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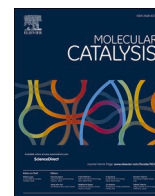
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Modification of commercial Y zeolites by alkaline-treatment for improved performance in the isomerization of glucose to fructose

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ABSTRACT

Isomerization of glucose to fructose is a key reaction step in the efficient production of valuable renewable chemical intermediates from biomass. Zeolites have been widely used to promote glucose isomerization, but only limited structure-activity relationship has been established and applied to optimize the reaction. In this work, commercial Y zeolites were modified by alkaline-treatment and their physicochemical properties and structures were correlated in order to optimize the catalytic performance for glucose isomerization. For H-Y, the alkaline-treatment developed new mesoporous structures with larger pore, modified the Si-O(H)-Al bonds and extracted silica from framework structures creating more tetrahedral extra-framework Lewis acidic aluminum. This increased the isomerization selectivity towards fructose more than twelve times and decreased significantly acetalization/ketalization side reactions compared to the pristine zeolite. In contrast, Na-Y contained mainly micropores and had less tetrahedral non-framework acidic Al-species, resulting in low glucose conversion and low fructose yield due to limited substrate accessibility to the pores, although the number of acid sites was tenfold higher than in H-Y. The study demonstrates how commercial Y zeolites can be designed by alkaline-treatment to comprise mesopores and weak acid sites, which greatly improve the catalytic performance for glucose isomerization to fructose.

1. Introduction

Lignocellulosic biomass is an abundant carbon-neutral resource, and its conversion to renewable fuels and chemicals through green catalytic processes has become a promising strategy to mitigate energy shortage and CO₂ emission [1-4]. As a feedstock, lignocellulose predominantly comprises polymeric glucose (cellulose), which can be hydrolyzed to produce glucose on a commercial scale. The glucose can form fructose or mannose by aldose-to-ketose isomerization or epimerization, respectively. Especially, the interconversion and production of fructose is an essential step in the valorization strategy of lignocellulose, as fructose is a key intermediate compound to form value-added chemicals, such as 5-hydroxymethylfurfural and levulinic acid [5, 6].

Zeolites constitute a well-known family of porous materials with high porosity, surface area and stability, and they generally comprise

structural characteristics that are very important parameters for their catalytic function [7]. Furthermore, the materials can accommodate a wide variety of metal cations or cationic metal complexes, which modify the acidity and basicity of the material. This makes zeolites attractive solid catalysts for sugar transformations, including the isomerization of glucose to fructose [8, 9]. Hence, Holm et al. [10] applied purely Lewis acidic zeotypes, such as Sn-beta, for the catalytic conversion of mono- and disaccharides to methyl lactate in methanol at 160 °C (68 % yield with sucrose as substrate). Concurrently, Davis and co-workers [11, 12] reported Sn-beta to be a highly active, selective, and recyclable catalyst for the isomerization of glucose to fructose in water at low temperatures of 110–140 °C (31 % fructose yield). Using alternative Sn-modified zeolite catalysts, later studies have established that Lewis acidic sites comprising tin in zeolites provide attractive activity for the conversion of sugars [13-17].

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Table 1
Porosity characteristics of pristine and alkaline-treated Y zeolites.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Pore width ^a (Å)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)			$V_{\text{mic}}/V_{\text{total}}$ (%)
			V_{total} ^b	V_{mic} ^c	$V_{\text{mes+mac}}$ ^d	
HY0	828	24.9	0.515	0.255	0.260	49.5
HY1	819	25.3	0.518	0.249	0.269	48.1
HY2	359	43.1	0.386	0.008	0.378	2.1
HY3	453	44.6	0.505	—	—	—
HY4	296	59.3	0.423	—	—	—
HY5	224	67.6	0.378	0.001	0.377	0.3
HY6	276	58.3	0.401	—	—	—
HY7	173	75.4	0.326	0.004	0.322	1.2
NY0	727	19.1	0.348	0.319	0.029	91.7
NY1	737	19.1	0.353	0.323	0.030	91.5
NY2	715	19.1	0.342	0.312	0.030	91.2
NY3	723	19.2	0.347	0.316	0.031	91.1
NY4	729	19.2	0.350	0.318	0.032	90.9
NY5	726	19.2	0.348	0.318	0.030	91.4
NY6	719	19.2	0.346	0.314	0.032	90.8
NY7	730	19.3	0.353	0.318	0.035	90.1

^a Pore width = adsorption average pore width (4 V/A) determined from the BET surface area.

^b V_{total} = total pore volume obtained at relative pressure of 0.95.

^c V_{mic} determined from t -plot.

^d $V_{\text{mes+mac}} = V_{\text{total}} - V_{\text{mic}}$. Hyphen indicate that data was below the error of the instrument.

Besides Lewis acidic sites, zeolites also provide Brønsted acid sites in their protonated form (H-form). The role of the Lewis and Brønsted acidic sites in the catalyzed isomerization of glucose to fructose has been corroborated using H-Y (2.6) zeolite (more Lewis acid sites) and Dowex 50WX8-100 resin (purely Brønsted acid sites) in methanol. The results

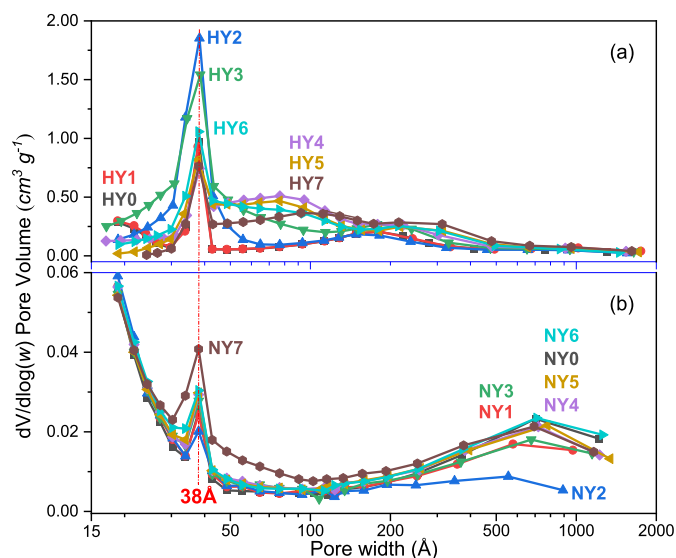


Fig. 2. The pore size distribution of pristine and alkaline-treated (a) H-Y and (b) Na-Y zeolites.

showed that the Lewis acid sites promoted the formation of fructose and methyl fructosides, while the Brønsted acid sites contributed to the formation of methyl glycosides [18]. Relying on this reactivity difference, conversion of glucose to fructose over commercial H-USY (6) zeolite resulted in a remarkable 55 % yield of fructose, when the

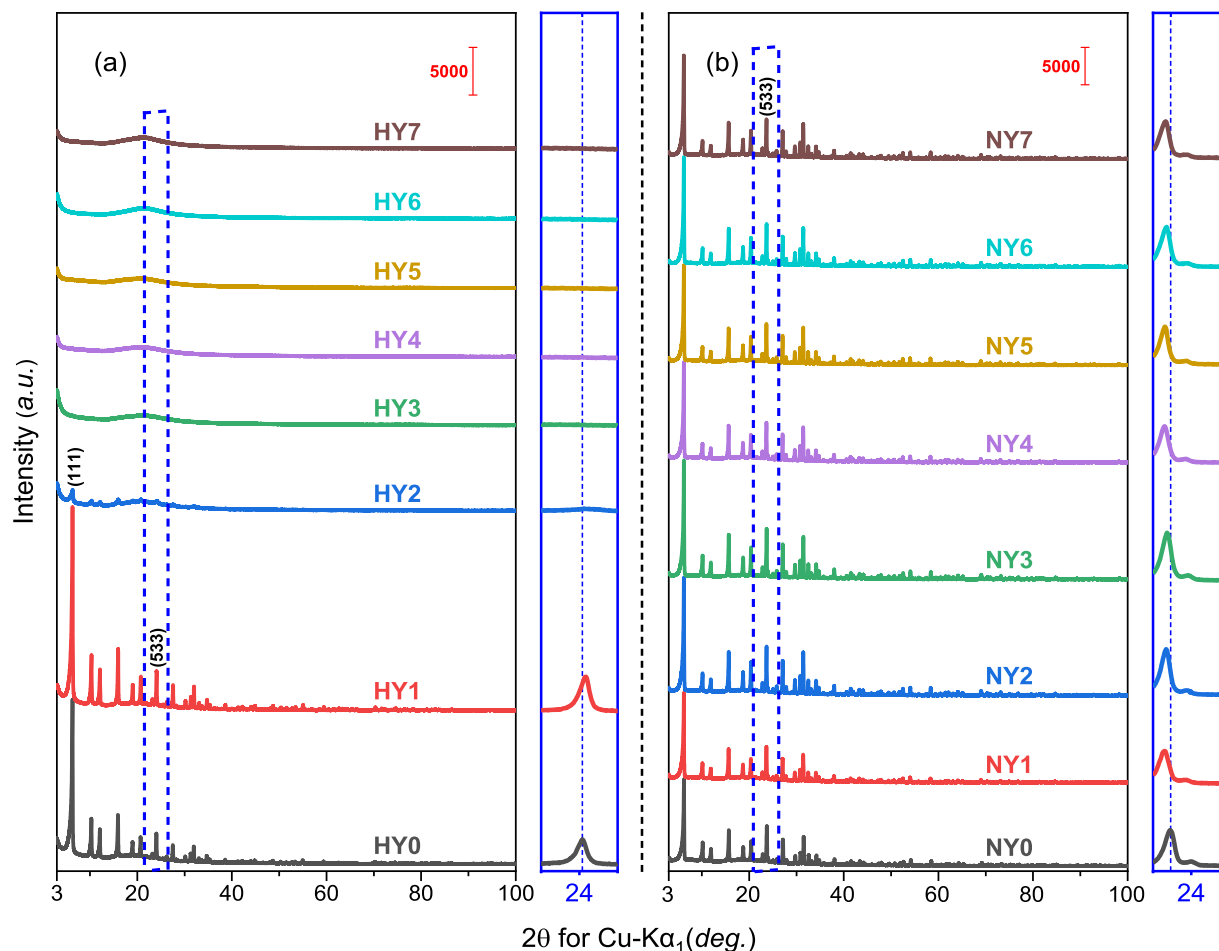


Fig. 1. XRD patterns of the pristine and alkaline-treated (a) H-Y and (b) Na-Y zeolites.

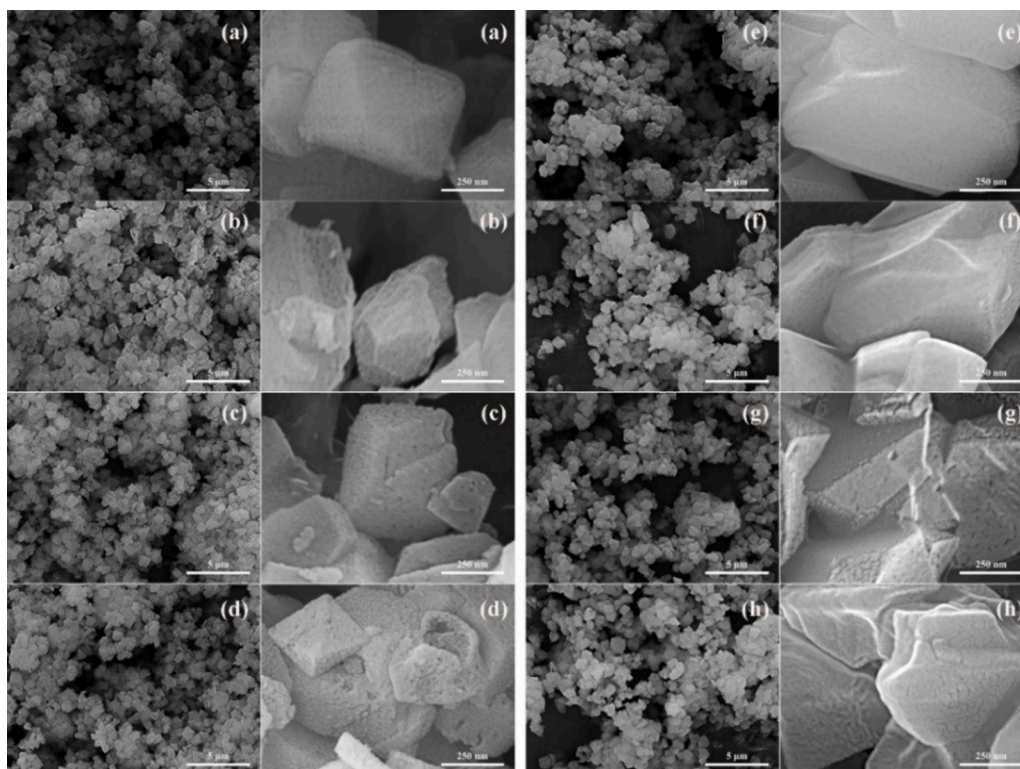


Fig. 3. SEM images of pristine and alkaline-treated H-Y zeolites (left) and Na-Y zeolites (right). (a) HY0, (b) HY3, (c) HY5, (d) HY7, (e) NY0, (f) NY3, (g) NY5 and (h) NY7 (5 μm scale bars on overview images and 250 nm scale bars on zoomed images).

reaction was separated into two steps performed in methanol and water, respectively [19, 20]. When a similar reaction approach was applied using longer alcohols, such as ethanol or propanol, instead of methanol significantly lower yields of fructose and alkyl fructosides were formed along with alkyl glycosides [19]. Alternative polar organic solvents with good sugar solubility have also proven less effective for the isomerization of glucose to fructose [21].

As an alternative to acidic zeolites, alkaline modified zeolites or zeolite-based materials also have great potential as basic catalysts and catalyst supports for glucose isomerization since aldose-to-ketose sugar isomerization can be facilitated with base [22]. Accordingly, alkali- and alkaline-earth metals have frequently been introduced into zeolites as solid base catalysts for glucose conversion [23, 24]. For example, Graça et al. [25–27] reported that the conversion of glucose and the yield of fructose (35 %) were greatly improved when magnesium ions were added to basic zeolites.

The studies reported in the literature on glucose isomerization with zeolites or zeotype materials comprise many different types of zeolites with the materials being used as an acidic or basic catalyst or as catalyst support [21, 28, 29], but few studies have investigated the relationship between physicochemical properties and structures of the zeolites and their catalytic performance [30, 31]. In this work, two commercial Y zeolites were modified by alkaline-treatment under different conditions and their structural variations were elucidated. Alkaline-treatment is a widely used method for desilication of zeolites, which results in changes in their pore structure and can improve performance in catalyzed reactions [32]. Based on the obtained results, we have attempted to establish the structure-activity relationship to optimize the catalytic performance in the isomerization of glucose to fructose, and provide a rational design of an improved zeolite catalyst for the conversion of sugar.

2. Experimental

2.1. Chemicals

Glucose (99.5 %), methanol (99.8 %, anhydrous), and NaOH (≥ 99.0 %, Assay) were purchased from Sigma-Aldrich and were used as received. The commercially available zeolites Na-Y (CBV 100, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5.1$) and H-Y (CBV 760, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 60$) were obtained from Zeolyst International, The Netherlands.

2.2. Catalyst preparation

The commercial Y zeolites were alkaline-treated with NaOH solutions with different concentrations (0.01, 0.1, and 0.2 mol L^{-1}) for various times (30, 60, and 300 min) at different temperatures (45, 65, and 90 $^{\circ}\text{C}$) (Table S1). Typically, the zeolite (0.5 g) and NaOH solution (10 mL) were mixed in a glass tube, which was immersed in an oil bath at the set temperature for a desired time under magnetic stirring. Afterwards, the zeolite was washed thoroughly with deionized water until the washing water had neutral pH, followed by drying overnight in an oven at 110 $^{\circ}\text{C}$. All samples were heated from room temperature to 550 $^{\circ}\text{C}$ (heating ramp 5 $^{\circ}\text{C min}^{-1}$) and calcined at 550 $^{\circ}\text{C}$ for 6 h.

2.3. Catalyst characterization

Nitrogen physisorption was performed with zeolite samples for porosity and BET surface area measurements using a Micrometrics ASAP 2020 analyzer. The samples were degassed in vacuum at 200 $^{\circ}\text{C}$ for 4 h prior to determining adsorption-desorption isotherms at -196 $^{\circ}\text{C}$.

X-ray diffraction patterns (XRD) of all zeolite samples were collected on a Huber G670 Guinier diffractometer using $\text{Cu-K}\alpha_1$ radiation ($\lambda = 1.5406$ \AA) from a focusing quartz monochromatic beam with an exposure time of 1 h at a step size of 0.005 $^{\circ}$ in the 2θ interval 3–100 $^{\circ}$.

Fourier-transform infrared spectroscopy (FTIR) analyses of zeolites

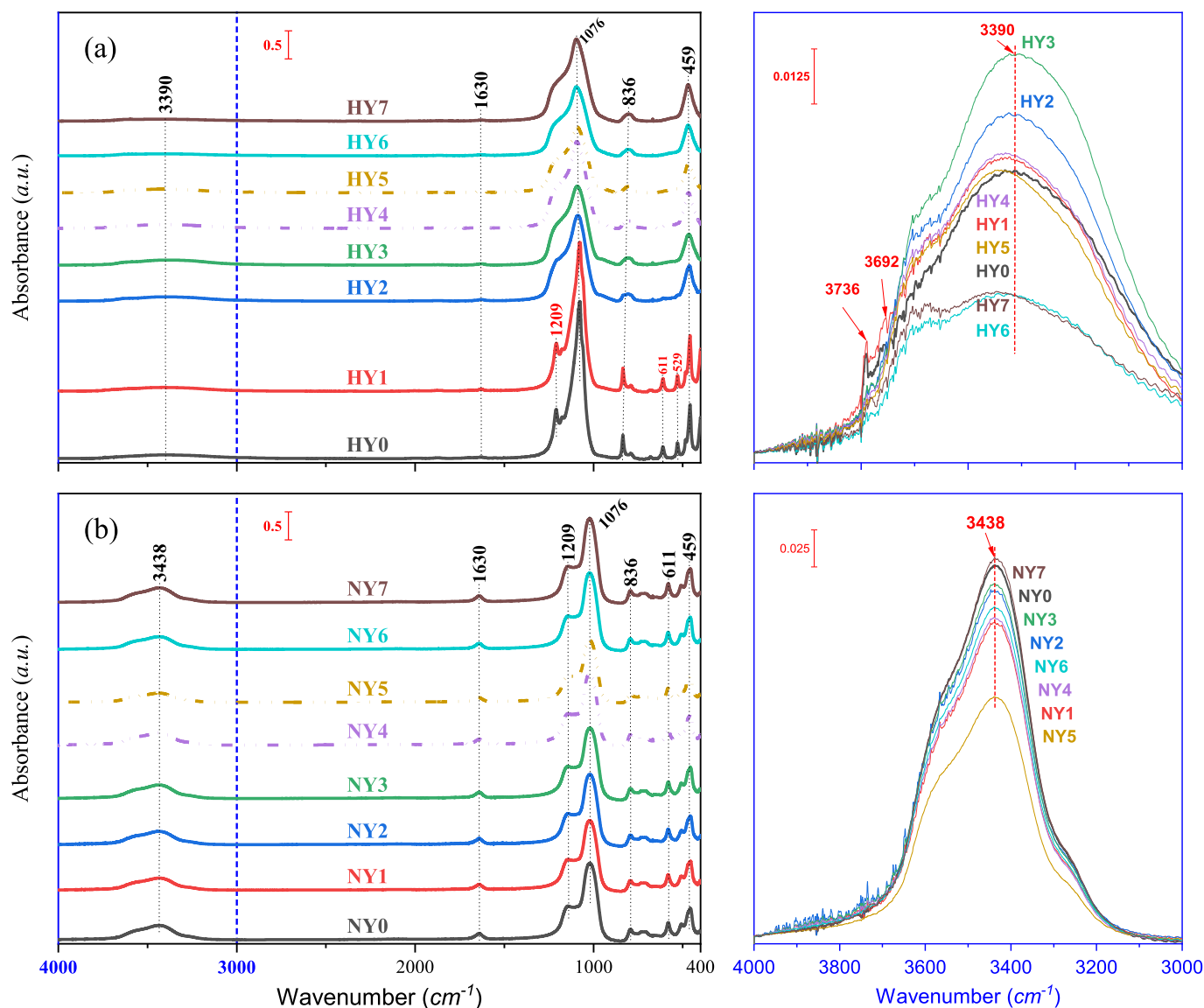


Fig. 4. FTIR spectra of the pristine and alkaline-treated (a) H-Y and (b) Na-Y zeolites (ν/cm^{-1} : 3736 (isolated Si-OH), 3692 (Al-OH), \sim 3400 (H-bond), 1630 (H-OH), 1209, 1076, 836 and 459 (Si-O-Si and Si-O-Al primary structural units), 611 and 529 (SiO₄ and AlO₄ pseudo-lattice tetrahedral)).

were performed on a Thermo Scientific Nicolet iS5 spectrometer with a measuring range of 4000–400 cm^{-1} , spectral resolution of 2 cm^{-1} and scan number of 128, respectively. All samples were mixed with KBr powder with a mass ratio of 1:100 (zeolite:KBr), pressed to a pellet and then analyzed.

²⁹Si and ²⁷Al magic angle spinning nuclear magnetic resonance (MASNMR) spectra of samples were acquired on a Bruker AVANCE III HD spectrometer operating at a magnetic field of 14.05 T using a 4 mm CP/MAS BBFO probe.

Ammonia temperature-programmed desorption (NH₃-TPD) was performed with zeolite samples using a Micrometrics AutoChem II 2920 chemisorption analyzer. About 100 mg sample was inserted into a glass U-tube reactor supported between two quartz wool plugs. In a typical analysis, the sample was pre-treated in He at 500 °C for 110 min (heating ramp 20 °C min⁻¹) followed by adsorption of ammonia (1 % NH₃ in He, 50 mL min⁻¹) at 150 °C for 30 min. Next, the gas flow was changed to He (50 mL min⁻¹), the physisorbed ammonia removed over 230 min, and ammonia desorption was carried out between 150 and 500 °C (heating ramp 10 °C min⁻¹) and quantified by analysis using a thermal conductivity detector (TCD).

Scanning electron microscopy (SEM) images were recorded of the samples using an FEI Quanta FEG 250 ESEM microscope operated at 15 kV, and the working distance was 5.0 mm.

2.4. Catalytic tests

Catalytic isomerization of glucose was performed with the zeolites in 15 mL Ace pressure tubes. Zeolite (75 mg), glucose (125 mg) and methanol (4 g) were mixed in the reaction tube under magnetic stirring (zeolite loading 1.8 wt. % and glucose concentration 0.13 M). The tube was closed and heated in an oil bath (preheated) at a set temperature for a desired time. After the reaction, the tube was quickly placed in cold water to quench the reaction, and the reaction mixture diluted to 100 mL with deionized water, followed by filtration through a 0.22 μm filter membrane. The reaction mixtures were analyzed by high-pressure liquid chromatography (HPLC) with an Agilent 1200 series instrument equipped with a refractive index detector (RID) and a Rezex-RCM-Monosaccharide Ca²⁺ column (300 \times 7.8 mm) using MilliQ water as eluent (flow 0.6 mL min⁻¹, column temperature 80 °C).

NMR analysis of reaction mixtures was performed on a Bruker

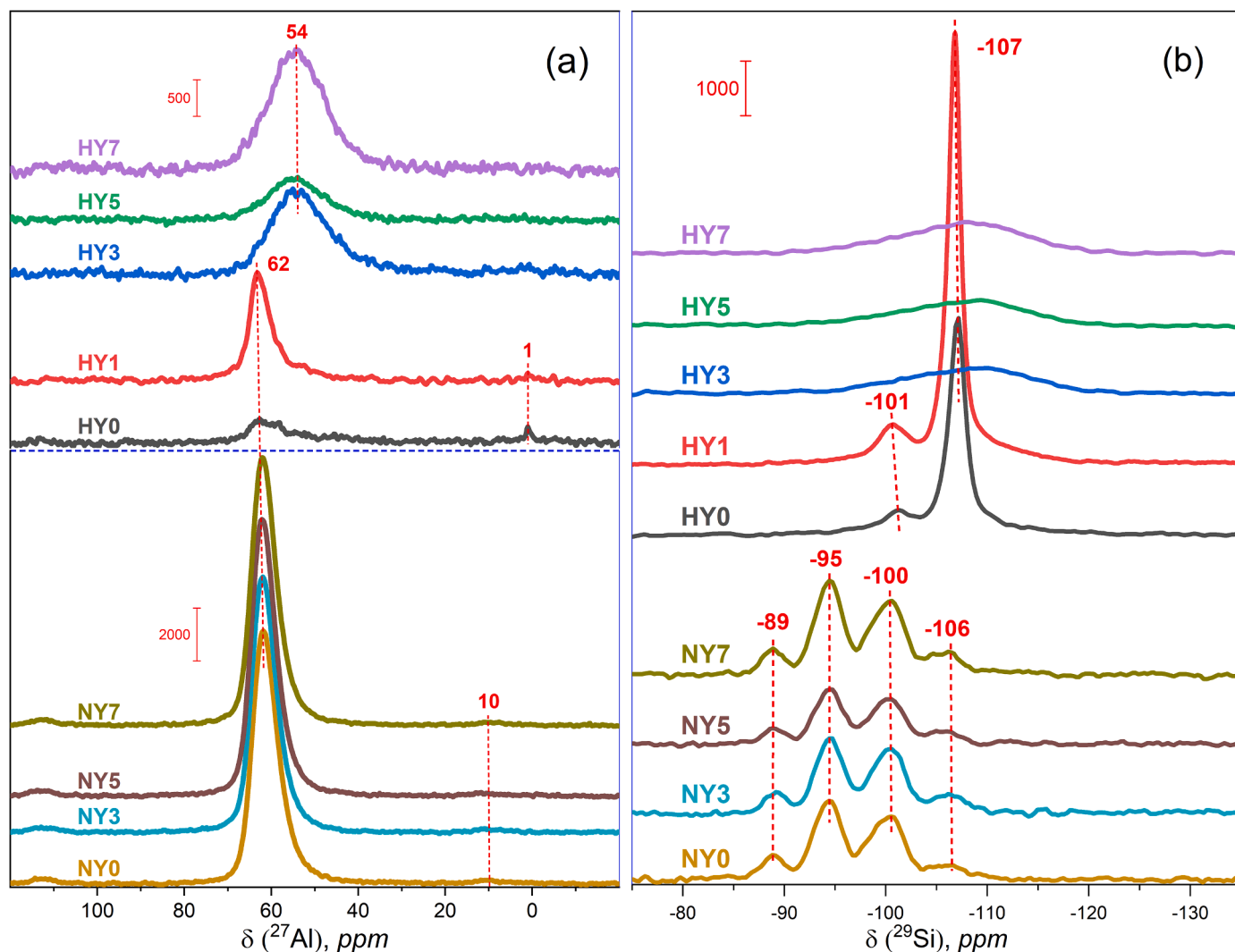


Fig. 5. (a) ^{27}Al and (b) ^{29}Si MAS NMR spectra of pristine and alkaline-treated Y zeolites (asterisks denote background signal from the empty rotor). $\delta(^{27}\text{Al})/\text{ppm}$: 62 (tetrahedral framework Al-species), 54 (tetrahedral non-framework Al-species), 1 and 10 (octahedral extra-framework Al-species). $\delta(^{29}\text{Si})/\text{ppm}$: -101 (Si[1Al,3Si]), -107 (Si[0Al,4Si]), -89 (Si[3Al,1Si]) and -95 ppm (Si[2Al,2Si]).

AVANCE III 800 MHz spectrometer equipped with a TCI z-gradient CryoProbe and a SampleJet sample changer. Samples contained 500 μL of crude reaction mixture mixed with 100 μL of methanol- d_4 as the lock substance and a defined mass (~ 20 mg) of DMSO as the internal quantification standard. Yields of reaction products were quantified by quantitative ^{13}C NMR and ^1H - ^{13}C NMR analysis as previously described [33].

3. Results and discussion

3.1. Catalyst characterization

Two commercial Y zeolites and a series of corresponding alkaline-treated zeolites were prepared by treating the zeolites with aqueous NaOH solution at various reaction conditions (Table 1). XRD patterns of the pristine and alkaline-treated Y zeolites are shown in Fig. 1. For HY1 the (111) peak intensity ($2\theta = 6.5^\circ$) increased and the (533) peak ($2\theta = 24.0^\circ$) shifted to higher angle compared to HY0 when treated with 0.01 M NaOH (Fig. 1a). This suggested removal of extra-framework aluminum and silicon and an accompanying decrease in unit cell, respectively [34]. Moreover, at alkaline concentrations above 0.1 M NaOH the crystallinity of the H-Y zeolites decreased dramatically causing the framework structure to collapse and to become amorphous

(Fig. 1a) [35, 36]. By contrast, the peak intensity of the Na-Y zeolites remained nearly unaffected by the alkaline-treatment revealing an intact structure (Fig. 1b), though a shift of the (533) peak ($2\theta = 24.7^\circ$) to lower angle indicated some exchange of protons to Na^+ in the structure and a corresponding increase in unit cell volume and interplanar spacing [34, 37].

The porosity and morphology of the resulting samples were analysed by N_2 physisorption and SEM, respectively, and the characteristics are summarized in Table 1. Fig. 2 shows the pore size distributions of the samples obtained from the nitrogen adsorption-desorption isotherms (Figs. S1 and S2). As the concentration of the alkaline NaOH solution increased, larger pores formed in the alkaline-treated H-Y zeolites (HY1-HY3), resulting in an increased total pore volume with no micropores and lower surface area (Fig. 2a, Table 1). Prolonged treatment or treatment at higher temperature using 0.2 M NaOH (HY3-HY5 or HY4, HY6 and HY7) similarly indicated that closed structures opened when silicon dissolved during the alkaline-treatment and micropores merged to form new mesopores in the range of 43–480 \AA [38]. Overall, the alkaline-treatment allowed altering the average pore width of the H-Y zeolites from 24.9 to 75.4 \AA .

The NY0 is an ultra-stable zeolite having a mainly microporous structure with the micropore volume making up above 90 % of the total pore volume (Table 1 and Fig. S2). In contrast to HY0, the pore size

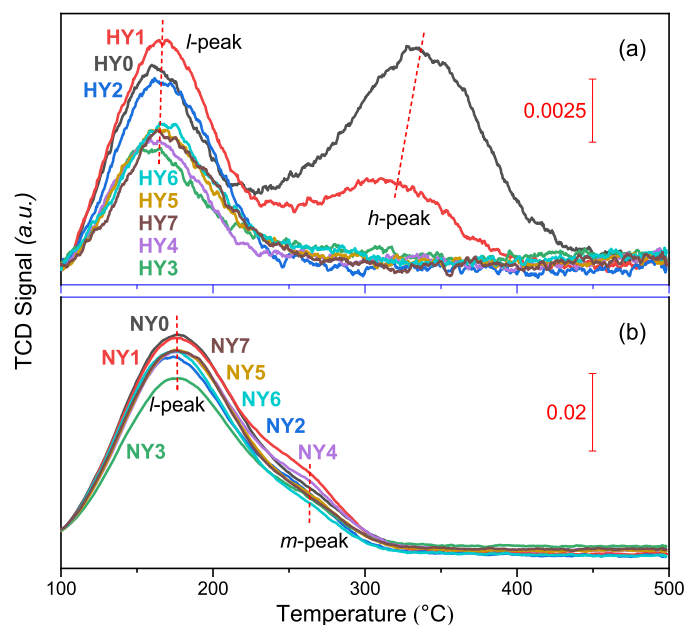


Fig. 6. NH_3 -TPD profiles of pristine and alkaline-treated (a) H-Y and (b) Na-Y zeolites.

Table 2
Isomerization of glucose over pristine and alkaline-treated Y zeolites.^a

Sample	Glucose Conv. (%)	Fructose Yield (%)	Selectivity (%)	Balance (%) ^d
HY0 ^b	93.5	6.2 ^c	6.6	12.7
HY1 ^b	25.3	<2.0	<2.0	<76.7
HY2	21.2	16.1	75.7	94.8
HY3	24.7	17.9	72.4	93.2
HY4	19.5	13.5	69.0	94.0
HY5	27.7	19.8	71.3	92.1
HY6	21.3	17.1	80.0	95.7
HY7	22.6	19.1	84.6	96.5
NY0	20.3	10.4	51.0	90.0
NY1	11.9	2.9	24.2	91.0
NY2	9.5	2.1	22.2	92.6
NY3	11.0	2.6	23.9	91.6
NY4	15.4	2.7	17.7	87.3
NY5	15.9	2.7	17.0	86.8
NY6	15.5	3.9	24.9	88.4
NY7	18.8	4.1	21.7	85.3

^a Reaction conditions: 125 mg glucose, 75 mg catalyst, 4 g methanol, 120 °C, 120 min.

^b Quantified by ^1H - ^{13}C HSQC NMR (Fig. S3), see Table S3 for more detailed data.

^c Yield of methyl fructosides.

^d Sum of the yields of glucose and fructose.

distribution of NY0 remained almost unchanged upon alkaline-treatment (Fig. 2b), and only treatment at high temperature with high base concentration (90 °C, 0.2 M NaOH) resulted in an increased pore width range of 30–400 Å and a slightly enlarged average pore width (NY7). Analogous to HY0, the silicon here likely dissolved from the NY0 merging some of the smaller pores into larger pores [39].

SEM images of the pristine and alkaline-treated zeolites are shown in Fig. 3. Opposite to pristine HY0, the alkaline-treated HY0 zeolites had surface roughness and obvious pores (Figs. 3a-3d) [40] with increasing pore sizes according to the harshness of the treatment condition. On the other hand, the alkaline-treated Na-Y zeolites were less rough with less visible pores, suggesting that the NaOH solution could have a significant effect on the structures of H-Y zeolite (Figs. 3e-3h).

FTIR spectra of the zeolites were also recorded after alkaline-treatment (Fig. 4) and the peaks were assigned according to previous

studies [41] as $\nu/\text{cm}^{-1} = 3736$ (isolated Si-OH), 3692 (Al-OH), ~ 3400 (H-bonding), 1630 (H-O-H), 1209, 1076, 836 and 459 (Si-O-Si and Si-O-Al primary structural units), 611 and 529 (SiO_4 and AlO_4 pseudo-lattice tetrahedral). The alkaline-treatment first predominantly removed extra-framework silicon/aluminum species and surface hydroxyl groups causing the peaks at 3736 cm^{-1} for HY2-HY7 to disappear or decrease significantly in intensity. At alkaline concentrations above 0.2 M, several other peaks (1209, 611 and 529 cm^{-1}) also disappeared or decreased in intensity (1076 and 836 cm^{-1}) in the H-Y zeolites spectra due to framework desilication and breakage and/or partial hydrolysis of framework Si-O-Si(Al), eventually forming Si-OH and Al-OH linkages [42]. This likely resulted in loss of crystallinity and developed mesoporosity as confirmed by the XRD and porosity analysis results (vide supra) [43]. The newly formed Si-OH or Al-OH groups increased the amount of H-bonded water molecules ($\sim 3400\text{ cm}^{-1}$) adsorbed on these sites in HY1-HY5. However, at higher alkaline-treatment temperatures the framework structures of the H-Y zeolites was further deformed resulting in a significantly decreased surface area (Table 1) with less surface OH groups and an accompanying lower amount of H-bonded water (HY6-HY7).

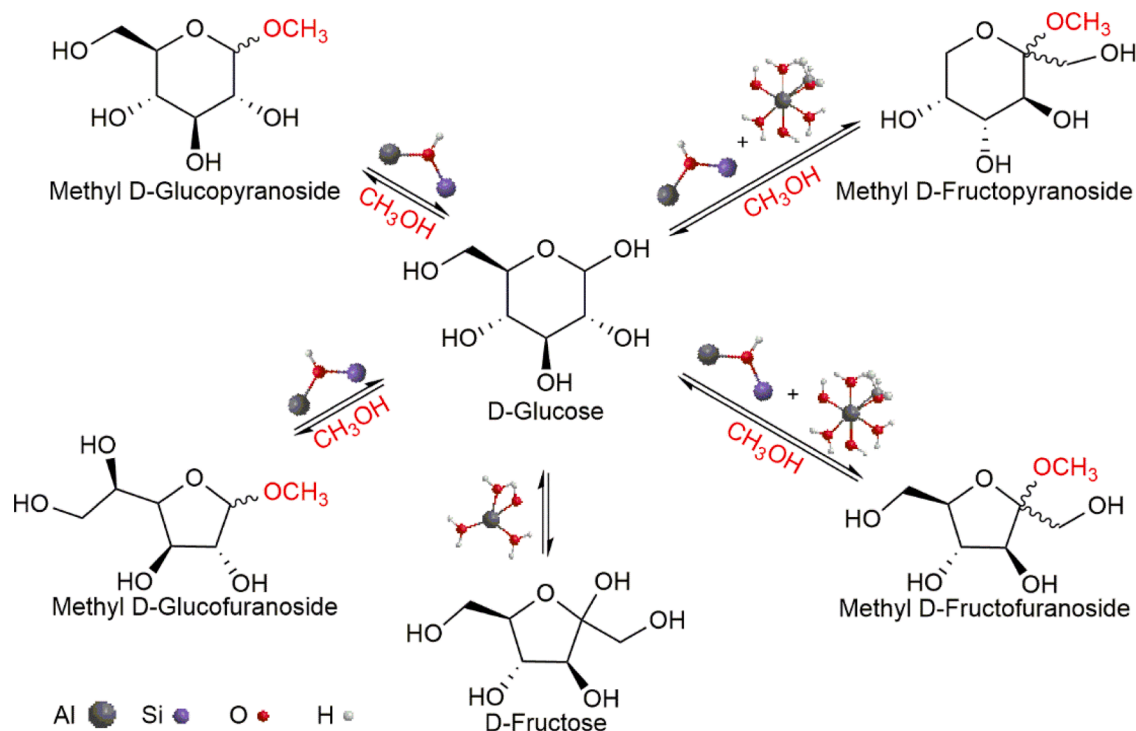
Compared to the pristine H-Y zeolite, Na-Y had a higher relative content of Al (i.e., lower Si/Al ratio) and thus more surface Al-OH groups (3438 cm^{-1} peak more intense), which are known to hinder desilication [44]. Accordingly, the intensities of the Na-Y peaks only slightly changed by the alkaline-treatment, confirming that the structure remained largely intact. Here, longer treatment time favoured the removal of surface Si-OH groups (Fig. 4b; NY5 treated for 300 min), and higher treatment temperature allowed the alkaline solution to perturbate the framework structure, leading to the formation of more exposed Si-OH groups (Fig. 4b; NY7 treated at 90 °C) and larger pore size (Table 1).

Solid state NMR spectroscopy is a unique tool to characterize the local chemical environments in zeolites [45] and selected samples were characterized by ^{29}Si and ^{27}Al MAS NMR (Fig. 5). The ^{27}Al MAS NMR spectra (Fig. 5a) of the Na-Y zeolites revealed a strong signal at 62 ppm that can be assigned to tetrahedral framework Al-species, and weaker signals at 1 and 10 ppm that can be attributed to octahedral extra-framework Al-species in (AlO_6) [46, 47]. Especially the peak at 10 ppm correlated with non-acidic terminal Al-OH (six-coordinated Al site) groups on the surface of zeolites [48], and the FTIR spectra also showed that the surface of Na-Y zeolites possessed OH hydroxyl groups (Fig. 4b).

In the case of H-Y zeolites, the signal at 1 ppm disappeared after the alkaline treatment (Fig. 5a) corroborating that the alkaline solution preferentially reacted with the weak acidic Si/Al surface species and removed extra-framework Al-species. Afterward, desilication likely occurred on the framework structures, especially under higher treatment temperatures. The extraction of framework-silicon significantly modifies the chemical environment of Al-species from the tetrahedral framework Al-sites to tetrahedral extra-framework Al-sites and thus increasing the relative content of Al [49, 50]. Consequently, the signals at 62 ppm for the HY3, HY5 and HY7 zeolites were shifted to 54 ppm and broadened. A similar signal shift was not observed with the series of Na-Y zeolites, because the framework structures of Na-Y zeolites are protected by negatively charged $\text{Al}(\text{OH})_4^-$ species formed due to the higher Si/Al ratio [51].

Moreover, the ^{29}Si MAS NMR spectrum of pristine H-Y showed two signals at -101 and -107 ppm (Fig. 5b) corresponding to Si[1A1,3Si] and Si[0Al,4Si], respectively, while the spectra of the Na-Y zeolites revealed two additionally signals at -89 and -95 ppm (Fig. 5b) corresponding to Si[3Al,1Si] and Si[2Al,2Si], respectively [46]. Hence, desilication of H-Y by the alkaline-treatment broadened the signals and reduced signal intensity, and destroyed Si[1A1,3Si] and Si[0Al,4Si] sites, whereas longer treatment time extracted silicon from the Na-Y zeolites, especially the surface Si-species, most likely the weak acidic Si-OH, leading to an obvious decrease in the intensity of H-bonds (Fig. 4b).

The number and strength of acid sites in the Y zeolites were



Scheme 1. Illustration of the role of zeolite sites on the glucose conversion in methanol.

examined by NH_3 -TPD. The individual desorption profiles are shown in Fig. 6 and the calculated amount of acid sites summarized in Table S2. The pristine H-Y zeolite had two obvious desorption peaks at 165 and 335 °C that can be assigned to weak acid sites (*l*-sites) and strong acid sites (*h*-sites), respectively [52]. The TPD profiles of the Na-Y zeolites revealed a maximum at 175 °C corresponding to weak acid sites (*l*-sites), and a shoulder peak was appeared around 265 °C, which can be assigned to medium-weak acid sites (*m*-sites) in contrast with the weak and strong acid sites. The alkaline-treatment effectively removed the *h*-sites, while harsher treatment conditions were needed to remove the weaker sites, as expected.

3.2. Catalytic testing

Initially, the catalytic isomerization of glucose was examined with all H-Y and Na-Y zeolites in methanol at 120 °C and the result are shown in Table 2. The conversion of glucose decreased significantly with the H-Y catalysts from 93.5 % with pristine HY0 to less than 30 % for the alkali-treated catalysts HY1-HY7. However, the corresponding fructose selectivities increased by more than twelve-fold from initially 6.6 % (HY0) to 84.6 % (HY7), with no methyl fructosides being formed with the latter catalyst. This improvement in selectivity also resulted in a notably increase in fructose yields for some of the catalysts, especially HY5, where the yield increased from 6.2 to 19.8 %. For these catalysts (HY2-HY7), the competing methyl glucoside formation also decreased markedly (products were not detected by ^1H - ^{13}C HSQC NMR, Figs. S3a-S3c). For the alkali-treated Na-Y zeolites (NY1-NY7) both glucose conversions and fructose selectivities (and the corresponding fructose yields) were lower than for the pristine Na-Y zeolite as well as for the H-Y zeolites treated under the same alkaline conditions.

The catalytic conversion of glucose in methanol with H-Y zeolites is prone to form methyl glycosides, including methyl glucofuranosides and methyl glucopyranosides, as by-products in the presence of strong Brønsted acidic sites, i.e. Si-O(H)-Al [18, 52]. Such strong acid sites were most likely present in the pristine zeolite HY0 but to a much lower extent in the alkaline-treated catalysts HY1-HY7, resulting in a decreased yield of these by-products. In line with this, the NH_3 -TPD profiles clearly

indicated that HY0 possessed strong acid sites (0.232 mmol; *h*-sites) (Fig. 6a and Table S3) which greatly decreased upon desilication (HY1), and these sites were responsible for the formation of methyl glucosides as mentioned above. The yield of methyl fructosides formed with HY0 reached a maximum of 9.8 % after 5 h of reaction (Table S3), whereas no significant formation of fructose or methyl fructosides occurred with HY1 due to its lower amount of weak acid sites (*l*-sites) or higher strong acid sites (*h*-sites). The mild alkaline-treatment removed the weak surface acid sites, especially the extra-framework Lewis acid sites (Fig. 5a), and suggests that no new active sites responsible for glucose isomerization was generated. The harder treatment conditions, i.e. higher temperature or longer reaction time, remarkably destroyed the framework structure of H-Y (Figs. 1 and 3a), leading to the extraction of framework silicon and subsequently converted tetrahedral framework Al-species to tetrahedral extra-framework Lewis acidic Al-species as also found in previous reports (Fig. 5a) [23, 53]. The generation of these new active Al-species catalyzed the glucose isomerization and enhanced the fructose selectivity. Moreover, the generation of mesoporosity by the alkaline-treatment (Table 1) likely also increased the conversion of glucose.

The amount of weak acid sites (*l*-sites) in pristine NY0 was about ten times higher than in HY0 (Table S2). Nevertheless, the conversion of glucose with both NY0 and the alkaline-treated zeolites NY1-NY7 was found to be low, and even more, the alkaline-treatment decreased the fructose yield (Table 2). The Na-Y zeolites contained mainly micropores with limited substrate accessibility to the pores (Table 1), which likely contributed to lower the glucose conversion. In addition, the alkaline-treatment removed extra-framework Al-species and some weakly acidic Si-OH (Figs. 4b, 5a and 6b, and Table S2), which possibly also contributed to reducing the glucose conversion as well as the yield and selectivity of fructose. Scheme 1 illustrates the dominant role of zeolite sites on the glucose conversion in methanol.

After the initial screening of zeolite reactivity, the effect of reaction time on the glucose isomerization was investigated with selected zeolite catalysts and the results are shown in Fig. 7. The conversion of glucose reached >93.5 % for the pristine HY0 after 10 h of reaction (Table S3), whereas the conversion only reached up to 42 % for the alkaline-treated

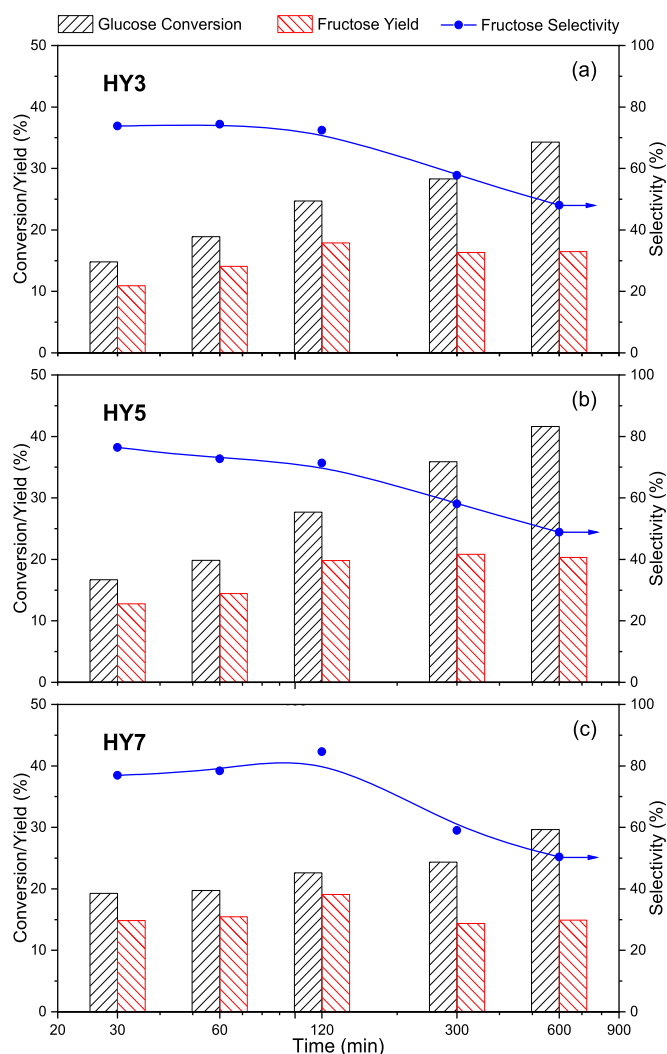


Fig. 7. Effect of reaction time on the isomerization of glucose using alkaline-treated (a) HY3, (b) HY5 and (c) HY7 zeolites (Reaction conditions: 125 mg glucose, 75 mg catalyst, 4 g methanol, 120 °C).

zeolite HY5 after 10 h of reaction (Fig. 7a). The corresponding fructose yields remained unchanged around 16.5 % for HY3 and 15 % for HY7, but gradually increased over time to 20 % for HY5 after 10 h. Notably, a large amount of methyl glucosides formed with HY0 (up to 48.4 % methyl glucofuranosides after 1 h of reaction, and 54.4 % methyl glucopyranosides after 0.5 h of reaction, Table S3) due to its relative high Brønsted acidity [54], while none formed with the alkaline-treated catalysts (HY2-HY7) where all Al-O(H)-Si bonds were destroyed and the strong Brønsted acidic sites removed. Hence, the alkaline-treatment of the H-Y zeolites significantly decreased acetalization into methyl glucosides compared to the pristine zeolite.

Finally, the influence of reaction temperature was investigated at 80–140 °C with the alkaline-treated catalysts HY3, HY5 and HY7 and the results are compiled in Fig. 8. At increased reaction temperature, the conversion of glucose increased with HY5 up to 35.8 %, and the yield of fructose increased and reached 20.2 %. Similarly, for the HY3 and HY7 catalysts the glucose conversion increased up to 30–35% and also the yields of fructose increased reaching 18–20 % while the yield of methyl glucosides remained low at <2 %. Combined, the results show that glucose isomerization occurred already at low temperature of 80 °C (albeit slowly), and that increasing temperature resulted in higher glucose conversion, lower fructose selectivity and higher by-product formation.

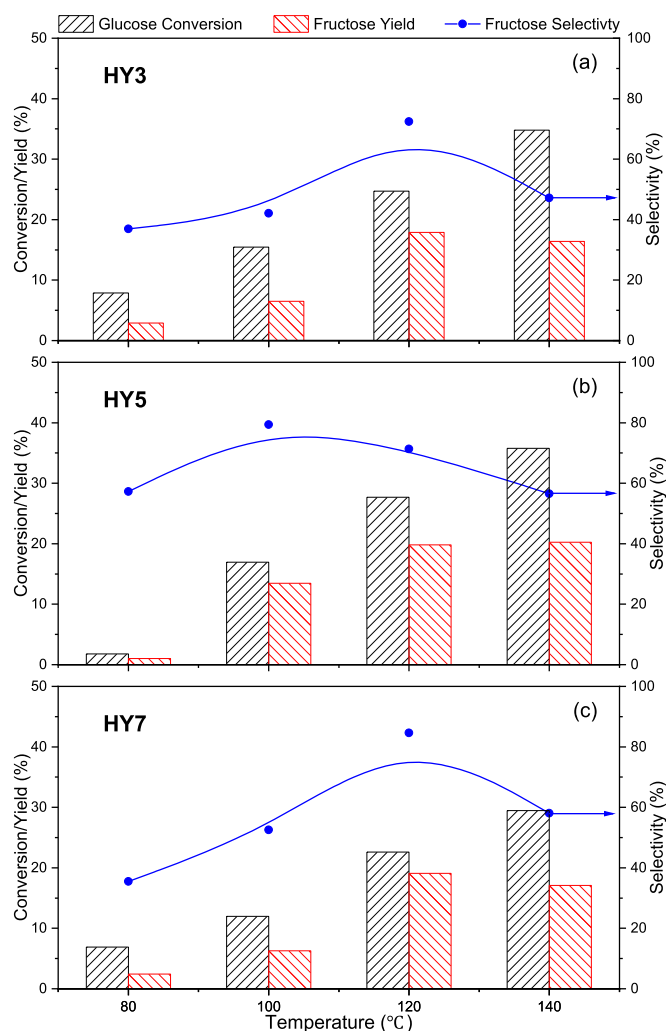


Fig. 8. Effect of reaction temperature on the isomerization of glucose using alkaline-treated (a) HY3, (b) HY5 and (c) HY7 zeolites (Reaction conditions: 125 mg glucose, 75 mg catalyst, 4 g methanol, 2 h).

4. Conclusions

In this work, two commercial H-Y and Na-Y zeolites were treated with NaOH solution under different conditions and their physicochemical characteristics were thoroughly examined and correlated with their catalytic performance in glucose isomerization. Alkaline-treatment of the H-Y zeolite removed strong acid sites, i.e., Si-O(H)-Al bonds, and the surface extra-framework acidic sites. The desilication of H-Y zeolites also influenced the crystallinity significantly, resulting in loss of structural integrity, whereby mesopores generated with a pore size range of 43–480 Å. Glucose isomerization with moderately alkaline-treated H-Y zeolite resulted in a fructose selectivity (84.6 %) approximately twelve times higher than the selectivity obtained with the pristine H-Y zeolite (6.6 %) without formation of methyl glucosides. In contrast, the pore structure of the Na-Y zeolite remained microporous and its framework structure remained intact upon alkaline-treatment. The number of acid sites in Na-Y was ten times that of H-Y zeolite, but it possessed less tetrahedral non-framework acidic Al-species. In combination with the structural features, this gave catalytic materials that provided lower glucose conversion and fructose yield for the glucose isomerization compared to the pristine Na-Y zeolite.

Further studies aim to evaluate the alkaline-treated H-Y zeolites as catalysts and catalyst supports for the isomerization of C3-C5 aldoses, substantiating the selective isomerization of aldoses to ketoses and

design strategies for synthesis of zeolite or zeotype materials containing more extra-framework Al and larger pore sizes. Furthermore, stability and reusability will be addressed.

Declaration of Competing Interest

There are no conflicts to declare.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.mcat.2021.111686](https://doi.org/10.1016/j.mcat.2021.111686).

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