**Bioresources and Bioprocessing**

# Isomerization of glucose into fructose with homogenous amine-type base catalysts: amine structure, chain length, and kinetics

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**Abstract**

Three homogeneous organosilanes amine and aliphatic primary amine were used as amine catalysts to evaluate their catalytic activity and kinetic towards glucose isomerization. Catalysts structure (primary, secondary, tertiary amine), terminal groups and alkyl chain length were investigated and compared elaborately. Result showed organosilanes tertiary amine behaved the best and amine generated $OH^-$ and amine itself contributed the isomerization reaction. The generated acidic by-product not only decreased fructose selectivity but also affected glucose conversion kinetic. The effect of siloxane ($-Si-O-CH_3$) substituent with methyl ($-CH_3$) can be insignificant, but it provided guiding significance for selecting amine-type homogeneous or grafted amine catalysts for glucose isomerization reaction. Longer alkyl chain resulted in lower glucose conversion because of the alkyl chain curls that would weaken the amine catalytic effect and hydration ability. Catalyst loading and initial glucose concentration investigations further showed that amine would effectively catalyze the isomerization reaction under varied operational conditions. This work will provide more details about organic amine catalysts on glucose isomerization into fructose and promote synthesis of platform chemicals in the applications of biorenewable chemicals and fuel.

**Keywords:** Organosilanes, Aliphatic primary amine, Amine structure, Isomerization kinetic, Terminal substitution, Alkyl chain length, Operational conditions

## Introduction

With gradual depletion of traditional fossil resources, several promising biomass-derived products have been identified to be attractive due to the advantages of them being renewable, globally available, and environmentally friendly (Shen et al. 2019). Biomass feedback is of 75% carbohydrates with an empirical formula of $C_6H_{12}O_6$, which is produced by sunlight photosynthesis with $CO_2$ and $H_2O$ (Mika et al. 2018). Therefore, the conversion of carbohydrates into various chemicals and biofuels is one of the most important tactics in bioeconomy chain according to the idea of "biorefinery concept" (Mika et al. 2018). Among those biomass-derived carbohydrates,
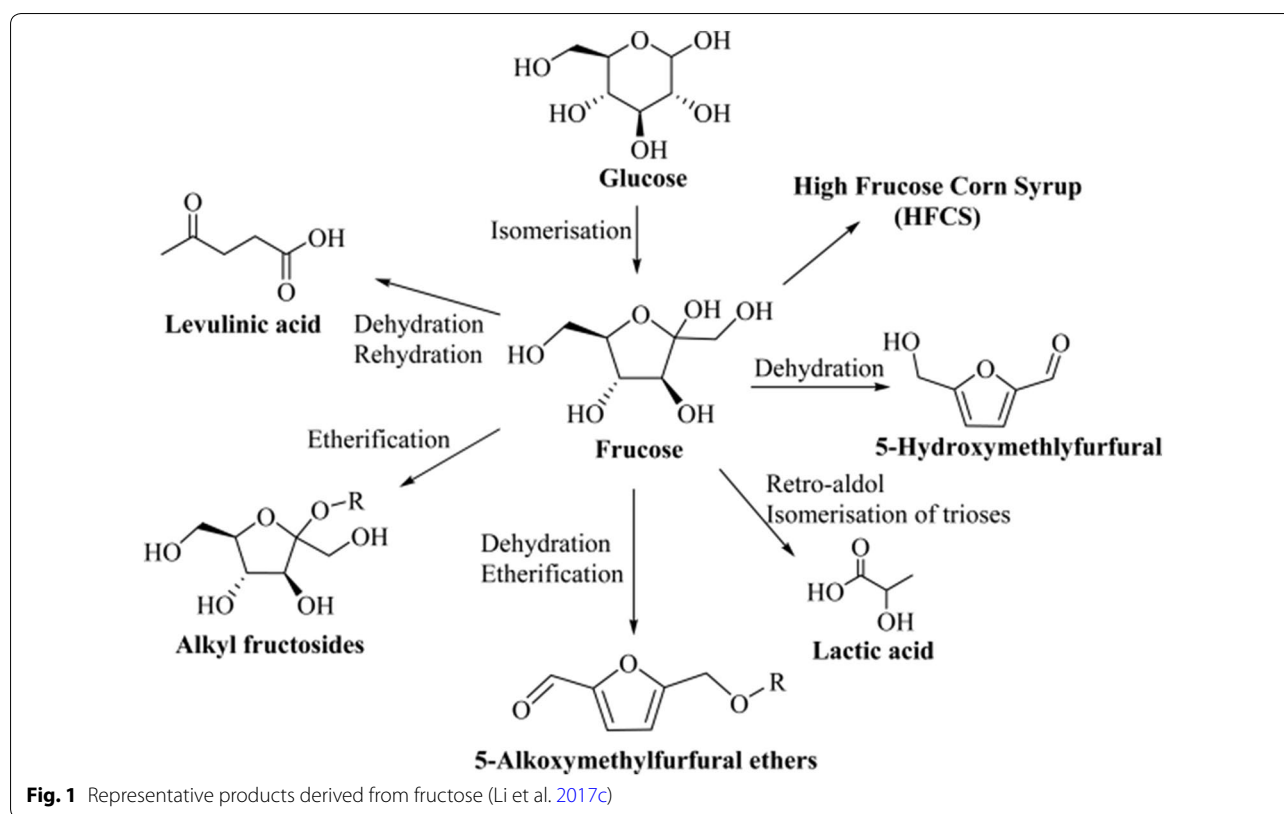
fructose is a crucial feedstock (Li et al. 2017c). Except as a well-known sweetener that alternates as conventional table sugar (sucrose) (Yabushita et al. 2019), fructose could also be as a raw material for the production of 5-hydroxymethylfurfural (5-HMF) (Du et al. 2019; Morales-Leal et al. 2019; Shaikh et al. 2018). 5-HMF is a popular chemical that can be further processed into 2,5-furandicarboxylic acid (FDCA), which is a renewable substitute of petroleum-based terephthalic acid in polyester (Gorbanev et al. 2009; Zhang and Deng 2015). In some similar manners, fructose acts as an intermediate to synthesise some other platform compounds, such as levulinic acid and its esters, alkyl fructosides and 5-ethoxymethylfurfural as shown in Fig. 1 (Corma et al. 2007; Lam and Luong 2014; Li et al. 2016, 2017b, c).

Fructose is the product of glucose isomerization. Recently, immobilized enzymes have been used as biocatalyst for industrial fructose production, and a fructose yield of 42% was obtained (Lee and Hong 2000; Li

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**Fig. 1** Representative products derived from fructose (Li et al. 2017c)

et al. 2017a). However, the biological catalyst suffers from various drawbacks, such as the poor stability, high cost, needed by buffers and irreversible deactivation (Lee and Hong 2000; Shen et al. 2019; Yang et al. 2016). Meanwhile, the glucose isomerase is vulnerable to the surroundings (temperature, pH and feed purity, etc.) that strict control over operating conditions is required. Therefore, chemical catalytic process for glucose isomerization into fructose is an alternative approach of enzyme process fructose production (Li et al. 2017c).

Seminal work discovered that glucose isomerization could be catalyzed by the Lewis acidic zeolite Sn-Beta (Moliner et al. 2010). Despite of the existence of Sn active sites' leaching, this work has sparked interest in searching chemical catalysts for glucose isomerization (Olson et al. 2019). Later, several intriguing chemical catalysts for this reaction have been investigated, including homogeneous and heterogeneous Lewis acids, inorganic Brønsted bases (Carraher et al. 2015), organic bases (Liu et al. 2014) and so on.

Among those chemical catalysts, amine-type organic bases catalysts are intriguing for their high tunability and no cation–ketose complex forming according to Lobry de Bruyn–Alberda van Ekenstein mechanism (de Bruijn et al. 1986; Liu et al. 2014; Yang and Montgomery 1996) and broader range of p$K$a (Liu et al. 2014). Besides,

amines could easily be found in a variety of natural products such as food and drugs. In addition, their availability and low toxicity make them ideal candidates to produce fructose for food, chemical, and fuel applications (Liu et al. 2014). Chemical structure (acyclic vs. cyclic amine), nature of the amine groups (primary, secondary, tertiary amine), and p$K$a are the major factors that affect amine catalyst activity. In previous study, morpholine, piperazine, ethylenediamine, triethylamine, piperidine and pyrrolidine were selected and tested to compare their catalytic activity towards glucose isomerization into fructose (Liu et al. 2014). Yield of 32% with 63% fructose selectivity was reached after 20 min at 100 °C (Liu et al. 2014), which with the similar performance as state of the art Lewis acid catalysts (Souza et al. 2012). To improve catalysts' stability, PS particles or $Fe_3O_4$ supported 1-(3-aminopropyl) imidazole (API), tetramethylguanidine (TMG) and 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) were also developed (Yang et al. 2015). Higher glucose-to-fructose yield and selectivity were achieved in water under a wide range of temperature with excellent catalysts stability and reusability (Yang et al. 2015). Besides, tertiary amine functionalized SBA-15 was created and acted as heterogeneous catalytic materials for glucose-to-fructose isomerization, alkyl linker length of the amine tether was investigated (Deshpande et al.

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2017). Results revealed that decreasing the length of the active site tether could improve the catalyst performance significantly (Deshpande et al. 2017). Most recently, the impact of tertiary amines alkyl substituents structure on their catalytic performance for the isomerization of glucose to fructose was studied (Deshpande et al. 2019). Results demonstrated that amines with less bulky substituent achieved higher glucose conversion (Deshpande et al. 2019).

Although some efforts have been taken to investigate the relationship between amine structure and their performance in glucose isomerization reaction, the role of the amine in glucose isomerization has received limited understanding because of their wide variety. More detailed understanding of the catalytic process was desired (Liu et al. 2014). Especially the overall influence of amine substituents is not fully understood. In this present work, first, three homogeneous amine type organosilanes amine (primary, secondary, and tertiary amine) were chosen as catalysts to screen their catalytic activity and catalytic kinetic towards glucose isomerization. Second, the substituents of siloxane (–Si–O–CH$_3$) group with methyl (–CH$_3$) were performed and their activity was compared elaborately. Finally, three kinds of aliphatic primary amine, which with 2, 6 and 8 alkyl chains, were adopted as amine catalysts to directly investigate the influence of chain length on glucose isomerization. Meanwhile, catalysts loading and glucose feed concentration were illustrated. This work will provide more details about amine catalysts on glucose isomerization into fructose and will promote synthesis of platform chemicals in the biorenewable chemicals and fuel applications.
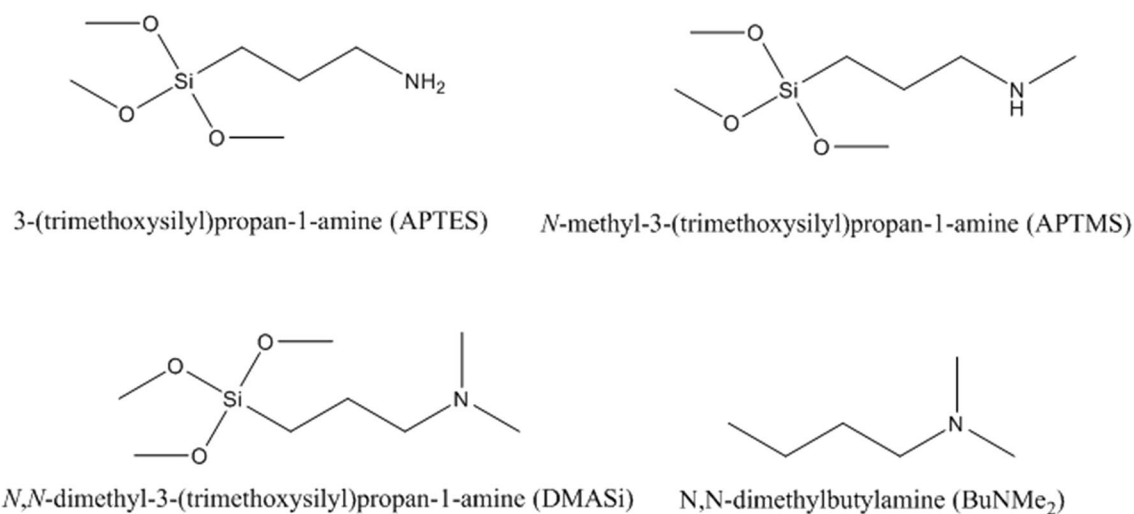
## Experimental

### Materials

Deionized water (DI water, 18.25 MΩ cm) was prepared using a water purification system (Water Purifier, WP-UP-UV-20, Sichuan Water Technology Development Co. Ltd, China). Fructose and glucose (Alfa Aesar Tianjin China, 99%) were used as received. Structures and their abbreviations of the three homogeneous amine type organosilanes and aliphatic primary amine with 2, 6 and 8 alkyl chain are shown in Figs. 2 and 6. All other chemicals are of analytical grade or higher and were used without further treatment.

### Reaction testing

The glucose isomerization into fructose reaction was performed in a 10 mL thick-walled glass reactor made by Alltech. An oil bath was used to heat the reactor rapidly to the desired temperature. In a typical experiment, a certain amount of glucose, amine-type catalyst, and 5 mL deionized water were added to the glass reactor. A triangular magnet stir bar (Fisher Scientific) was also added to allow for adequate agitation. After a certain period, the reaction was quenched with flowing water.

### Products analysis

After each step of reaction finished, the resulting solution was analyzed by HPLC without any pretreatment. HPLC was equipped with an Aminex HPX-87H column and refractive index detectors. 5 mM $H_2SO_4$ was used as the mobile phase at a flow rate of 0.6 mL/min and the column temperature was maintained at 60 °C. According to our previous work (Xu et al. 2019), the mannose yield



**Fig. 2** The structures of organosilanes amine catalysts

3-(trimethoxysilyl)propan-1-amine (APTES)

*N*-methyl-3-(trimethoxysilyl)propan-1-amine (APTMS)

*N*,*N*-dimethyl-3-(trimethoxysilyl)propan-1-amine (DMASi)

N,N-dimethylbutylamine (BuNMe$_2$)

from glucose catalyzed by organosilanes amines was < 1%, so the mannose could be negligible in this work.

$$\text{Conversion of glucose (\%)} = \frac{\text{moles of glucose reacted}}{\text{moles of glucose supplied}} \times 100$$

$$\text{Yield of fructose (\%)} = \frac{\text{moles of fructose formed}}{\text{moles of glucose supplied}} \times 100$$

$$\text{Selectivity for fructose (\%)} = \frac{\text{moles of fructose formed}}{\text{moles of glucose reacted}} \times 100$$

## Results and discussion

### Comparison of primary, secondary and tertiary amine

Some organic bases have been investigated as homogeneous catalysts for the isomerization of glucose to fructose in water (Carraher et al. 2015; Liu et al. 2014). However, homogeneous organosilanes amines have been not

involved. Initial catalytic testing focused on determining the effect of the amine structures for homogeneous amines on fructose yield and selectivity. Thus, organosilanes amines with different chemical structures (primary, secondary, and tertiary amine) were selected. Effects of reaction conditions (time, temperature) on fructose yields and selectivity are shown in Fig. 3.

Under designed experiment conditions, a 34% fructose yield and 75% selectivity was achieved with DMASi (with tertiary amine) at 110 °C for 60 min. This result is superior to previous reports, which obtained a 32% fructose yield and 63% selectivity (Liu et al. 2014), which indicates the organosilanes amines are more active for fructose production. In terms of fructose yield, DMASi (with tertiary amine) and APTMS (with secondary amine) exhibit similarly and both are higher than APTES with primary amine. While the fructose selectivity for DAMSi is around 80% that is far higher than APTES (∼ 70%) and APTMS (∼ 55%) for all the screened temperature. This indicates that for organosilanes amines, the tertiary
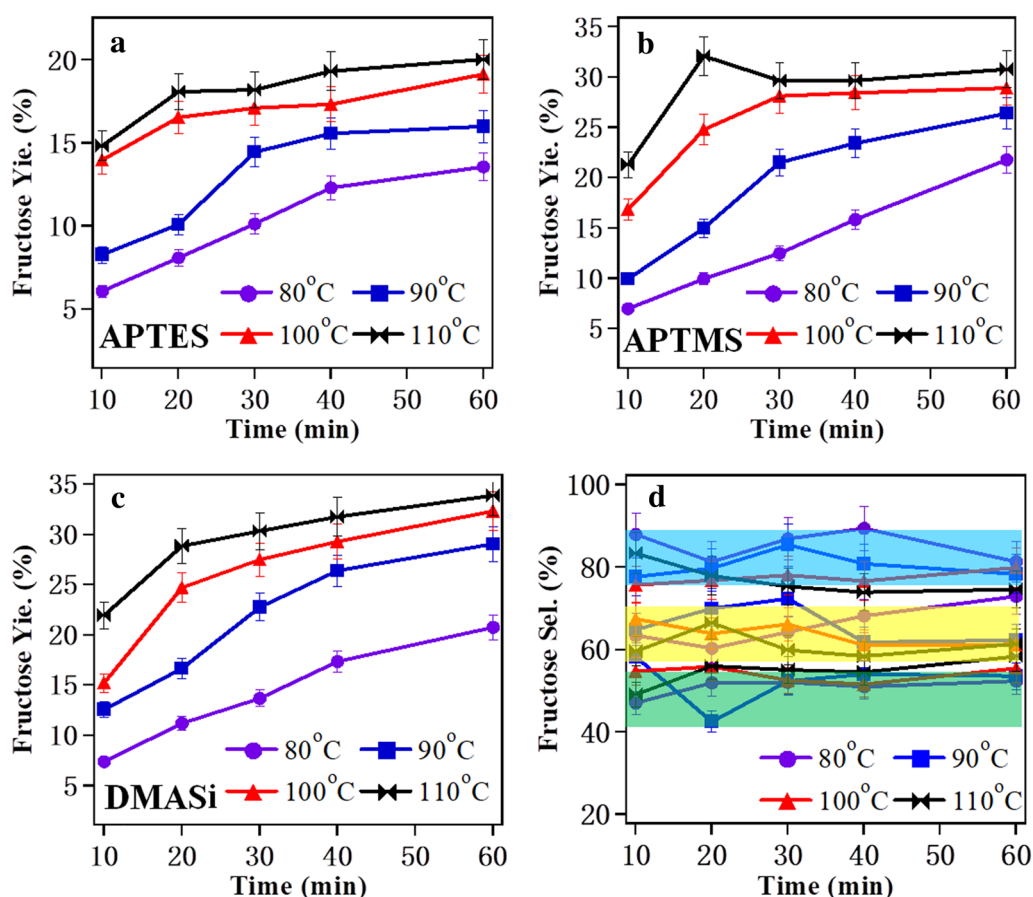


**Fig. 3** Fructose yield versus time profiles for organosilanes amines. **a** APTES, **b** APTMS and **c** DMASi. Blue, yellow and green checkers present DMASi, APTMS and APTES separately in **d**. Reaction conditions: 0.5 g glucose, 5 mL H$_2$O, organosilanes amine (mol% relative to glucose), 10–60 min, 80–110 °C

amine is a higher efficient isomerization catalyst for glucose-to-fructose isomerization, which is consent with some other reports (Deshpande et al. 2019; Yang et al. 2015).

Previous research demonstrated that amine-generated hydroxide ion ($OH^-$) catalyzes glucose isomerization reaction (Carraher et al. 2015). Hence the p*K*a for amine is regarded as a decided factor in glucose isomerization. Interaction between nitrogen atom and $H_2O$ could affect its $OH^-$ generation ability (Liu et al. 2014). The lone electron pair of nitrogen held in a $sp^3$ orbital is much easier to protonate than the one held in a $sp^2$ or sp orbital (Liu et al. 2014; Yang et al. 2015). Besides, an NMR study confirmed that triethylamine did not participate in the Maillard reaction, which explained the tertiary amine performed better in glucose isomerization catalytic reaction (Liu et al. 2014). Recently, the contribution of the amine itself is emphasized, and current thinking is that the role of the amine itself is more important than the generated $OH^-$. However, it is hard to distinguish the contribution of amine itself and its generated $OH^-$. While, an indisputable fact is that amine with tertiary amine resulted in the higher fructose selectivity than primary and secondary amine. In this study, the p*K*a values of the three adopted organosilanes amines are close, while their glucose catalytic effects are obviously diverse, so the role of amine itself is considered as more important in organosilanes. According to the proposed glucose isomerization mechanism (Liu et al. 2014; Yang et al. 2015), trimethylamine participated in the isomerization reaction but not in side reactions that led higher fructose selectivity than primary amine and secondary amine. Surely, deeper investigation is needed for further correlating the structural properties and catalytic performance for the amines.

### Kinetics of glucose conversion

To explain the observed temperature effect and gain more insight on the glucose isomerization with organosilanes amines, the kinetics analysis and rate-constant fitting were estimated. First-order rate reaction was assumed and the reaction rate could be expressed as follows (Carraher et al. 2015):

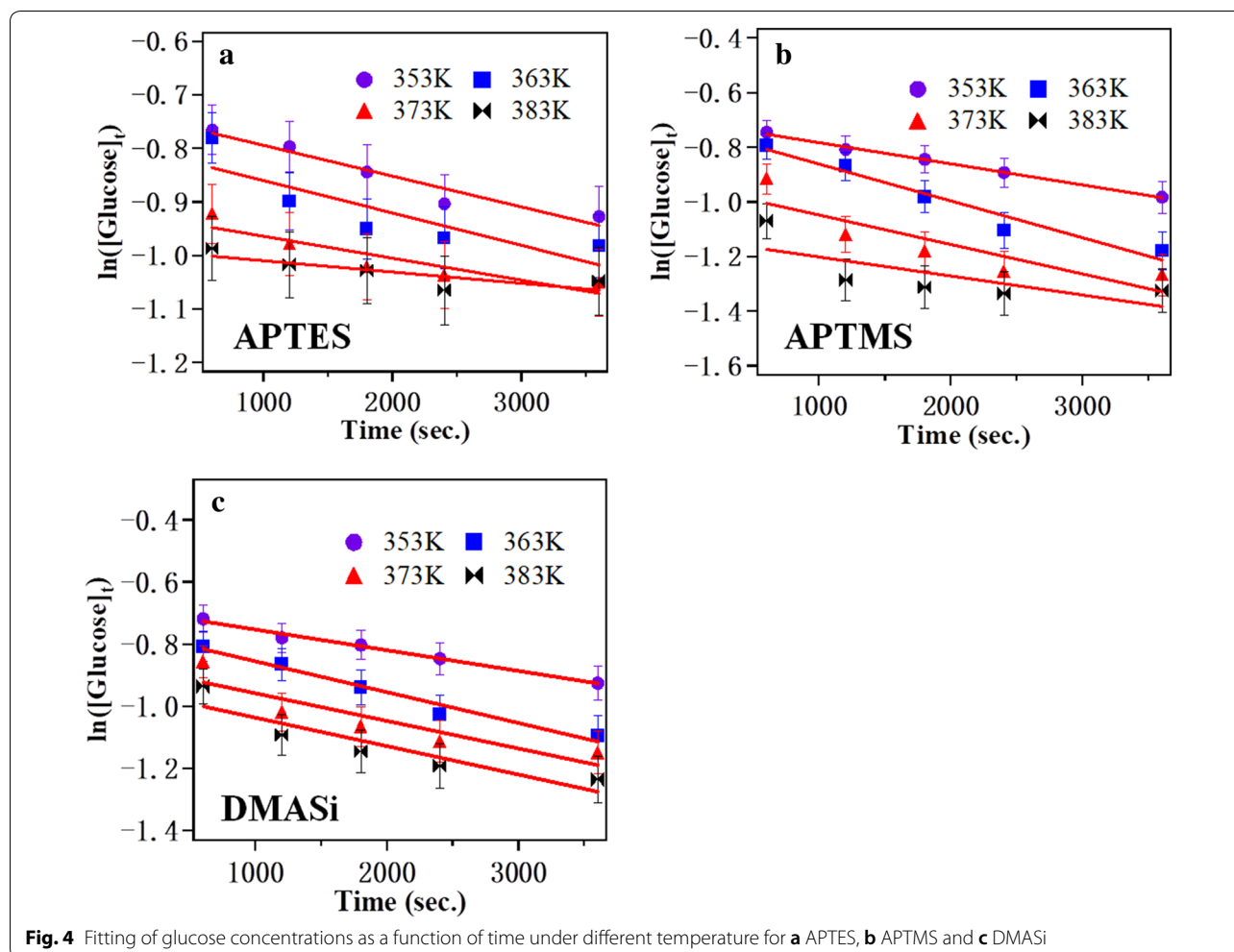$$\ln\left([[\text{Glu}]_t\big/[\text{Glu}]_0\right) = -kt$$

where $[\text{Glu}]_t$ = glucose concentration at time t with unit of mol/L, $[\text{Glu}]_0$ = initial glucose concentration, $k$ = observed rate constant, and $t$ stands for time in seconds. A linear correlation between $\ln([[\text{Glu}]_t])$ and reaction time $t$ was plotted. The $k$ obtained under different temperature was obtained. The results are shown in Fig. 4 and Table 1 respectively.

As shown in Fig. 4, when the adopted temperature is lower, the First-order rate reaction assumption fits the data points better. While at high temperature, the experimental points deviate from the kinetic model seriously. This can be explained by the fact that the higher the temperature, the more by-products produced, leading the selectivity of fructose to be lower as demonstrated in Fig. 3d. The color of the solution after the reaction turned to brown, which is similar to previous reports (Liu et al. 2014). Those color by-products have been mainly assigned to the 1,2-enediol intermediate, which is acidic (Kim and Lee 2008; Liu et al. 2014). The acidic by-products hindered the activity of bases in turn that resulted lower rate constant at higher temperature as shown in Table 1. The generated acidic by-products not only decreased fructose selectivity but also reduced glucose conversion kinetic. Thus, the rate constants for 100 °C and 110 °C are lower than 80 °C and 90 °C. Those acidic by-products can be removed with commercially activated carbon as reported (Liu et al. 2014). So the separation of targeted fructose is not difficult.

### Effects of terminal groups

Noteworthy structural feature for the three organosilanes amines is their end group of $-Si-O-CH_3$. As well known, the $-Si-O-CH_3$ could undergo hydrolysis and form Si–O network. While, to our knowledge, whether Si–O network can affect the glucose isomerization to a certain degree has not been investigated before. Although, the tertiary amine interacting with the surface of silica (also mainly Si–O network) has been reported (Deshpande et al. 2019), whereas whether the prepared silica (SBA-15) have different behavior compared with the hydrolysis in situ-formed Si–O network is not clear. In this study, direct substituent of siloxane ($-Si-O-CH_3$ in DMASi) with methyl ($-CH_3$ in BuNMe$_2$) was performed and their activity was compared elaborately under 100 °C and 110 °C. The results are shown in Fig. 5.

It was observed that for DMASi and BuNMe$_2$ at 100 and 110 °C, taken the experimental bias into account, the glucose conversion and fructose selectivity followed almost identical variation trend. A 40% glucose conversion with 75% fructose selectivity could reach, which is close to the reaction thermodynamic equilibrium in $H_2O$ (Moliner et al. 2010). This result demonstrates that the considered in situ hydrolysis effect of $-Si-O-CH_3$ group could be negligible in the present experimental conditions. Although no different performance is observed, this result may also have guided significance for selecting amine-type homogeneous or grafted amine catalysts for glucose isomerization into fructose reaction.

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**Fig. 4** Fitting of glucose concentrations as a function of time under different temperature for **a** APTES, **b** APTMS and **c** DMASi

**Table 1 Fitted rate constants for APTES, APTMS and DMASi in glucose isomerization**

| Catalysts | $k_{80°C} \times 10^{-5}$ $(s^{-1})$ | $k_{90°C} \times 10^{-5}$ $(s^{-1})$ | $k_{100°C} \times 10^{-5}$ $(s^{-1})$ | $k_{110°C} \times 10^{-5}$ $(s^{-1})$ |
|---|---|---|---|---|
| APTES | 5.74 | 6.05 | 4.10 | 2.12 |
| APTMS | 7.75 | 13.48 | 10.80 | 6.94 |
| DMASi | 6.62 | 9.93 | 8.90 | 9.17 |

### Effects of chain length and experimental parameters

As mentioned, the impact of alkyl substituent structure of amines on their catalytic performance for the glucose-to-fructose isomerization is obvious (Deshpande et al. 2019). The steric bulk of substituent was considered as a major factor that affected glucose isomerization catalytic activity (Deshpande et al. 2019; Liu et al. 2014). While more direct evidence is limited. In this part, three kinds of aliphatic primary amine with 2, 6 and 8 alkyl chain (as shown in Fig. 6), which have particular pronounced structure difference, were adopted as amine catalysts to investigate the effect of alkyl chain length on glucose isomerization into fructose reaction. The result is shown in Table 2.

Table 2 shows that when adopting aliphatic primary amine, ~61 to ~70% fructose selectivity could be reached, which is close to APTES under the 110 °C as illustrated in Fig. 3d. This result shows for primary amine, fructose selectivity is not sensitive to their substituents structure. From organosilanes primary amine (APTES) to aliphatic primary amines, under the same temperature, the close fructose selectivity could be reached. Thus, it can be seen the importance of reaction temperature in glucose isomerization that impacts the fructose selectivity.

Another obvious phenomenon is when the alkyl chain of aliphatic primary amine is 2 and 6 (ethylamine and hexylamine), their catalytic glucose isomerization performance is similar with ~40% glucose conversion and ~61% fructose selectivity. While when the alkyl chain added to
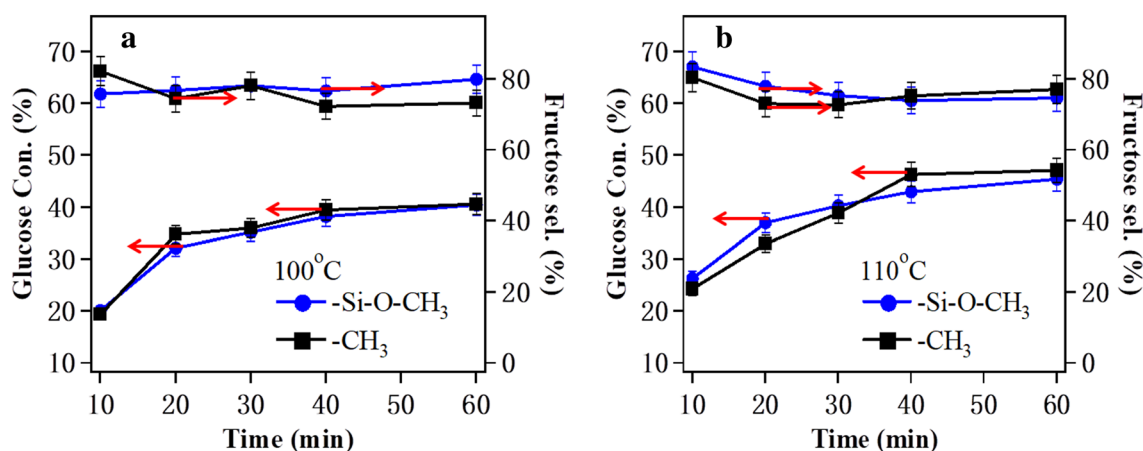
**Fig. 5** Glucose conversion and fructose selectivity versus time profiles as a function of time under **a** 100 and **b** 110 °C for DMASi and BuNMe$_2$. Reaction conditions: 0.5 g glucose, 5 mL H$_2$O, amine (mol% relative to glucose), 10–60 min, 80–110 °C
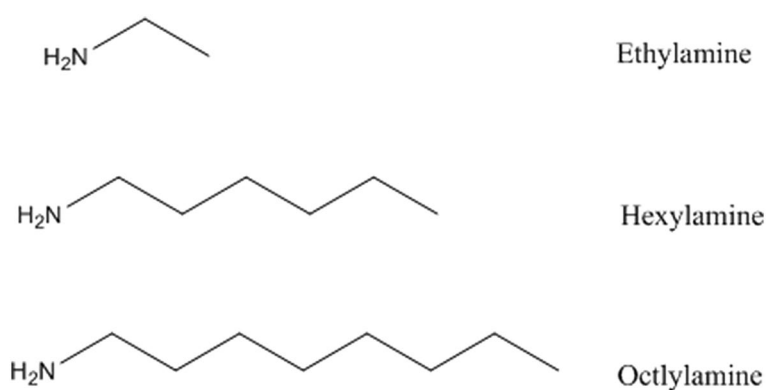


**Fig. 6** The structure of aliphatic primary amine with 2, 6 and 8 alkyl chain

**Table 2  Isomerization of glucose to fructose by aliphatic primary amine catalysts with different alkyl chain length**

| Catalysts (alkyl chain length) | p$K$a | Glucose con. (%) | Fructose yie. (%) | Fructose sel. (%) |
|---|---|---|---|---|
| Ethylamine (2) | 10.70 | 38.85 ± 1.9 | 23.69 ± 1.2 | 60.98 ± 2.8 |
| Hexylamine (6) | 10.56 | 39.14 ± 2.0 | 24.34 ± 1.2 | 62.19 ± 2.4 |
| Octylamine (8) | 10.65 | 27.72 ± 1.4 | 19.38 ± 0.9 | 69.91 ± 1.8 |

Reaction conditions: 0.5 g glucose, 5 mL H$_2$O, aliphatic primary amine catalyst (mol% relative to glucose), 10 min, 110 °C

8 (octylamine), the glucose conversion dropped to ∼ 28% with ∼ 70% fructose selectivity. The higher fructose selectivity can be explained by the fact that more glucose conversion lead to lower glucose conversion because of more acidic by-product generation as discussed above. As shown in Table 2, the three aliphatic primary amines are of close p$K$a values, all water-soluble and formed homogenous solutions. Thus, their OH$^-$ generation ability should not be very different, while ethylamine

and hexylamine are significantly more active than octylamine. Thus the steric bulk is regarded as the main reason. In this work, we explain the difference by the fact that longer alkyl chain length leads to more flexibility, the chain may curl that weakens the amine catalytic effect.

In an industry producing process, the concentration of feedstock and catalyst loading is also important, which determines the target products' production capacity and cost. So the influence of initial hexylamine concentrations

on the glucose conversion and fructose yield is evaluated in this part and the results are shown in Fig. 7.

Figure 7a shows an increase of the hexylamine dosage from 0.5 to 10 mol%, stable fructose selectivity (around 65%) fructose selectivity are obtained. More ethylamine leads to higher glucose conversion because of the more amine existence. While initial glucose concentration evaluation shows the glucose concentration varies from 0.1 to 0.5 g in 5 mL $H_2O$, stable glucose conversion and fructose yield reached, and higher glucose initial concentration (> 0.5 g in 5 mL $H_2O$) resulted in a decrease in the glucose conversion due to the absence of enough catalysts. All above results demonstrate ethylamine can effectively catalyze the isomerization reaction under a variety of operational conditions.

As discussed above, the reaction condition (mainly residual time, temperature, initial glucose concentration and catalysts loadings) and whether being immobilized could affect the amine catalytic effects largely. Comparison of the adopted organosilanes amine and aliphatic primary amine in this work with representative homogeneous base catalysts is shown in Table 3.

As analyzed, for homogeneous base catalysts listed in Table 3, catalysts type and reaction conditions affect the glucose isomerization reaction. Different alkyl substituents also influence the glucose conversion and fructose selectivity. For our results, 45% of glucose conversion with 75% fructose selectivity could be obtained when DMASi acted as catalyst, which indicates DMASi is promising industrial homogenous catalyst for fructose production from glucose isomerization.

## Conclusions

In the present work, three homogeneous amine type organosilanes (primary, secondary, and tertiary amine) were selected first as amine catalysts to screen their catalytic activity and kinetic toward glucose isomerization reaction. Results showed amine-generated $OH^-$ and amine itself played important roles in the isomerization reaction and organosilanes tertiary amine behaviors best. The generated acidic by-product not only causes the decrease of fructose selectivity but also reduced the glucose conversion kinetic. The substituent of siloxane ($-Si-O-CH_3$) with methyl ($-CH_3$) investigation showed in situ hydrolysis effect of $-Si-O-CH_3$ group could be negligible, which provided guided significance for selecting amine-type homogeneous or grafted amine catalysts for the glucose isomerization reaction.

The substituent structure of amines on their isomerization performance was investigated by adopting aliphatic primary amine with different alkyl chain length. Higher alkyl chain resulted in lower glucose conversion for the alkyl chain curls that weaken the amine catalytic effect and hydration ability. Catalyst loadings and initial glucose concentration effects showed that hexylamine could effectively catalyze the isomerization reaction under a variety of operational conditions. This work will provide more details about amine catalysts on glucose isomerization into fructose and promote synthesis of platform chemicals in the biorenewable chemicals and fuel applications.
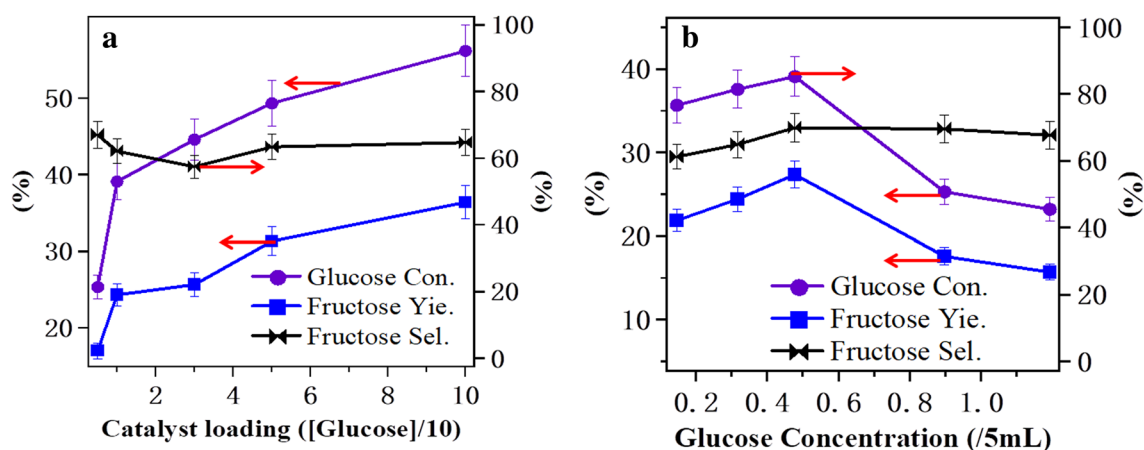


**Fig. 7** Glucose conversion and fructose selectivity versus **a** hexylamine loading and **b** initial glucose concentration profiles under 110 °C and 10 min. Ethylamine loading are 0.5, 1, 3 5 and 10 (mol% relative to glucose); glucose concentrations are 0.1, 0.3, 0.5, 0.9 and 1.2 g in 5 mL $H_2O$

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**Table 3  Isomerization of glucose to fructose with representative homogenous catalysts at different reactions conditions**

| Catalysts (loading) | Conditions (solvent, temperature, time, glucose concentration) | Glu conv. (%) | Fru yie. (%) | Fru sel. (%) | Ref |
|---|---|---|---|---|---|
| Triethylamine (10 mol%) | $H_2O$, 100 °C, 20 min, 10 wt% | 51 | 32 | 63 | Liu et al. (2014) |
| Quinuclidine (10 mol%) | $H_2O$, 100 °C, 2 h, 10 wt% | 54 | 29 | 54 | Deshpande et al. (2019) |
| Triethylamine (10 mol%) | $H_2O$, 100 °C, 2 h, 10 wt% | 48 | 27 | 56 | Deshpande et al. (2019) |
| Diisopropylethylamine (10 mol%) | $H_2O$, 100 °C, 2 h, 10 wt% | 33 | 23 | 70 | Deshpande et al. (2019) |
| Tri-*n*-propylamine (10 mol%) | $H_2O$, 100 °C, 2 h, 10 wt% | 12 | 9 | 75 | Deshpande et al. (2019) |
| Imidazole (160 mol%) | $H_2O$, 120 °C, 0.5 h, 10 wt% | 60 | 33 | 55 | Yang et al. (2015) |
| 1-(3-Aminopropyl) imidazole (7.5 mol%) | $H_2O$, 120 °C, 0.5 h, 10 wt% | 47 | 20 | 43 | Yang et al. (2015) |
| Tetramethylguanidine (3 mol%) | $H_2O$, 120 °C, 0.5 h, 10 wt% | 59 | 30 | 51 | Yang et al. (2015) |
| 1,5,7-Triazabicyclo[4.4.0]dec-5-ene (3 mol%) | $H_2O$, 120 °C, 0.5 h, 10 wt% | 64 | 32 | 50 | Yang et al. (2015) |
| Trimethylamine (3 mol%) | $H_2O$, 100 °C, 0.5 h, 10 wt% | 43 | 28 | 65 | Yang et al. (2015) |
| Tris(2-aminoethyl)amine (3 mol%) | $H_2O$, 100 °C, 0.5 h, 10 wt% | 43 | 24 | 56 | Yang et al. (2015) |
| Polyethylenimine (0.5 mol%) | $H_2O$, 100 °C, 0.5 h, 10 wt% | 38 | 21 | 55 | Yang et al.(2015) |
| Arginine (10 mol%) | $H_2O$, 120 °C, 20 min, 10 wt% | 41 | 31 | 76 | Yang et al. (2016) |
| Polyethylenimine (0.05 mol%) | $H_2O$, 110–120 °C, 15 min, 10 wt% | 47–50 | 33–36 | 66–77 | Yang and Runge (2016) |
| Hexylamine (10 mol%) | $H_2O$, 110 °C, 10 min, 10 wt% | 39 | 24 | 62 | This work |
| APTES | $H_2O$, 110 °C, 60 min, 10 wt% | 34 | 20 | 58 | This work |
| APTMS | $H_2O$, 110 °C, 60 min, 10 wt% | 50 | 31 | 61 | This work |
| DMASi | $H_2O$, 110 °C, 60 min, 10 wt% | 45 | 34 | 75 | This work |

*Glu conv.* glucose conversion, *Fru yie.* fructose yield, *Fru sel.* fructose selectivity

## Abbreviations
5-HMF: 5-Hydroxymethylfurfural; FDCA: 2,5-Furandicarboxylic acid; API: 1-(3-Aminopropyl)imidazole; TMG: Tetramethylguanidine; TBD: 1,5,7-Triazabicyclo[4.4.0]dec-5-ene; DMASi: *N,N*-Dimethy1-3(trimethoxysily)propan-1-amine; APTMS: *N*-Methyl-3-(trimethoxysily)propan-1-amine; APTES: 3-(Trimethoxysily)propan-1-amine; BuNMe2: *N,N*-Dimethylbutylamine.

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