Effect of different acidity modifications on the activity and selectivity on H-ZSM5 zeolites in *n*-butene isomerization

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Abstract H-ZSM-5 was modified by silylation [tetraethylorthosilicate (TEOS) and triaminopropyltriethoxysilane], alkali (NaOH), acid (HCl) and ammoniumhexafluorosilicate (AHFS) treatments. The parent and modified zeolite forms were tested in *n*-butene isomerization. Modifications affected total acidities, the strength of the acid sites, pore sizes and surface areas of the H-ZSM-5 differently. The modifications decreased the conversion obtained by the parent catalyst. TEOS and alkali modifications did not promote formation of isobutene. Pre-alkali treatment before acid treatment increased selectivity to isobutene from 56.0 to 66.7 %, while conversion changed a little, it dropped from 52 to 50 %. AHFS modification provided the highest enhancement in selectivity to isobutene (87.5 %) for which *n*-butene conversion was dropped by about 10 % compared to H-ZSM-5. This was attributed to a slight modification of the pore size and to the reduction in strong and weak acid sites and generation of new Lewis acid sites.

Keywords H-ZSM5 · Modification · Acidity · Isomerization · Isobutene

Introduction

In the last decades, skeletal isomerization of *n*-butene to isobutene has attracted much interest [1–5]. The studied catalysts varied from metal oxides to amorphous or crystalline aluminosilicates. These studies showed that improvements in isobutene selectivity could be achieved by the choice of catalyst type, suitable pore size and shape, or by varying parameters such as crystallite size, morphology, and Si/Al

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ratio, or by modifications such as extra framework cation exchange, isomorphous substitution, pore blockage and elimination of acid sites.

Three different mechanisms, monomolecular, bimolecular and pseudo-monomolecular, have been proposed in the literature for skeletal isomerization of *n*-butene [1, 6–10]. Monomolecular mechanism occurs on the Brønsted acid sites of the catalyst. This mechanism requires a highly energetically and thermodynamically unfavorable ring opening to form primary carbenium ion as an intermediate. Monomolecular mechanism could explain the high selectivity to isobutene. The bimolecular mechanism includes dimerization, isomerization and cracking steps. Through this mechanism, the main by-products, propenes and pentenes, are formed. The dimerization of *n*-butene does not directly occur since this would require a primary carbenium ion. In the pseudo-monomolecular mechanism, the active sites would be the coke instead of the Brønsted acid sites and would not, therefore, require a primary carbenium ion. The suppression of cracking by-products can be obtained by adjusting pore size (shape selectivity) of the catalyst such that bimolecular intermediate cannot form due to space constraints, or by adjusting the acidity of the catalysts, such that the rate of formation of $C4^=$ dimer intermediate is lowered.

The most promising catalysts for the selective isomerization of *n*-butenes are found to be 10-membered ring (10-MR) molecular sieves, such as ferrierite, SAPO-11 and ZSM-22 [6] and ZSM-5 zeolites [11]. Their pore sizes are optimal for *n*-butene diffusion, and they can suppress the bimolecular mechanism. Yang et al. [4] studied 1-butene isomerization over aluminophosphate molecular sieves (SAPO-11, MeAPO-11) and ZSM-22. They found that acidic sites of medium strength were responsible for high selectivity.

Various methods have been applied to modify acidity (strength, acid type and amount) and textural properties of zeolites. Houzvicka et al. [6] tried to change acidity of H-ZSM5 by isomorphous substitution of different metals (Ga, Fe, B) into its lattice. It was found that acidity of the catalysts was not significantly affected; as a result, selectivity to isobutene was not improved. Song et al. [12] modified the acidity of the H-ZSM5 catalyst by alkali (NaOH) and acid treatment (HCl). It was shown that mild alkali treatment led to the reduction in strong acid sites and did not distinctly change the pore structure. However, severe alkali treatment resulted in the creation of the stronger acid sites and new mesopores. Weber et al. [13] showed that chemical liquid deposition of tetraethylorthosilicate (TEOS) onto H-ZSM5 reduced acid sites without changing pore structure. On the other hand, pore mouth narrowing and pore blocking occurred after chemical vapor deposition. Canizares et al. [3] treated H-ferrierite with ammoniumhexafluorosilicate [$(NH_4)_2SiF_6$, AHFS]. This led to a little framework dealumination although Si/Al ratio increased slightly, indicating that the most of the extracted aluminum atoms remained in the pores. High AHFS amounts decreased crystallinity, micropore area and volume. AHFS removed external acid sites. Their catalytic activity was evaluated in the skeletal isomerization of *n*-butene. The modified catalyst improved selectivity to isobutene from 45 to 75 %. However, *n*-butene conversion was reduced from 53 to 43 %.

In light of the literature, it was decided to modify H-ZSM5 zeolites by silylation (TEOS, 3-APES), acid (HCl), alkali (NaOH) and ammoniumhexafluorosilicate

(AHFS) treatments to understand and assess the role of different modifications on zeolite activity and selectivity in *n*-butene isomerisation. Evaluation of different modifications on the same zeolite will provide more insight into what controls isobutene selectivity.

Materials and methods

Preparation of H-ZSM5 catalysts

Na-ZSM-5 was synthesized with SiO_2/Al_2O_3 ratio of 77 following a method given in literature [2]. Synthesized Na-ZSM-5 was calcined as follows. It was first heated to 300 °C and kept there for 30 min. This was followed by heating to 540 °C at a rate of 3 °C/min where it was kept for 8 h. After calcination, Na-ZSM-5 was ion-exchanged with 0.1 M NH_4Cl (Sigma-Aldrich, 99.5 %) solution for 6 h at room temperature under continuous agitation in a water bath to obtain NH_4-ZSM5. The ion exchange was applied twice. The sample obtained was washed thoroughly with deionized water until it was free of chloride ions, which was checked using silver nitrate. After drying at 110 °C for 24 h, it was calcined slowly by heating (3 °C/min) to 540 °C and holding at this temperature for 4 h to form H-ZSM-5. This material was also referred to as parent zeolite.

Finally, the catalyst powders pelletized under 825 MPa were ground and sieved to obtain particles in the size range of 106 and 250 μm. This particle size minimizes internal diffusional limitations [14].

Modification of H-ZSM-5

Modification methods and conditions which will affect H-ZSM-5 properties slightly (acidity, pore size and structure) were selected based on literature studies.

Silylation

Silylation was performed by chemical liquid deposition method using TEOS and 3-APES [15]. For TEOS deposition, 1.5 g zeolite was added to 10 ml hexane. Then, 0.03 ml of TEOS/g-catalyst was added into this mixture and stirred for 1 h at room temperature. The slurry obtained was washed thoroughly with deionized water to remove excess TEOS and centrifuged to obtain modified zeolites. After drying overnight at ambient conditions, they were dried at 110 °C for 24 h and calcined at 550 °C for 6 h.

3-APES-modified zeolite catalyst was prepared by immersing 9.6 g parent zeolites into a 100 ml ethanol solution containing 1.46 g of 3-APES. Ethanol was subsequently removed by evaporation at 90 °C [16]. The remaining sample was washed thoroughly with deionized water, centrifuged and allowed to dry overnight at ambient conditions. The sample was then dried at 110 °C for 24 h and calcined at 540 °C for 8 h in order to decompose the organosilane precursors and to form silica-modified H-ZSM5.

Mild alkali treatment

A method given in the literature was applied for mild alkali treatment of H-ZSM-5 [12]. A zeolite sample of 3.5 g was added to 200 ml of 0.05 M aqueous NaOH (Fluka, 98 %) solution at 70 °C and stirred for 2 h. The slurry was then cooled down immediately using an ice-water bath, filtered and washed thoroughly till the pH of the filtration solution decreased to 7. This was followed by drying at 120 °C for 10 h and calcination at 520 °C for 8 h.

Pre-alkali treatment and acid treatment

H-ZSM-5 weighing 3.5 g was first treated with 200 ml of 0.1 M aqueous NaOH solution at 70 °C in a shot bottle for 8 h (severe alkali treatment) [12]. Subsequently, it was washed, dried and calcined as for mild alkali treatment. The severe alkali-treated sample was then subjected to acid treatment by adding 5 g of alkali-treated sample to 200 ml of 0.1 M HNO_3 (Merck, 65 %) solution heated to 70 °C. The slurry obtained was stirred for 24 h. After cooling down the slurry immediately in an ice bath and filtering, the remaining sample was then successively washed thoroughly with deionized water, centrifuged and allowed to dry at ambient conditions overnight. The modified sample was then dried in oven and calcined as for alkali treatment. For acid modification alone, only the same acid treatment was applied.

AHFS treatment

First, 1.0 g H-ZSM-5 was added into the 100 ml of 0.8 M sodium acetate solution at pH 6.7 [17]. Second, the mixture was heated to 80 °C under stirring. Third, 20 ml of 1.2 mmol AHFS was added drop wise to the mixture under stirring for 3 h at 80 °C. Fourth, the modified zeolite was recovered by filtration and washed thoroughly with deionized water to eliminate the unreacted AFHS. The solution was centrifuged and powder washing was repeated till solution pH became 7. After that it was allowed to dry at ambient conditions overnight. This was followed by drying at 110 °C for 24 h and calcination at 550 °C for 4 h.

Characterization of catalysts

The crystalline structures of the catalysts were determined by Philips X'Pert diffractometer with CuK_α radiation. The scattering angle 2θ was changed from 5° to 70°, with a step length of 0.02°/s.

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

The textural properties of the catalysts were determined by Micromeritics ASAP 2010 model static volumetric adsorption instrument. The samples were dried in an oven at 110 °C overnight prior to degassing. Prior to adsorption experiments, the zeolites were outgassed at 300 °C for 24 h under 5 μmHg vacuum.

The acidity of the samples were determined by temperature-programmed desorption of ammonia (NH$_3$-TPD) using a 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 keeping 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$_3$–He gas mixture at the rate of 30 ml/min for 30 min. Physically adsorbed NH$_3$ was removed by degassing the sample at 90 °C under a He flow of 70 ml/min for 120 min and then at a flow rate of 30 ml/min for 150 min. NH$_3$ desorption from the sample was analyzed by heating the sample at the rate of 10 °C/min from 90 to 600 °C. TCD signal was recorded during the NH$_3$-TPD.

The acidity measurements of the catalysts were also carried out by IR spectroscopy with pyridine adsorption/desorption method. IR analysis was carried out between 400 and 4,000 cm^{-1} with Shimadzu FTIR-8201 model Fourier transform infrared spectrometer using the KBr pellet technique. KBr pellets were prepared by pressing a mixture of 4.5 mg catalyst sample and 150 mg KBr. The pellets prepared were dehydrated under vacuum (2×10^{-2} mmHg) at 400 °C for 2 h. The pellets were contacted with pyridine pellets at 150 °C for 30 min. After removing physically absorbed pyridine by keeping pellet under vacuum (2×10^{-2} mmHg) at 150 °C for 30 min, the samples were analyzed by FTIR.

Catalyst testing

A fixed bed reactor was used for testing the catalysts in *n*-butene skeletal isomerization. Tests were carried out in a quartz tubular reactor (10 mm in diameter and 65 cm in length) heated by a tubular furnace. The reactor feed consisted of 7.27 % 1-butene in N$_2$. Flow rates of gases were set and controlled by mass flow controllers. The reaction was performed at 375 °C for a catalyst loading of 50 mg into the reactor (WHSV of 22 h^{-1}).

The reactor effluent was connected to the sampling loop system of gas chromatography (Agilent Technologies 6890N Network GC System) for online gas analysis. The online gas chromatograph was equipped with a flame ionization detector (FID) and a fumed silica KCl column (GS Alumina KCl, 50 m × 0.53 mm).

Results and discussions

Characterization results

SEM analysis showed that synthesized H-ZSM5 had spherical crystallites which were not affected by modifications (results not given). An average crystallite size was calculated as 700 nm from the sizes of 30 particles taken from the SEM images. XRD results showed that ZSM5 structure was preserved after the modifications (results not shown).

Textural and physicochemical properties of the parent catalyst and its modified forms are shown in Table 1. TEOS deposition reduced the surface area, pore size

Table 1 Textural and physicochemical properties of H-ZSM5 and its modified forms

Catalysts	BET surface area (m^2/g)	Micropore area (m^2/g)	Micropore volume (cm^3/g)	H.K. pore diameter (Å)	SiO$_2$/Al$_2$O$_3$	Al content (mmol/g)
H-ZSM5	401.2	348.2	0.159	5.9	76.3	0.29
H-ZSM5–TEOS	362.4	289.6	0.145	5.3	79.4	0.25
H-ZSM5–3APES	276.5	213.9	0.122	3.5	170.2	0.18
H-ZSM5–AHFS	394.3	323.5	0.150	5.8	85.1	0.26
H-ZSM5–NaOH	438.1	336.8	0.171	5.5	77.1	0.23
H-ZSM5–NaOH–HCl	375.4	292.3	0.196	5.5	78.1	0.25
H-ZSM5–HCl	355.9	296.5	0.138	4.9	154.2	0.15

and micropore volume. SiO$_2$/Al$_2$O$_3$ ratio increased slightly. The external surface area increased. These results indicated that silylation took place on the surface and caused pore narrowing and blockage. Hibino et al. [20] and Weber et al. [13] reported pore narrowing and increase in the external surface area of ZSM-5 upon silicon alkoxides deposition [13, 15, 18–20].

The most significant decrease in BET surface, micropore volume and pore size was observed by 3-APES treatment. A large increase in SiO$_2$/Al$_2$O$_3$ ratio was obtained (Table 1). A significant silica deposition was achieved, and it narrowed and blocked zeolite channels. Since 3-APES is a large molecule, most of silica probably deposited on the external surface as reported by Ding et al. [21].

The textural properties of the H-ZSM-5 were affected the least by AHFS treatment compared to other modifications. The surface area loss was not significant and the pore size dropped a bit (Table 1). SiO$_2$/Al$_2$O$_3$ ratio increased slightly, which indicated dealumination. This was in agreement with study by Canizares et al. [17]. They reported that AHFS caused dealumination and extracted Al atoms remained in the pore. Kumar et al. [22] also found mild dealumination by AHFS treatment. Accordingly, Triantafillidis et al. [23] reported that AHFS treatment was appropriate for preparation of moderately dealuminated H-ZSM5 samples, which were free from extra framework Al.

As opposed to other treatment methods, the mild alkali treatment increased the BET surface area and micropore volume. Slight dealumination was also observed as Al content decreased. Dealumination is reported to accompany desilication [24] which might explain the slight increase in SiO$_2$/Al$_2$O$_3$ ratio observed. The drop in the pore size was probably due to precipitation of silica and alumina species dissolved from zeolite onto the surface of ZSM-5 crystals. Severe alkali pre-treatment and acid treatment decreased surface area and increased micropore volume. It dropped aluminum content which raised SiO$_2$/Al$_2$O$_3$ ratio. These could be related to a slight desilication and dealumination taking place as discussed by Song et al. [12]. This led to a drop in the pore size. The acid treatment alone decreased BET surface area, micropore volume and pore size. Al content was dropped significantly due to dealumination which doubled SiO$_2$/Al$_2$O$_3$.
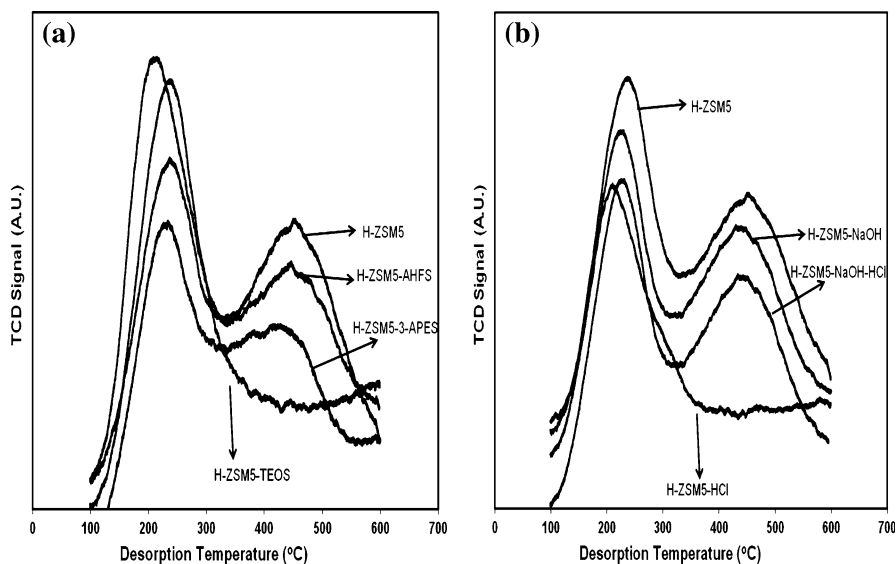
Fig. 1 NH$_3$-TPD profiles of different catalysts, **a** H-ZSM5, H-ZSM5–TEOS, H-ZSM5–APES, H-ZSM5–AHFS, **b** H-ZSM5, H-ZSM5–NaOH, H-ZSM5–NaOH–HCl, H-ZSM5–HCl

Temperature-programmed desorption of ammonia allows quantitative determination of the total amount of the acid sites. The NH$_3$-TPD profiles of the parent H-ZSM5 and their modified samples are presented in Fig. 1. It can be seen that most samples exhibited the typical double-peak characteristic of zeolites with MFI structure [25]. The desorption peaks centered at a low temperature (240 °C) and a high temperature (450 °C) are referred as weak and strong acid sites, respectively [26]. The total acidity of each catalyst was calculated and tabulated in Table 2. There were no large differences between the total acidity of parent and modified catalysts. This indicated that besides the total influence of acidity, the strength and type of acid must be taken into account to explain results obtained in the skeletal isomerization of *n*-butene to isobutene. However, the quantity of weak and strong acid sites changed differently with different modifications pursued.

The acidity types of H-ZSM5 and their modified forms were determined by pyridine adsorption. It was observed from each spectrum that all the catalysts had Brønsted and Lewis acid sites (results not given). Brønsted and Lewis sites amounts were determined from the areas under the IR peaks centered at wavenumbers of 1,450 and 1,545 cm^{-1}, respectively (Table 2). Since pyridine adsorption on H-ZSM5 (at low temperatures and short adsorption times, as in our case) is reported to occur only in the outer part of the crystallites [17], these values can be interpreted as a measure of surface acidity.

TEOS modification decreased total concentration of acid sites of H-ZSM5; strong acid sites were decreased by half while weak acid sites increased slightly. TEOS molecules react with two adjacent hydroxyl groups on the zeolite surface during TEOS deposition [27]. TEOS decomposes to the Si(C$_2$H$_5$)$_3$ and C$_2$H$_5$OH. Ethanol diffuses into the solution from the surface, whereas Si(C$_2$H$_5$)$_3$ molecules remain on

Table 2 Acidity of H-ZSM5 and its modified samples

Catalysts	Total Acidity (mmolNH$_3$/g$_{cat}$)	Weak Acid Sites (mmolNH$_3$/g$_{cat}$)	Strong Acid Sites (mmolNH$_3$/g$_{cat}$)	Brønsted Area (1,540 cm^{-1})	Lewis Area (1,450 cm^{-1})
H-ZSM5	0.394	0.189	0.205	2.51	0.89
H-ZSM5–TEOS	0.319	0.213	0.106	–	–
H-ZSM5–3APES	0.262	0.129	0.133	1.79	0.34
H-ZSM5–AHFS	0.353	0.167	0.187	1.60	0.98
H-ZSM5–NaOH	0.368	0.173	0.195	1.36	0.71
H-ZSM5–NaOH–HCl	0.338	0.175	0.163	0.91	0.61
H-ZSM5–HCl	0.319	0.196	0.123	1.92	0.67

the acid sites. After the calcination, the acid sites on the surface were coated by SiO$_2$.

3-APES modification reduced the number of strong and weak acid sites substantially. This could be due to pore blockage and high amount of silica deposition observed. The amounts of both Brønsted and Lewis acid sites were also decreased significantly. 3-APES adsorb strongly on acid sites [16]. After the combustion of the organic component in the anchored organosilane molecules, SiO$_x$ species selectively replace external hydroxyls with SiO$_x$ species lacking acidic hydroxyls.

AHFS also decreased the amount of strong and weak acid sites. Brønsted sites were decreased to some extent. The reduction in acidity could be due to substitution of Al in the framework by Si atoms (Table 1). Al atoms extracted from the framework might remain in the pores and might form new Lewis acid centers ([3, 22]). This might be the reason for the slight increase observed in the amount of Lewis acid sites. Similarly, Canizares et al. [17] found that AHFS treatment removed mainly external Brønsted and Lewis acid sites of ferrierite with a marked improvement in the number of medium strength acid sites.

After alkali treatment, some reduction in strong and weak acid sites was observed. The change in acidity could be due to dealumination and desilication observed (Table 1). Both Brønsted and Lewis acid sites were reduced. That is, external surface acidity was lowered. The pre-alkali (severe) and acid treatment decreased strong acid sites significantly while it dropped weak acids slightly. The change in acidity was due to desilication and dealumination. Song et al. [12] reported that severe alkali treatment (high NaOH concentration) caused extra framework alumina formation which was removed after HCl treatment. External acidity was decreased significantly.

Acid treatment alone decreased strong acid sites significantly while weak acid sites did not change much. The substantial removal of Al from the structure led to decrease in acidity. Dealumination of H-ZSM5 by HCl was also reported by Kooyman et al. [28]. The drop observed in Brønsted and Lewis acid sites showed removal of external acid sites upon acid treatment.

Reaction tests

Conversion of 1-butene and selectivity to isobutene were calculated from the following equations,

$$\text{Conversion (mole\%)} = \frac{(1 - \text{butene}_{\text{in}}) - (n - \text{butene}_{\text{out}})}{(1 - \text{butene}_{\text{in}})}$$

$$\text{Selectivity (mole\%)} = \frac{\text{Isobutene}_{\text{out}}}{(1 - \text{butene}_{\text{in}}) - (n - \text{butene}_{\text{out}})}$$

Initial product distributions obtained over H-ZSM5 and its modified forms except H-ZSM5–HCl (which gave low conversion and selectivity) are given in Table 3. Different product distributions were obtained with the catalysts prepared. These products include various hydrocarbons such as C1, C2, C3 and C5+ as well as isobutene. Large amounts of secondary products, propene, propane and pentenes, formed indicated that bimolecular mechanism was significant over H-ZSM5 catalysts at short time on stream. C1, C2, C3 and C5 hydrocarbons are formed through dimerization or oligomerization followed by cracking. And isobutene is formed through skeletal isomerization. A geometric isomerization between *cis*-2-butene and *trans*-2-butene and a double-bond migration can proceed on solid acid catalysts simultaneously. Therefore, the product distribution is very complicated because the extent of reaction varies according to reaction conditions and catalysts. Byggningsbacka et al. [7] proposed a detailed mechanism for product distribution for skeletal isomerization of *n*-butene.

Table 3 Product distributions, conversions and selectivity to isobutene obtained over H-ZSM5 and its modified forms for the reaction time of 10 min at T = 375 °C and WHSV = 22 h^{-1}

| Comp. (mol%)	Sample				
	H-ZSM5	H-ZSM5–TEOS	H-ZSM5–NaOH–HCl	H-ZSM5–AHFS	H-ZSM5–NaOH
Methane	0.01	0.03	0.06	0.01	2.17
Ethane	2.71	3.34	2.14	0.59	1.12
Ethylene	8.15	2.85	1.14	1.03	1.50
Propane	2.59	1.18	3.01	1.29	2.11
Propylene	5.94	2.96	4.43	1.74	5.24
Isobutane	0.72	2.32	3.57	0.49	3.48
n-Butane	0.56	1.98	2.41	0.51	3.64
Trans-2-butene	18.81	16.61	14.88	19.93	10.63
1-Butene	10.73	19.82	15.51	19.96	19.57
Isobutene	29.41	31.38	33.40	37.88	29.93
Cis-2-butene	17.86	15.08	18.02	15.52	17.84
1-Pentene	2.14	1.77	1.64	0.67	1.41
(C2 + C3)$^{=}$/C5$^{=}$	6.58	3.28	3.40	4.13	4.78
Selectivity	55.91	64.71	64.74	84.95	57.60
Conversion	52.60	48.49	51.59	44.59	51.96

(a)

(b)
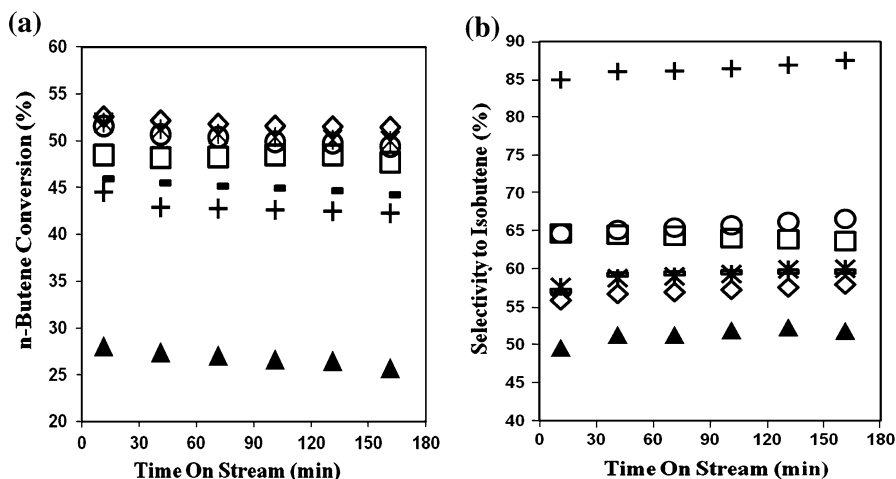
Fig. 2 Comparison of *n*-butene conversions (**a**), selectivities to isobutene over different catalysts (**b**). Reaction conditions, T = 375 °C and WHSV = 22 h^{-1}. Catalysts: ◆H-ZSM5; ▲H-ZSM5–3APES; ⬯ H-ZSM5–NaOH–HCl; ➡H-ZSM5–HCl; ✛H-ZSM5–AHFS; ✳ H-ZSM5–NaOH; ⊟H-ZSM5–TEOS

Modifications decreased selectivity toward the by-products, pentene, ethylene and propylene, strongly but not all with the same trend. Houzvicka et al. [6] and Lee et al. [26] stated that strong acid sites present on zeolites were responsible for the formation of by-products mainly propane and propylene, through the bimolecular mechanism. As discussed in the introduction, bimolecular reactions involve cracking reactions. Propylene and ethylene are predominant over strong acid sites. The decrease in (ethylene + propylene)/pentenes ratio with the modifications indicated drop in the extent of bimolecular mechanism [17]. Reduction in the acid site density would decrease contact time, as a result less consecutive reactions could occur which might also contribute to increase in selectivity.

The conversions and selectivities obtained over the catalysts are given in Fig. 2a, b. *n*-Butene conversion decreased and selectivity to isobutene increased with reaction time on stream. This was attributed to coke formation. It reduced the catalyst activity and increased selectivity by blockage of unselective active sites and reduction in the space in the pores due to coke deposition, as discussed in literature [1, 7, 8]. H-ZSM5 provided 51.5 % conversion of *n*-butene with 58.0 % selectivity to isobutene. The modifications decreased conversion of *n*-butene obtained over the parent catalyst. The highest drop, about 33 %, was obtained after 3-APES deposition. Although this modification caused pore blockage, decreased acidity and surface area significantly, selectivity to isobutene was affected slightly.

The TEOS modification decreased conversion obtained with parent zeolite by 8 %. This was attributed to a decrease in strong acid sites. However, it improved the selectivity to isobutene from 58.0 to 63.7 %. This was probably due to elimination of easily accessible, non-shape selective acid sites found on the external surface.

The AHFS treatment lowered the conversions obtained over parent catalyst by about 10 %; i.e., to 42.3 %. On the contrary, the selectivity to isobutene was enhanced dramatically, from 58.0 to 87.5 %. Reduction in conversion was attributed to drop of weak and strong acid sites and to noteworthy drop of Brønsted acid sites and slight increase Lewis acid sites. This acidity change together with slight decrease in pore size enhanced the selectivity.

Mild alkali treatment did not change activity and selectivity of the parent catalyst significantly; the conversion decreased by about 3 % while selectivity to isobutene increased slightly, to 60.1 %. This might be due to the reduction observed in strong and weak acid sites. Pre-alkali and acid treatment affected activity as for alkali alone. However, it improved parent catalyst selectivity by 10 %. This was probably due to significant drop in strong acid sites and the decrease in the external acidity. Acid treatment alone reduced parent's catalysts conversion by 10 %. However, selectivity to isobutene was not affected. The drop in activity was related to the removal of strong acid sites.

Conclusions

The crystal structure of the H-ZSM-5 was preserved after modifications. The modifications affected the acidity and textural properties of the H-ZSM5 differently. The distribution of acid site strength and pore size had considerable effects on isobutene selectivity. The TEOS modification narrowed and blocked pores and decreased strong acid sites substantially. However, no significant change in conversion and selectivity was obtained. 3-APES narrowed and closed the pore openings and reduced acidity. It deteriorated the parent catalysts selectivity. AHFS treatment provided the best improvement in selectivity. By this modification, strong and weak acid sites were decreased and Lewis acidity was increased while pore size changed slightly. The alkali treatment caused dealumination and desilication. Although the total acidity decreased to some extent and external acidity decreased considerably, selectivity to isobutene was almost the same as that of the parent catalyst. Pre-alkali and acid treatment decreased strong acids and external acidity strongly. Nevertheless, conversions similar to the parent catalyst were obtained as the selectivity increased by about 10 %. Acid treatment affected acidity significantly. It gave lower conversions and selectivities than the parent catalyst.

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