPABr) was dissolved in 75 ml of water. Solution C was added to the homogeneous solution of A and B.

After the addition of 110 ml deionised water, the mixture was agitated for 15 min. Then, the gel was transferred into an autoclave. The autoclave was then put into an oven at 150 °C and kept for 96 h. After quenching to room temperature, zeolite formed was filtered and washed with deionised water. After drying at room temperature, it was calcined by keeping at 300 °C for 30 min and then heating to 540 °C with a heating rate of 3 °C/min and kept at this temperature for 8 h. Eventually, the organic template was removed and Na-ZSM-5 zeolite was obtained.

The synthesized Na-ZSM-5 were ion-exchanged with 0.1 M  $\text{NH}_4\text{Cl}$  (Sigma-Aldrich, 99.5 %) solution for 6 h at 80 °C under continuous agitation in water bath to obtain H-ZSM5. This method was applied twice. After ion exchange, the zeolites were washed thoroughly with deionized water until they were free of chloride ions which was checked using silver nitrate. Then, the samples were dried at 110 °C for 24 h. The dried sample was calcined by slowly heating to 540 °C (3 °C/min) and keeping at this temperature for 4 h to remove  $\text{NH}_3$ . Synthesized H-ZSM5 was labeled as H-ZSM5.

## 2.2. Modification of H-ZSM-5 and H-FER

H-ZSM5, H-ZSM5-C (Si/Al = 50, Sud Chemie) and H-Ferrierite (Si/Al=20, Sud Chemie) were used in CLD. TEOS modification was carried out as follows. Zeolite weighing 1.5 g was added to 10 ml hexane. After they were mixed, 0.03 ml of TEOS/g cat was added into the mixture and stirred for 0.5 or 1 h at room temperature. The slurry was filtered and then washed with hexane to remove excess TEOS. Then centrifuged and solid remained left overnight. It was then calcined in air at 550 °C for 6 h. This procedure was repeated for second cycle deposition. The same procedure was also used for  $\text{SiCl}_4$  deposition.

Modification by 3-APTES was performed by immersing 9.6 g zeolite into 100 ml ethanol solution containing 1.46 g of 3-APTES. Subsequently, ethanol was evaporated at 353 K. The sample was then dried and calcined at 540 °C in order to decompose the organosilane precursors and to form the silica-modified zeolites (Ding et. al., 2002).

## 2.3. Characterization of Catalysts

The crystalline structures of the samples were determined by Philips X'Pert diffractometer with  $\text{CuK}\alpha$  radiation. The scattering angle  $2\theta$  was varied from 5 °C to 40 °C, with a step length of 0.02.

The morphology of the samples was investigated by Philips SFEG 30S scanning electron microscopy (SEM).

Elemental analysis was determined by Varian-96 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) with fusion dissolution method. The method can be summarized as: 0.2 g of sample was mixed with 2 g of lithium tetra borate, and then mixture was fused in furnace at 1000 °C for 1 h and allowed to cool. Formed glass bead was dissolved in 1.6 M HNO<sub>3</sub> solution on a magnetic stirrer. Solution was completed to 250 ml and diluted if necessary.

Nitrogen physisorption studies were performed using Micromeritics ASAP 2010 model static volumetric adsorption instrument. The samples were dried in oven at 100 °C over night prior to degassing. Prior to adsorption experiments, the zeolites were out gassed at 300 °C for 24 h under 5 µmHg vacuum.

The acidity measurements of catalysts were made by IR spectroscopy with pyridine adsorption/desorption method. The samples were degassed at 400 °C under vacuum ( $2 \times 10^{-2}$  mmHg) for 1 h. Adsorption of pyridine was carried out at 150 °C for 30 min. Before FTIR analysis, the samples were kept at 150 °C under N<sub>2</sub> flow for 1 h and then under vacuum ( $2 \times 10^{-2}$  mmHg) for 1 h in order to desorb the physisorbed pyridine. KBr pellets were prepared by pressing a mixture of 6 mg pyridine adsorbed catalyst sample and 200 mg KBr. IR characterizations were carried out between 400 and 4000 cm<sup>-1</sup> with Shimadzu FTIR-8201 model Fourier Transformed Infra-red Spectrometer.

The acidities of the catalysts were also determined by Temperature-Programmed Desorption of Ammonia (NH<sub>3</sub>-TPD) method using Micromeritics AutoChem II Chemisorption Analyzer instrument. The sample was heated up to 500 °C by increasing the temperature at a rate of 5 °C/min and kept at this temperature for 1 h under He flow of 70 ml/min. Then the sample was cooled under He flow of 30 ml/min to 90 °C at a rate of 5 °C/min. This was followed by switching the flow to NH<sub>3</sub>-He gas mixture at the rate of 30 ml/min for 30 min. Physically adsorbed NH<sub>3</sub> was removed by degassing the sample at 90 °C under He flow of 70 ml/min for 120 min and then at the rate of 30 ml/min for 150 min. NH<sub>3</sub> desorption from the sample was analyzed by heating the sample at the rate of 10 °C/min from 90 °C to 600 °C. TCD signal was recorded during the NH<sub>3</sub>-TPD.

#### 2.4. Reactor Set-up and n-Butene Isomerization

The isomerization reaction tests were performed in quartz fixed bed reactor (10 mm diameter and 65 cm length) at 375 °C under atmospheric pressure by flowing 1-butene (98 %, 8 ml/min) and nitrogen (100 ml/min) mixture to the reactor. Before the reaction, the catalyst (0.05 g) was heat treated at 440 °C for 60 min

under 100 ml/min flow of N<sub>2</sub> and then maintained at this temperature for 45 min. The reaction products were analyzed with on-line gas chromatograph (Agilent Technologies 6890N Network GC System) equipped with a capillary column (GSA alumina KCl, 50 m × 0.53 mm) and FID. The three n-butene isomers (1-butene, cis-2-butene, and trans-2-butene) were considered as reactants.

### 3. RESULTS AND DISCUSSIONS

#### 3.1. Catalysts Characterisation

The modified samples were labeled as M-X-C where M indicates the modification agent (T=tetraethylorthosilicate, S=silicontetrachloride, A=3-aminopropyltriethoxysilane), X indicates the deposition time (h), C indicates number of deposition cycle. The XRD patterns of the H-ZSM5, H-ZSM5-C and H-FER and their modified samples are given in Figure 1. They all had sharp and obvious diffraction patterns.

The diffraction patterns of HZSM-5 (Figure 1.a) and its modified samples were well consistent with those reported in the literature (Song et al., 2009). The intensity of the characteristic peaks after 2-cycle TEOS modification decreased slightly, but the relative crystallinity values of all TEOS modified H-ZSM5 samples showed no significant changes indicating that smaller amounts of silica deposited on the H-ZSM5 sample (Weber et al., 2000). Shang et al., (2008) reported that TEOS deposition had little influence on structure. In the SiCl<sub>4</sub> and 3-APTES modifications, peak at 2θ=23° decreased. This could be due to dealumination during modification. This is also supported by the decrease of Al amount in 3-APTES modified zeolites, Table 1-3.

The XRD patterns of the commercial H-ZSM5-C and its modified samples (Figure 1.b) were similar for all the three samples. The crystal structure and intensity values of parent catalyst were completely same with the TEOS modified sample. Decrease in the peak intensities was observed in the 3-APTES modified sample. This was also attributed to silica deposition on the surface and to some dealumination, as discussed for H-ZSM5.

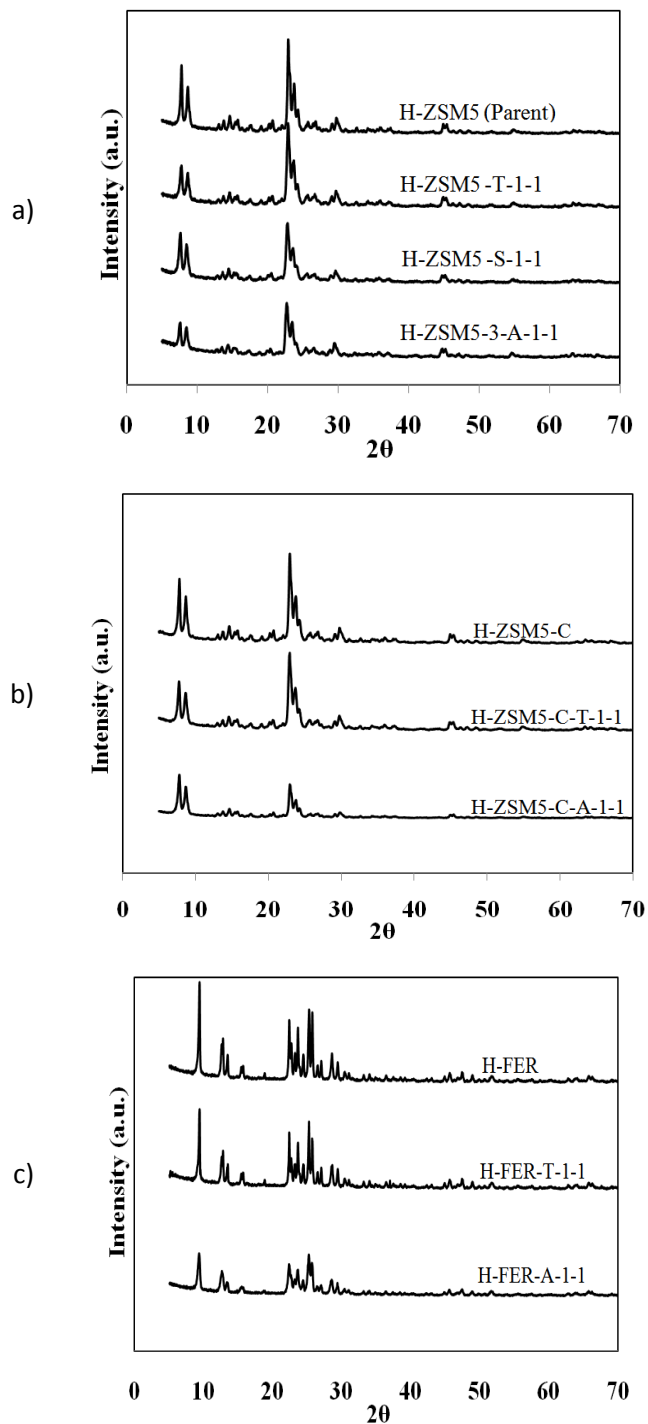


Figure 1. XRD patterns of H-ZSM5 and its modified forms (a), H-ZSM5-C and its modified forms (b), H-FER and its some modified forms (c).



The XRD patterns of the commercial H-FER and its modified forms (Figure 1.c) were the same with literature (Song et. al., 2009). There was no change in the peak positions. However, peak intensities decreased to some extent by 3-APTES modification. This was related to the decrease in surface area (Yue et. al., 1996) which was probably caused by deposition of silica on the surface.

The SEM images of parent H-ZSM5, HZSM5-C and HFER and only 3-APTES modified samples are given for comparison in Figure 2. Parent zeolites had different morphologies: H-ZSM5 had larger spherical particles, HZSM5-C had much smaller particles and H-FER had irregular particulates. It was found that the appearance of the crystals did not change compared with the parent samples.

The textural parameters of parent H-ZSM5, H-ZSM5-C and H-FER and their modified forms are summarized in Tables 1 to 3, respectively. BET surface area, and pore volume and micropore surface decreased markedly with silylation treatments. The largest decrease was observed for 3-APTES modification. Surface area of the modified samples was reduced dramatically after second cycle of deposition. The reason for this would be as follows. During the first silylation cycle, deposition agents molecules preferentially interacted with acid sites which were easily accessible, so high passivation effects were achieved. In the second cycle, the concentration of accessible sites was strongly reduced some of the pores might be blocked as noted in surface area measurements (Table 1-3).

Since molecular diameters of deposition agents used (10.3 Å for  $\text{Si}(\text{OC}_2\text{H}_5)_4$ , 7.1 Å for  $\text{SiCl}_4$ ) in the present work were larger than the pores of the H-ZSM5 (0.54-0.56 nm), and H-FER (0.54-0.56 nm), it was difficult for them to penetrate into zeolites. The increase in Si/Al ratio of the samples (Table 1) after TEOS deposition was attributed to small amount of TEOS deposition on the samples during modification by Weber et al. (1998). Canizares et al. (2000) reported that modification of H-FER by the liquid deposition of  $\text{SiCl}_4$  narrowed pore size and a little framework dealumination. Ying et al. (1996), on their study on the of H-ZSM-5 pore size controlling by chemical liquid deposition, found that the external surface area was affected by deposition. This reflected the silica deposition on the external surface. Formation of a thin layer of oxide was formed upon  $\text{SiCl}_4$  deposition on the external surface of the zeolite as a result of the deposition reaction and pore opening of the zeolites were narrowed. Niwa et al (1986, 1988) found that alkoxide deposition formed silica layer on H-ZSM5 and H-FER, and narrowed pore size.

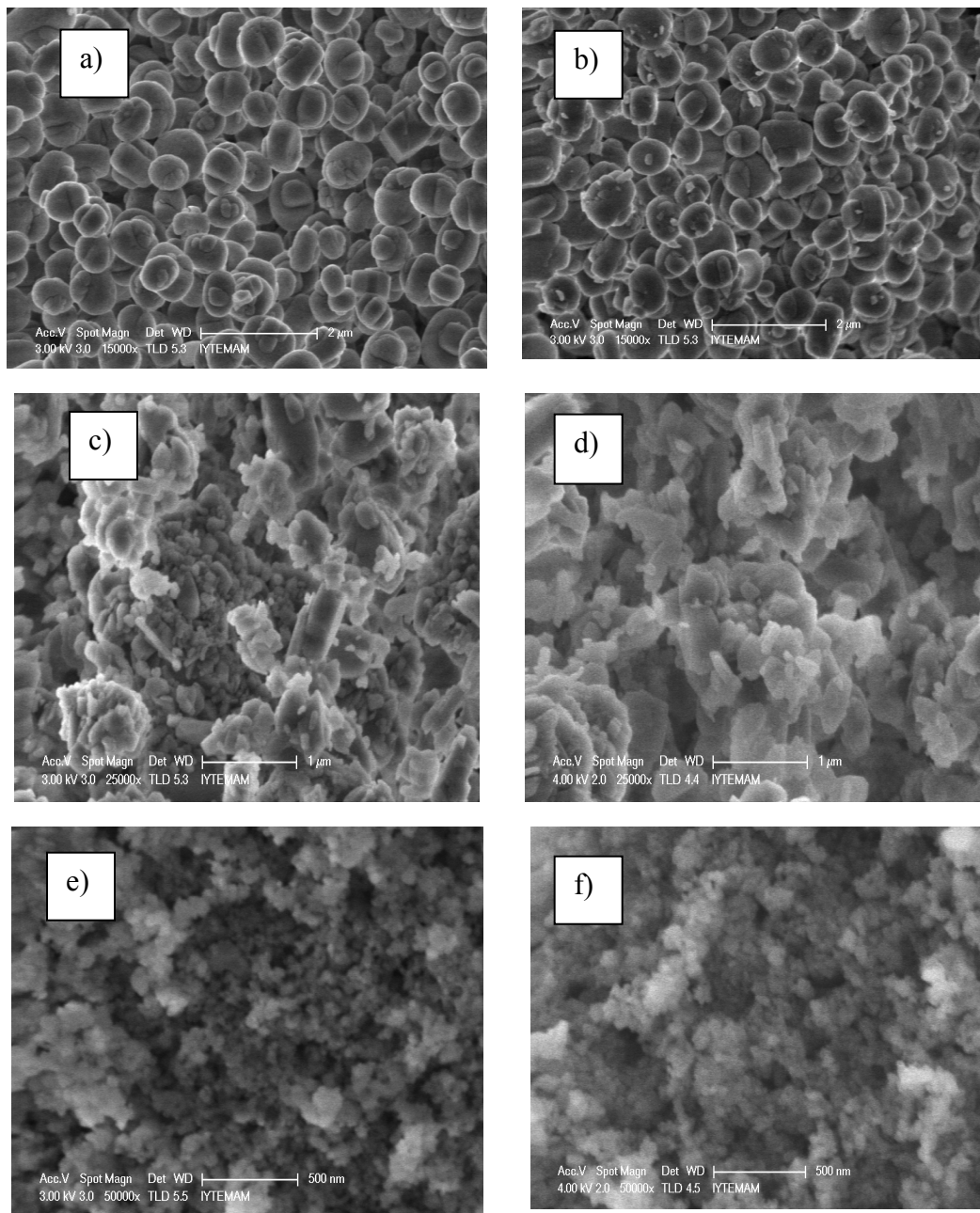


Figure 2. SEM images of H-ZSM5, H-ZSM5-C and H-FER and their modified samples: a) H-ZSM5, b) H-ZSM5-A-1-1, c) H-FER, d) H-FER-A-1-1, e) H-ZSM5-C, f) H-ZSM5-C-A-1-1.

The acidities of H-ZSM5, H-ZSM5-C and H-FER and their modified forms determined by  $\text{NH}_3$ -TPD are given in Figure 3. It can be seen that all the samples exhibited the typical double-peak characteristic of zeolites with MFI structure (Shang et al., 2008). The desorption peaks centered at low temperature (240 °C) and high temperature (450 °C) are referred to as weak and strong acid sites, respectively (Baerlocher et. al., 2001). Parent zeolites had both weak and strong acid sites. After the TEOS modification, peak areas of weak acid sites and strong acid sites decreased slightly. For  $\text{SiCl}_4$  and 3-APTES modification, it could be deduced that both weak and strong acids reduced significantly while affecting mostly strong acid sites. As the severity of the modification increased in  $\text{SiCl}_4$  and 3-APTES modification, total acid sites, both strong and weak acid sites decreased. This decrease was probably not only due to a  $\text{SiO}_2$  layer covering external surface acid sites, but also to reduced access of probe molecules to the internal acid sites as result of pore narrowing and pore mouth blockage. Canizares et al. (2000) reported that modification of Ferrierite zeolite by the liquid deposition of  $\text{SiCl}_4$  diminished the strong/weak and Brønsted/Lewis acid sites ratio. Ding et al (2002) reported that 3-APTES had strongly basic amino groups and this led to strong adsorption on acid sites. Moreover, silica deposition deactivated only the external surface of H-ZSM5.

Quantitative change in total amount of the acid sites is given in table 1 to 3. H-FER had the highest acidity and it was followed by H-ZSM5-C and then by H-ZSM5. This result was in accordance with their Si/Al ratio (Table 1 to 3). Acidity change by deposition agents decreased in the following order, 3-APTES >  $\text{SiCl}_4$  > TEOS.

The least decrease in the acidity was obtained by TEOS deposition among the modification agents. This could be due to larger diameter of the TEOS which prevent its diffusion into pores of H-ZSM5 and H-FER. Thus, modification by TEOS affected mainly external surface and pore mouth of HZSM5 (Weber et al 1998, Shang et al 2009, Manstein et al). Zheng et al. (2002) found that silylation by TEOS reduced the concentration of Brønsted acid sites, preferentially in the pore mouth region of the zeolites, and led to a blocking of Lewis acid sites.  $\text{SiCl}_4$  can be deposited on the outer surface and inside the pore channels of the zeolites based on the relatively smaller molecular size of  $\text{SiCl}_4$ , which is much easier to react with  $-\text{OH}$  groups compared with TEOS. Therefore, the concentration of Bronsted acid can be reduced markedly by the CLD treatment with  $\text{SiCl}_4$  (Figure 3.a). The results are consistent with the literature (Manstein et al., 2002). The strong basic amino groups in 3-APTES molecules lead to strong adsorption on acid sites, but the large size of the organosilane molecules prevent the titration of acidic OH groups within zeolite channels. Thus, only acid sites at the external surfaces react with these bulky silica precursors. After combustion of the organic

component in anchored organosilane molecules, SiOx species selectively replace external hydroxyls with SiOx species lacking acidic hydroxyls (Ding et al., 2002).

The acidities of some of the catalysts determined by pyridine adsorption are given in Figure 4. There is a broad band at  $1548\text{ cm}^{-1}$  which is assigned to Brønsted acid sites. The intense band at  $1490\text{ cm}^{-1}$  assigned to Brønsted and Lewis acid sites. And small band at  $1455\text{ cm}^{-1}$  is related to Lewis acidity. It was observed from each spectrum that the all the catalyst had Brønsted and Lewis acid sites. Acidity of the catalysts affected with modifications. As the severity of modification increased the amount of acid sites decreased. They reduced both Brønsted and Lewis acid sites. With 3-APTES acidity decrease was the largest and then followed by  $\text{SiCl}_4$  and TEOS.

Table 1 Textural properties of H-ZSM5 and its modified samples.

Sample	Si/Al	Al Content (mmol/g)	BET Surface Area ( $\text{m}^2/\text{g}$ )	External Surface Area ( $\text{m}^2/\text{g}$ )	Micropore Area ( $\text{m}^2/\text{g}$ ) (t-plot)	Micropore Volume ( $\text{cm}^3/\text{g}$ ) (H.K.)	Total Acidity (mmol $\text{NH}_3/\text{gcat}$ )
H-ZSM5	78.43	0.69	421.3	30.1	391.2	0.166	0.376
H-ZSM5-T-0.5-1	79.26	0.67	412.2	49.0	363.2	0.157	0.336
H-ZSM5 -T-1-1	83.75	0.65	405.3	56.6	348.7	0.155	0.354
H-ZSM5 -T-1-2	93.61	0.55	359.4	65.3	294.1	0.142	0.298
H-ZSM5 -S-1-1	102.48	0.51	254.6	11.1	243.5	0.144	0.154
H-ZSM5 -S-1-2	116.79	0.41	217.3	21.0	196.3	0.128	0.078
H-ZSM5-A-0.5-1	90.12	0.56	366.0	60.7	305.3	0.138	0.206
H-ZSM5-A-1-1	89.25	0.58	319.4	60.4	259.0	0.134	0.227
H-ZSM5-A-1-2	97.06	0.52	239.7	34.6	205.1	0.119	0.054

Table 2. Textural properties of H-ZSM5-C and its modified samples.

Sample	Si/Al	Al Content (mmol/g)	BET Surface Area (m <sup>2</sup> /g)	External Surface Area (m <sup>2</sup> /g)	Micropore Area (m <sup>2</sup> /g) (t-plot)	Micropore Volume (cm <sup>3</sup> /g) (H.K.)	Total Acidity (mmol NH <sub>3</sub> /gcat)
H-ZSM5-C	48.12	0.93	441.2	18.1	423.1	0.173	0.432
H-ZSM5-C-T-1-1	49.08	0.94	401.6	26.4	375.2	0.163	0.382
H-ZSM5-C-A-1-1	59.11	0.79	286.3	28.1	258.2	0.146	0.368

Table 3. Textural properties of H-FER and its modified samples.

Sample	Si/Al	Al Content (mmol/g)	BET Surface Area (m <sup>2</sup> /g)	External Surface Area (m <sup>2</sup> /g)	Micropore Area (m <sup>2</sup> /g)	Micropore Volume (cm <sup>3</sup> /g) (H.K.)	Total Acidity (mmol NH <sub>3</sub> /gcat)
H-FER	20.20	2.06	336.3	40.1	296.2	0.172	1.17
H-FER -T-1-1	34.11	1.54	295.4	61.2	234.2	0.158	0.99
H-FER-A-1-1	56.17	0.93	232.5	81.1	151.6	0.121	0.43

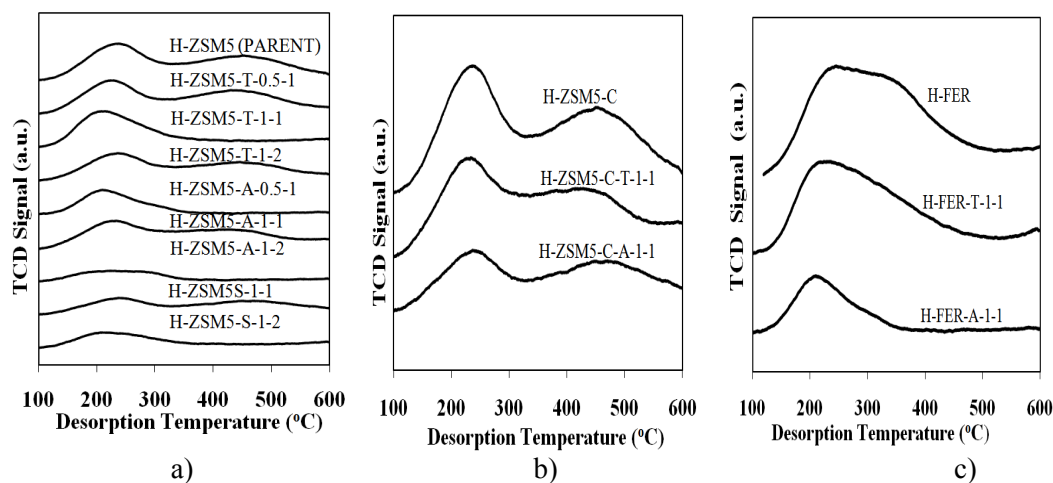
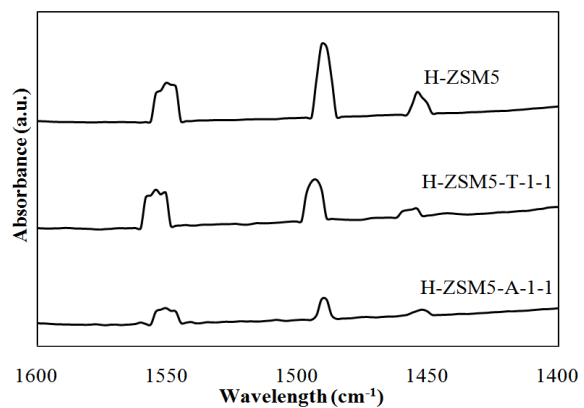


Figure 3.  $\text{NH}_3$ -TPD profiles of H-ZSM5 and its modified forms (a), H-ZSM5-C and its modified forms (b), H-FER and its some modified forms (c).

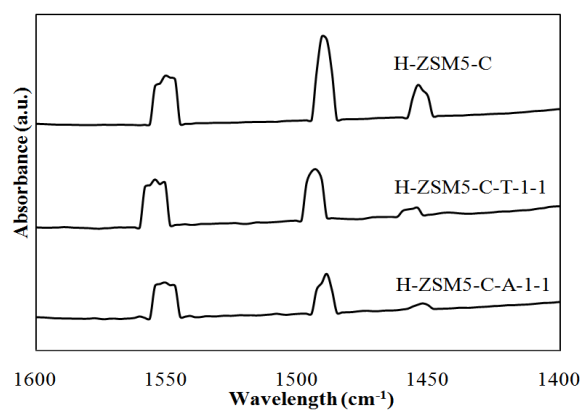
### 3.2. Catalytic Tests

The product distribution obtained over some of the selected catalysts is given in Table 4. The parent catalysts gave different product distributions. And also modification affected products formed. Main products were ethylene, propane, propylene, isobutene and butane.

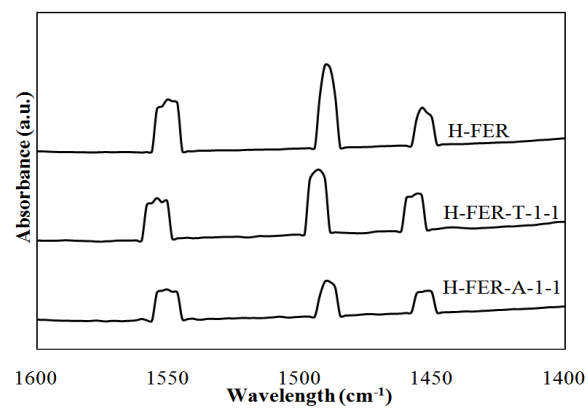
The n-butene conversions and the selectivities to isobutene forms in n-butene skeletal isomerization over different parent zeolites and some of their modified are given in Figure 5. Conversion decreased at the beginning of the reaction, which showed some deactivation of the catalysts. And then it remained almost constant with time on stream. Similar deactivation is reported in literature (Menorval et al., 2005, Houzvicka et al., 1997b). This was attributed to the deactivation of strong acid sites. Activities of the catalysts dropped significantly after modifications while the largest change was observed by  $\text{SiCl}_4$  and 3-APTES. This could be attributed to change in the acid sites and pore sizes upon modification. The significant activity decrease in  $\text{SiCl}_4$  and 3-APTES modified samples were due to decrease in number of acid sites as determined in the characterization part. The highest conversion (62.20 %) was obtained with H-ZSM5-C while it was 51.48 and 54.16 % for H-ZSM5 and H-FER, respectively.



a)



b)



c)

Figure 4. FTIR profiles of H-ZSM5, H-ZSM5-C, H-FER and their modified samples after pyridine adsorption.

Table 4. Product distributions of parent and some of their modified catalysts at reaction time of 180 min.

Sample	H-ZSM5	H-ZSM5-C	H-FER	H-ZSM5-1-1	H-ZSM5-C-1-1	H-FER-1-1
Product Distribution (mol %)						
Methane	0.00	1.05	0.00	0.06	1.11	0.06
Ethene	0.00	2.13	0.00	0.00	2.21	0.00
Ethylene	5.21	6.31	5.31	0.84	3.86	1.68
Propane	2.96	11.91	2.91	1.38	6.04	2.54
Propylene	5.67	11.51	1.04	3.17	7.37	2.17
Isobutane	0.99	2.29	0.09	1.53	5.58	1.43
n-Butane	0.74	3.87	0.87	0.38	5.11	0.38
Trans-2-butene	19.43	14.21	16.77	16.78	16.75	18.17
1-Butene	10.95	11.75	11.34	20.83	19.19	18.14
Isobutene	29.84	16.65	34.95	30.41	17.30	37.53
cis-2-butene	18.14	11.85	17.74	14.68	10.86	17.48
1-pentene	6.07	3.34	9.82	0.82	4.62	0.42
Other	0.11	3.13	0.03	9.12	0.09	0.13
Reaction Parameters (%)						
Conversion	51.48	62.20	54.15	47.71	53.20	46.21
Selectivity	57.97	26.78	64.54	63.74	32.52	81.23
Yield	29.85	16.65	34.15	30.41	17.30	37.54

Selectivity to isobutene was defined as the ratio of moles of isobutene to total number of moles of products. Among the parent catalysts H-FER was the most selective to isobutene (63.06 %) while H-ZSM5-C had the lowest selectivity (26.77 %). The crystallite size of H-ZSM5-C was much smaller than H-ZSM5. As a result most of the isomerization took place without the influence of the shape selectivity for H-ZSM5-C. This led to the low selectivity.

Among the modification agents only TEOS improved the selectivity of the parent catalysts. But significant change was observed with H-FER. TEOS 1 hour 1 cycle deposition increased H-FER selectivity from 63.06 to 81.23 %, and HZSM5 selectivity from 58.00 to 63.74 %. This improvement was attributed to slight changes in surface area and catalyst acidity after TEOS deposition. This suggested that the external surface acidity is the main reason for the formation of side products (propene and pentene). Therefore, it can be deduced that the Bronsted acid sites located inside the channels of H-ZSM5 and H-FER zeolite should be the main selective active sites for the skeletal isomerization of n-butene as discussed by Shang et al. (2008). However, selectivity of the parent catalysts were reduced after the SiCl<sub>4</sub> and 3-APTES deposition. This might be related to the pore blockage so less shape selectivity, and to the distribution of acid sites.



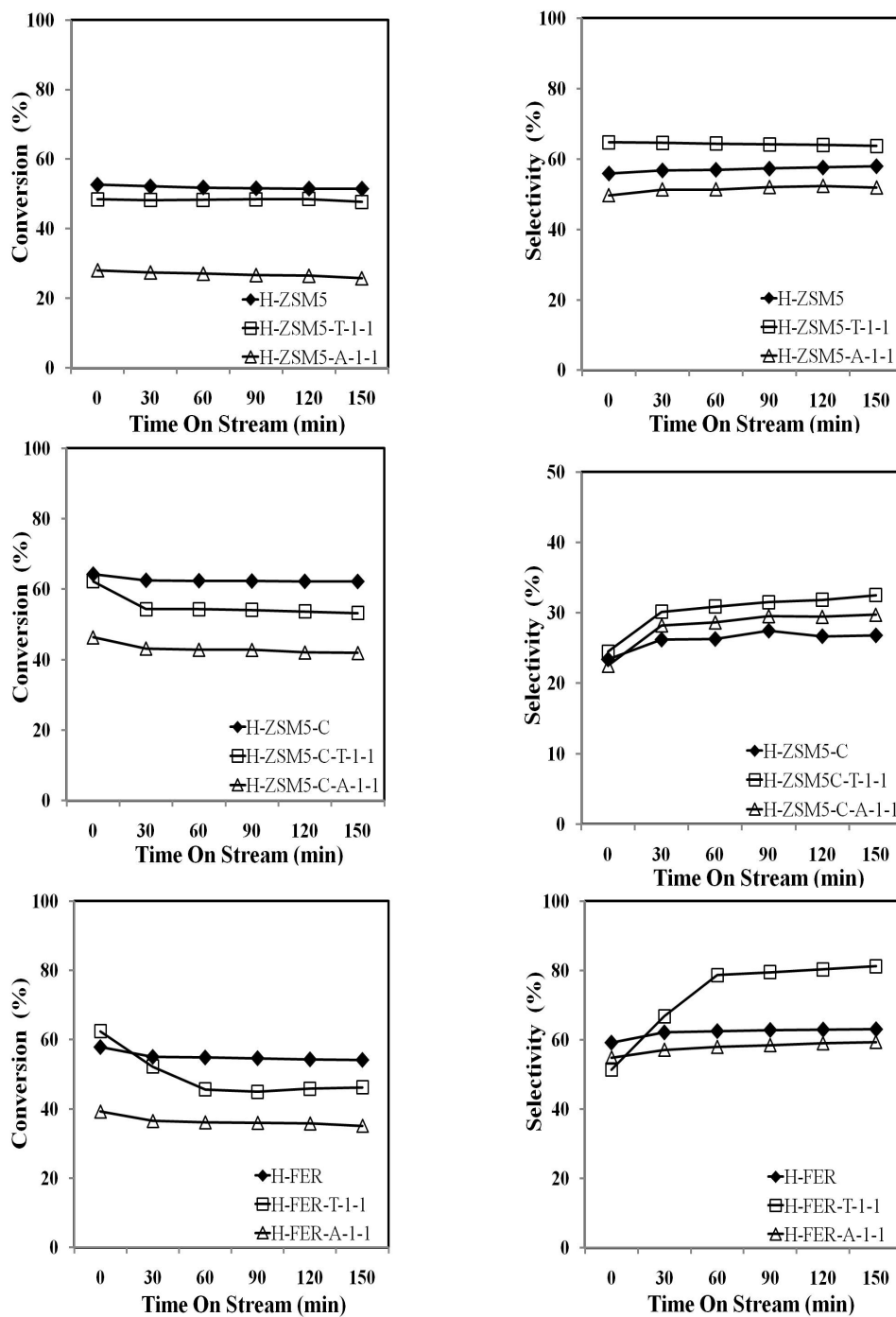


Figure 5. The catalytic activities and the selectivities of H-ZSM5, H-ZSM5-C, H-FER and their modified samples in n-butene isomerization.

Figure 6 shows the influence of time on stream (TOS) on the catalytic performance of H-ZSM5 and H-FER and their TEOS modified samples, which gave high selectivity to isobutene. For parent HZSM-5, the conversion of n-butene decreased gradually from 53.51 % to 46.10 %, while isobutene selectivity increased gradually from 50.26 % to 56.40 with TOS during the period of 16 h on stream studied. As for TEOS-1-1, it exhibited apparently similar tendency as parent H-ZSM5; conversion decreased from 48.33 to 41.05 % while corresponding selectivities were 56.11 % and 62.10 %. This showed that modification did not improve the deactivation characteristics of the parent catalyst as opposed to what is reported in literature (Weber et al., 1998). However, H-FER modified by TEOS improved deactivation properties.

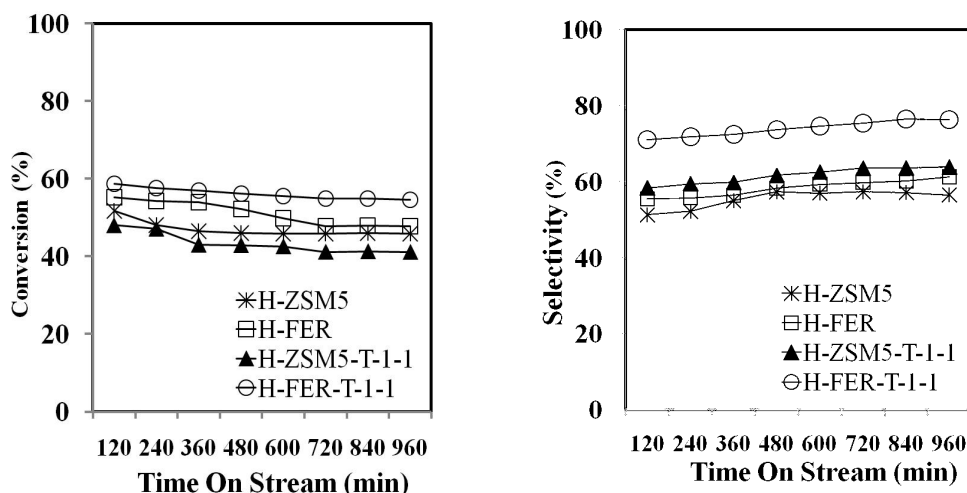


Figure 6. Influence of time on stream on the catalytic performance of H-ZSM5, H-FER and their TEOS modified forms.

#### 4. CONCLUSIONS

It has been demonstrated that the acidity of the synthesized H-ZSM-5, commercial HZSM-5 and H-FER can be changed by chemical liquid deposition method using TEOS,  $\text{SiCl}_4$  or 3-APTES. Crystal structure of the modified catalysts was same with the parent, slight decrease in crystallinity was observed as the severity of the modification increased. The acidity and surface area were reduced slightly after TEOS deposition. However, the acidity decreased dramatically after  $\text{SiCl}_4$  and 3-APTES modifications. The highest selectivities were obtained by controlled treatment with TEOS. This should mainly be due to

the greatly reduced non-shape selective Bronsted acidic sites after the deposition of TEOS, which were located on the external surface of zeolites. The Bronsted acidic sites located on the internal surface of the zeolites were supposed to be the main active centers for the selective skeletal isomerization of n-butene to isobutene. Modification did not improve the deactivation behavior of the parent catalysts.

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