



# Efficient formation of angelica lactones in a vapor-phase conversion of levulinic acid



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## ABSTRACT

Vapor-phase lactonization of levulinic acid to produce angelica lactones, which include  $\alpha$ -,  $\beta$ - and  $\gamma$ -form isomers, was performed in fixed-bed down-flow glass reactors over various oxide catalysts.  $\text{SiO}_2$  and  $\text{SiO}_2\text{-Al}_2\text{O}_3$  showed relatively high catalytic activity. The lactonization of levulinic acid to angelica lactones was found to be an endothermic equilibrium reaction, and the pressure equilibrium constant was calculated to be 0.2 atm at 275 °C. High temperatures and reduced pressures were effective for shifting the equilibrium from levulinic acid to angelica lactones, while the suitable reaction temperature was estimated to be 275 °C because temperatures higher than 275 °C decreased the selectivity to angelica lactones. The highest angelica lactones yield of 87.5% was achieved at a levulinic acid conversion of 95.3% over  $\text{SiO}_2$  under reduced pressure conditions of ca. 5 kPa at 275 °C. IR,  $\text{NH}_3$ -TPD and TG analyses were performed for characterizing the catalysts used after the reactions together with a silylated  $\text{SiO}_2$  prepared for studying the active species on  $\text{SiO}_2$ . The silanol groups of  $\text{SiO}_2$  with weak acidity were proposed to be the active species.

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## 1. Introduction

Applications of renewable biomass provide facile routes to alleviate the shortage of fossil fuels as well as to reduce  $\text{CO}_2$  emission. Biomass represents an abundant carbon-neutral renewable resource for the production of bioenergy and biochemicals, which can replace the energy and the materials produced from fossil resource [1]. Shifting society's dependence away from petroleum to renewable biomass resources is generally viewed as an important contributor to the development of a sustainable industrial society and effective management of greenhouse gas emissions [1–3]. Levulinic acid (LA) is an attractive chemical, which can be produced from cellulose [2,4] and hemicellulose [2,5–7] as well as sugars [8,9] presented in agricultural and forest residues. LA is used as a food flavoring agent and also a starting material for the preparation of a variety of industrial and pharmaceutical compounds [10,11]. Many useful C5 chemicals, such as angelica lactones (ALs),  $\gamma$ -valerolactone (GVL), 2-methyltetrahydrofuran, and 1,4-pentanediol, can be derived from LA [3,12]. Among these chemicals, attention has been highly focused on the production of GVL because of the important use of GVL as a solvent and an intermediate in the chemical industry for energy storage [13,14]. Although ALs have

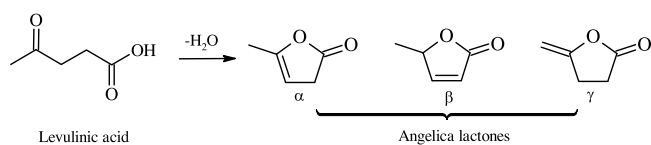
important uses in various fields, selective conversion of LA to ALs has rarely been reported.

ALs include three isomers,  $\alpha$ -,  $\beta$ - and  $\gamma$ -angelica lactone (AL) [15], as shown in Scheme 1.  $\alpha$ -AL has been widely used as a flavoring essence in the food and tobacco industry for its pleasant aromas [16]. In the application of ALs, ALs can be used for producing degradable polymers [17], alkyl levulinates [18], and GVL [15,19]. Recently, the conversion of ALs to C6–C13 gasoline-like hydrocarbons has attracted much attention [20,21]. In this process, dimerization and trimerization of ALs are efficiently catalyzed by  $\text{K}_2\text{CO}_3$ , and C6–C13 hydrocarbons can be selectively produced by the further hydrogenation of the corresponding dimers and trimers of ALs. Thus, ALs are expected to be novel feedstocks for the production of chemicals and transportation fuels. In some previous patents, production of ALs from LA was performed under reaction distillation conditions, and ALs yields higher than 90% could be achieved in the presence of sulfuric acid, phosphoric acid, sulfated  $\text{ZrO}_2$ , or  $\text{SiO}_2\text{-Al}_2\text{O}_3$  [3,22–25]. Mascal et al. performed LA lactonization over montmorillonite clay catalyst in a distillation flask, and 92% yield of ALs was achieved at 165 °C under a reduced pressure of 0.07 MPa [20]. Xin et al. also performed the same reaction under reaction distillation conditions, and ALs yield reached to 97% in the presence of H-ZSM5 at 130 °C under a reduced pressure of 0.01 MPa [21].

In this study, we firstly report a vapor-phase lactonization of LA to ALs over solid catalysts under continuous flow conditions using fixed-bed down flow reactors. The reaction equilibrium was investigated and the suitable reaction conditions for ALs forma-

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**Scheme 1.** Lactonization of levulinic acid to angelica lactones.

tion from LA were studied. The active species for the ALs formation from LA were also discussed and a detailed formation route for the lactonization of LA to ALs was proposed.

## 2. Experimental

### 2.1. Samples

LA was purchased from Tokyo Chemical Industries Co., Ltd., and it was used for the catalytic reaction without further purification. Three different silicas (CARIACT Q3, Q6 and Q10 with mean pore diameters of 3, 6 and 10 nm, respectively) were supplied by Fuji Silicia Chemical Ltd.  $\text{Al}_2\text{O}_3$  (N611) and  $\text{SiO}_2\text{-Al}_2\text{O}_3$  (N631L) were purchased from Nikki Chemical Co., Ltd. Monoclinic  $\text{ZrO}_2$  (RSC-100) and active carbon (A-BAC-LP) were supplied by Daiichi Kigenso Kagaku Kogyo Co. Ltd., Japan and Kureha Corporation, respectively. Rutile  $\text{TiO}_2$  (JRC-TiO3) was supplied by Catalyst Society of Japan. MFI and H-Y zeolites were supplied by Clariant Catalysts Industries Co., Ltd. and Catalysts & Chemicals Industries Co., Ltd., respectively.

A silylated  $\text{SiO}_2$  catalyst was prepared as the following procedures: 3 g of  $\text{SiO}_2\text{-Q3}$  and 3 g of chlorotrimethylsilane were stirred in a solvent of *n*-hexane of 30 g for 12 h, and the silylated  $\text{SiO}_2$  was obtained after a separation followed by drying at 110 °C for 12 h.

### 2.2. Catalytic reaction

Typically, at an ambient pressure, vapor-phase lactonization of LA was performed in a fixed-bed down-flow glass reactor with an inner diameter of 17 mm. Prior to the reaction, a catalyst of 0.5 g was placed in the catalyst bed and heated at a prescribed temperature for 1 h to stabilize the temperature of the catalyst bed. After that, either pure LA or its aqueous solution was fed through the top of the reactor at a liquid feed rate of 1.2 g h<sup>-1</sup> together with an  $\text{N}_2$  flow of 30 cm<sup>3</sup> min<sup>-1</sup>. In the reaction under reduced pressure conditions at ca. 5.3 kPa, LA was fed at a liquid feed rate of 2.9 g h<sup>-1</sup> over 2.0 g of  $\text{SiO}_2\text{-Q3}$  placed in the catalyst bed, and a vacuum pump was connected with the bottom of the reactor without using a carrier gas to reduce the pressure inside the reactor. The hydration of

ALs to LA was performed over 4.0 g of  $\text{SiO}_2\text{-Q3}$  at 275 °C using  $\alpha\text{-AL}$  as the reactant, while  $\alpha\text{-AL}$  and  $\text{H}_2\text{O}$  were individually fed at the same feed rate of 1.3 g h<sup>-1</sup>. The liquid effluents collected in a dry ice-acetone trap (-78 °C) every hour were analyzed by a FID-GC (GC-2014, Shimadzu) with a 30-m capillary column of RtxR-Wax (GL-Science, Japan). A GC-MS (QP5050A, Shimadzu) was used for identification of the products in the effluent. The details for the products separation and identification are shown in the supplemental file.  $\gamma\text{-Butyrolactone}$  was used as the internal standard. The conversion and selectivity were calculated as follows:

$$\text{Conversion (\%)} = \left( 1 - \frac{\text{moles of recovered reactant}}{\text{sum of moles of the reactant}} \right) \times 100 \quad (1)$$

$$\text{Selectivity (\%)} = \frac{\text{moles of specific product}}{\text{sum of moles of the reactant} - \text{moles of recovered reactant}} \times 100 \quad (2)$$

### 2.3. Characterization of the catalysts

The specific surface area of the catalysts was calculated by the BET method using  $\text{N}_2$  isotherm at -196 °C. The temperature-programmed desorption (TPD) of adsorbed  $\text{NH}_3$  was measured by neutralization titration using an electric conductivity cell immersed in an aqueous solution of  $\text{H}_2\text{SO}_4$ . The amount of desorbed  $\text{NH}_3$ , which was bubbled into the solution, was monitored by the change in the conductivity of the solution. A cumulative amount of desorbed  $\text{NH}_3$  was obtained as a function of the desorbed temperature and then differentiated to give a TPD profile as an acid strength distribution. The details of TPD experiment are described in our previous studies [26]. The thermogravimetry (TG) analysis was performed using Thermoplus 8120E2 (Rigaku) under the conditions: sample weight, ca. 10 mg; the rate of the increased temperature, 5 °C min<sup>-1</sup>; heating range, from the room temperature to 900 °C. The diffuse reflectance infrared Fourier-transform (DRIFT) spectra of catalysts were recorded on a spectroscopy using FT/IR-4200 (JASCO) under vacuum conditions, and the catalysts were pretreated at 150 °C in vacuum for 1 h in order to remove the  $\text{H}_2\text{O}$  adsorbed on the catalyst surface.

## 3. Results

### 3.1. Lactonization of LA to ALs over various catalysts

Table 1 shows the reaction results of lactonization of LA to ALs over various solid catalysts. The reactions were performed in  $\text{N}_2$

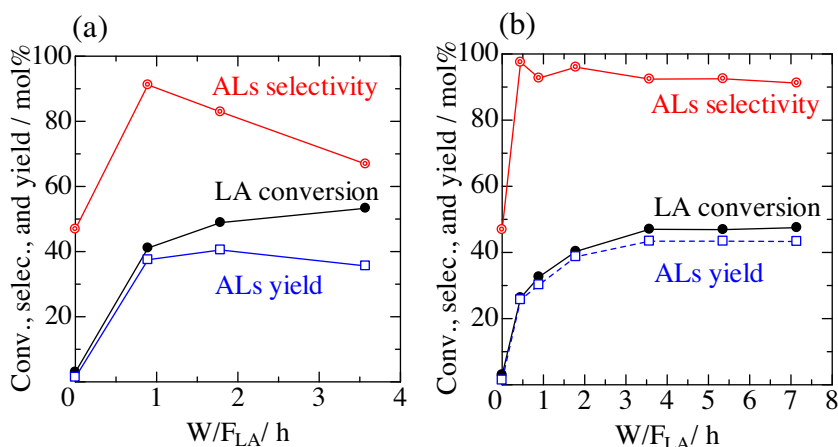
**Table 1**  
Lactonization of LA to ALs over various catalysts.<sup>a</sup>

Catalyst	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	Conversion <sup>b</sup> /mol%	Selectivity/mol% <sup>b</sup>				ALs yield <sup>b</sup> /mol%
			$\alpha\text{-AL}$	$\beta\text{-AL}$	$\gamma\text{-AL}$	Total of ALs	
$\text{SiO}_2\text{-Q3}$	705	19.6	45.3	44.8	4.9	95.0	18.6
$\text{SiO}_2\text{-Q6}$	451	13.6	43.2	42.9	6.7	92.8	12.6
$\text{SiO}_2\text{-Q10}$	295	13.0	42.5	43.6	6.7	92.8	12.1
$\text{SiO}_2\text{-Al}_2\text{O}_3$	440	25.0	45.2	38.3	3.8	87.2	21.8
$\text{TiO}_2$	40	8.0	27.0	25.5	8.6	61.1	4.9
MFI zeolite	431	20.1	34.3	35.6	2.4	72.3	14.5
HY zeolite	540	16.0	38.6	38.7	2.4	79.8	12.8
$\text{ZrO}_2$	106	14.1	26.4	26.2	5.1	57.8	8.1
$\gamma\text{-Al}_2\text{O}_3$	166	10.3	25.3	24.6	5.7	55.5	5.7
None	–	0	0	0	0	0	0
$\text{SiO}_2\text{-Q3}^c$	705	33.5	43.5	43.4	5.2	92.1	30.8
Active carbon <sup>c</sup>	1100–1300	19.5	38.0	38.1	4.8	80.9	15.8

<sup>a</sup> Reaction conditions: reactant, 50 wt.% LA aqueous solution; reaction temperature, 250 °C;  $\text{N}_2$  gas flow rate, 30 cm<sup>3</sup> min<sup>-1</sup>;  $W/F_{\text{LA}}$ , 0.8 h.

<sup>b</sup> Averaged activity in the initial 3 h.

<sup>c</sup> Reaction temperature, 275 °C.



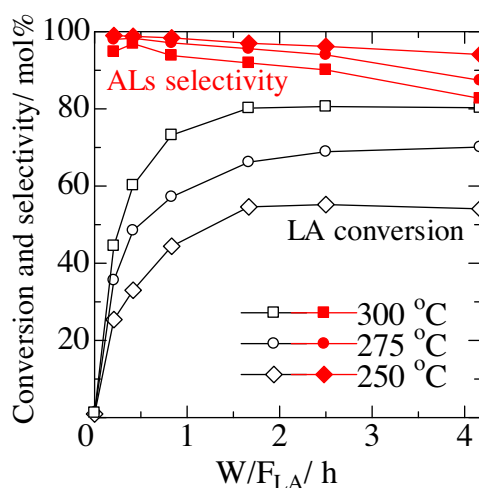
**Fig. 1.** Changes in catalytic activity of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> (a) and SiO<sub>2</sub>-Q3 (b) with W/F<sub>LA</sub>. Reaction conditions: reactant, 50 wt.% LA aqueous solution; reaction temperature, 275 °C; N<sub>2</sub> gas flow rate, 30 cm<sup>3</sup> min<sup>-1</sup>.

flow at 250 °C with a contact time of W/F<sub>LA</sub> of 0.8 h, where W and F<sub>LA</sub> were the catalyst weight (g) and the feed rate of LA (g h<sup>-1</sup>), respectively, using 50 wt.% LA aqueous solution as the reactant. The main products were α-, β- and γ-AL in all the reactions. The total selectivity to ALs exceeded 50% over each catalyst, and the residual selectivity was assigned to the undetectable products. Among the three AL isomers, α- and β-AL were mainly generated with a similar amount. The reaction did not proceed in the absence of a catalyst. SiO<sub>2</sub> catalysts showed relatively high selectivities to ALs, and SiO<sub>2</sub>-Q3 gave the highest ALs selectivity of 95.0% among all the tested catalysts. SiO<sub>2</sub>-Q3 had a higher surface area, and gave a high LA conversion of 19.6% comparing with those of SiO<sub>2</sub>-Q6 and Q10. On the other hand, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> showed the highest LA conversion of 25.0% and the highest ALs yield of 21.8% among all the tested catalysts. TiO<sub>2</sub> was not so active, and the conversion of LA was as low as 8.6%. MFI and HY zeolites had relative high surface areas and also gave relative high conversions of LA, whereas the selectivities to ALs were lower than 80%. ZrO<sub>2</sub> and γ-Al<sub>2</sub>O<sub>3</sub> showed poor activity for ALs formation, and the selectivity to ALs was even lower than 60%. The catalytic activity of active carbon and SiO<sub>2</sub>-Q3 was compared at a temperature of 275 °C. The active carbon with a higher surface area gave a lower conversion of LA than that of SiO<sub>2</sub>-Q3 as well as a lower selectivity to ALs.

At 250 °C, SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> showed the highest LA conversion and SiO<sub>2</sub>-Q3 gave the highest selectivity to ALs (Table 1). Thus, they were selected for the further study of LA lactonization to ALs. Fig. 1 shows the changes in activity of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>-Q3 with W/F<sub>LA</sub> at 275 °C using 50 wt.% LA aqueous solution as the reactant. Over SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, the conversion of LA increased with increasing the W/F<sub>LA</sub>, whereas the selectivity to ALs decreased at W/F<sub>LA</sub> higher than 0.8 h. Over SiO<sub>2</sub>-Q3, on the other hand, the conversion of LA increased monotonically with increasing the W/F<sub>LA</sub>, and kept a constant value of ca. 47% at W/F<sub>LA</sub> higher than 3.5 h. The selectivities to ALs kept at ca. 92% even at high W/F<sub>LA</sub> values. As a result, the yields of ALs kept at ca. 43% at W/F<sub>LA</sub> higher than 3.5 h.

### 3.2. Lactonization of LA to ALs under different reaction conditions

Fig. 2 shows the changes in catalytic activity of SiO<sub>2</sub>-Q3 with W/F<sub>LA</sub> at different reaction temperatures. At each temperature, the conversion increased with increasing the W/F<sub>LA</sub>, and tended to reach a constant value when the W/F<sub>LA</sub> was higher than 1.6 h. These results indicate that the lactonization of LA to ALs is an equilibrium reaction, and that the reactions performed at high W/F<sub>LA</sub> values have achieved the equilibrium. In Fig. 2, the conversion at the



**Fig. 2.** Changes in catalytic activity of SiO<sub>2</sub>-Q3 with W/F<sub>LA</sub> at different reaction temperatures. Reaction conditions: reactant, pure LA; N<sub>2</sub> gas flow rate, 30 cm<sup>3</sup> min<sup>-1</sup>.

same W/F<sub>LA</sub> increased with increasing the temperature, whereas the selectivity to ALs at the same W/F<sub>LA</sub> decreased. The selectivity to ALs also slightly decreased with increasing the W/F<sub>LA</sub> at each temperature.

In order to study the reaction equilibrium in LA lactonization to ALs, reactions were performed at 275 °C using aqueous LA solutions with different LA concentrations (Table 2 and Fig. 3). The catalyst weight was changed with the concentration of LA in order to achieve the same constant W/F<sub>LA</sub> of 3.6 h. The conversion of LA and the yield of ALs increased with increasing the concentration of LA, whereas the selectivity to ALs slightly decreased.

The lactonization of LA to ALs was also performed under reduced pressure conditions. Fig. 4 compares the changes in catalytic activity with W/F<sub>LA</sub> over SiO<sub>2</sub>-Q3 under atmospheric and reduced pressure conditions. Because the catalytic deactivation was observed at W/F<sub>LA</sub> values lower than 1.6 h, the initial activity of SiO<sub>2</sub>-Q3 was used for comparison. The conversion increased with increasing the W/F<sub>LA</sub> at low W/F<sub>LA</sub> values, and tended to reach to a constant value at high W/F<sub>LA</sub> values under both atmospheric and reduced pressure conditions. On the other hand, at a same W/F<sub>LA</sub>, the conversion under reduced pressure conditions was much higher than that under atmospheric pressure condi-

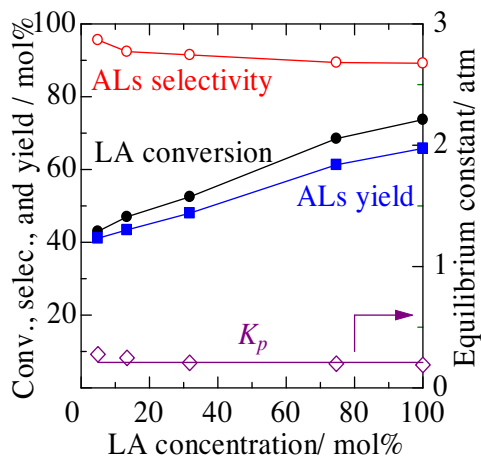
**Table 2**  
Lactonization of LA to ALs over SiO<sub>2</sub>-Q3 at different concentrations of LA aqueous solution.<sup>a</sup>

LA wt.% (mol%)	LA feed rate/g h <sup>-1</sup>	Catalyst weight/g	W/F <sub>LA</sub> /h	Conversion <sup>b</sup> /mol%	ALs selectivity <sup>b</sup> /mol%	ALs yield <sup>b</sup> /mol%	K <sub>p</sub> <sup>c</sup> /atm
25 (4.9)	0.28	0.98		43.0	95.6	41.1	0.28
50 (13.4)	0.56	2.00		47.0	92.4	43.4	0.24
75 (31.8)	0.91	3.26	3.6	52.5	91.5	48.0	0.20
95 (74.7)	1.14	4.07		68.5	89.4	61.3	0.20
100 (100)	1.20	4.27		73.7	89.2	65.8	0.19

<sup>a</sup> Reaction conditions: reaction temperature, 275 °C; N<sub>2</sub> gas flow rate, 30 cm<sup>3</sup> min<sup>-1</sup>.

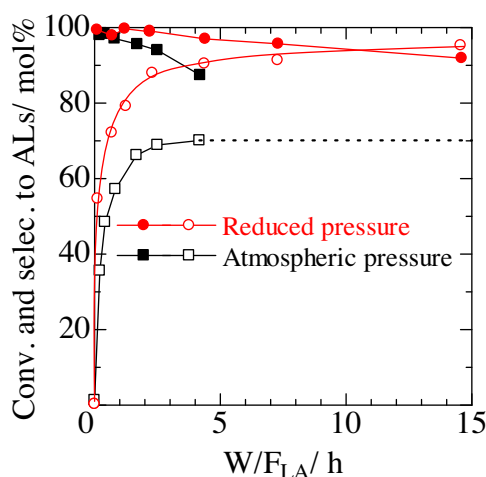
<sup>b</sup> Averaged activity in the initial 3 h.

<sup>c</sup> K<sub>p</sub>, pressure equilibrium constant of LA lactonization to ALs.



**Fig. 3.** Changes in catalytic activity of SiO<sub>2</sub>-Q3 with the concentration of aqueous LA solution.

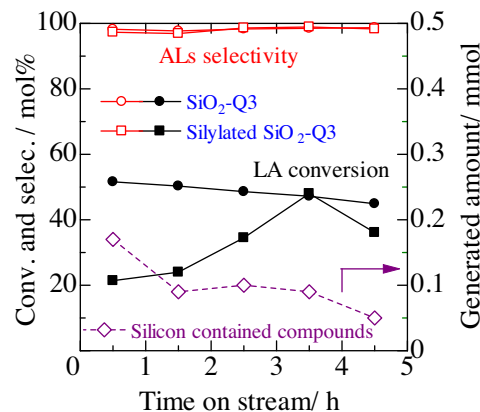
Reaction conditions: catalyst weight, 0.98–4.27 g; reaction temperature, 275 °C; N<sub>2</sub> gas flow rate, 30 cm<sup>3</sup> min<sup>-1</sup>; W/F<sub>LA</sub>, 3.6 h.



**Fig. 4.** Changes in catalytic activity with W/F<sub>LA</sub> over SiO<sub>2</sub>-Q3 under atmospheric and reduced pressure conditions. Open symbols, conversion of LA; Closed symbols, selectivity to ALs.

Reaction conditions: reactant, pure LA; reaction temperature, 275 °C. The values represent the initial activities for 1 h. No carrier gas was used under reduced pressure conditions, and the flow rate of N<sub>2</sub> was 30 cm<sup>3</sup> min<sup>-1</sup> under atmospheric pressure conditions.

tions. Although the selectivity to ALs decreased with increasing the W/F<sub>LA</sub> under both atmospheric and reduced pressure conditions, the selectivity to ALs under reduced pressure conditions was higher than that under atmospheric conditions at a same W/F<sub>LA</sub>. A high ALs yield of 87.5% with a LA conversion of 95.3% was achieved at a W/F<sub>LA</sub> of 14.6 h.



**Fig. 5.** Changes in activity with time on stream over SiO<sub>2</sub>-Q3 and silylated SiO<sub>2</sub>-Q3. Reaction conditions: catalyst weight, 0.5 g; reactant, pure LA; reaction temperature, 275 °C; N<sub>2</sub> gas flow rate, 30 cm<sup>3</sup> min<sup>-1</sup>; W/F<sub>LA</sub>, 0.4 h.

### 3.3. Catalyst stability and regeneration

Since the catalytic activity of SiO<sub>2</sub>-Q3 was stable in the initial 5 h at W/F<sub>LA</sub> higher than 1.6 h, we performed the reaction at a low W/F<sub>LA</sub> of 0.4 h in order to evaluate the catalytic stability (Table 3 and Fig. 5). The conversion of LA decreased from 51.6% to 44.9% during the initial 5 h, which indicated that SiO<sub>2</sub>-Q3 deactivated with time on stream. TG analyses of the as-received and used catalysts were performed to evaluate the amount of carbon accumulated on the catalysts after the reaction: the accumulated carbon was calculated to be 13.4 wt.% of the used catalyst.

The reaction over a reactivated SiO<sub>2</sub>-Q3 catalyst, which was prepared by calcination of a used catalyst in air at 500 °C for 6 h, was performed, and the catalytic activity of the reactivated SiO<sub>2</sub>-Q3 was compared with that of the as-received SiO<sub>2</sub>-Q3 (Table 3). The reactivated SiO<sub>2</sub>-Q3 showed a similar catalytic activity to that of the as-received SiO<sub>2</sub>-Q3, and only slight decrease in ALs yield was observed.

### 3.4. Hydration of ALs to LA over SiO<sub>2</sub>-Q3

In order to study the reaction equilibrium in the lactonization of LA to ALs, we performed the reverse reaction, the hydration of α-AL to LA, over SiO<sub>2</sub>-Q3 (Table 4). The reaction was performed at 275 °C under atmospheric pressure conditions. Under such reaction conditions, the conversion of α-AL, the selectivity to LA, and the yield of LA were 60.6, 82.4, and 49.9%, respectively. It is reasonable that SiO<sub>2</sub>-Q3 works as an acid catalyst in the hydration of α-AL to LA.

### 3.5. Lactonization of LA to ALs over silylated SiO<sub>2</sub>-Q3

The silylated SiO<sub>2</sub> was tested in order to understand the active species in SiO<sub>2</sub>-Q3. Fig. 5 also compares the changes in activity with

**Table 3**  
Comparison of the catalytic activity between reactivated SiO<sub>2</sub>-Q3 and as-received SiO<sub>2</sub>-Q3.<sup>a</sup>

Catalyst	Conversion <sup>b</sup> /mol%	Selectivity <sup>b</sup> /mol% α-AL	β-AL	γ-AL	Total of ALs	ALs yield <sup>b</sup> /mol%
As-received	48.5	45.9	46.2	6.2	98.3	47.7
Reactivated <sup>c</sup>	47.3	45.7	44.4	6.6	96.7	45.7

<sup>a</sup> Reaction conditions: reactant, pure LA; reaction temperature, 275 °C; N<sub>2</sub> gas flow rate, 30 cm<sup>3</sup> min<sup>-1</sup>; W/F<sub>LA</sub>, 0.4 h.

<sup>b</sup> Averaged activity in the initial 5 h.

<sup>c</sup> The catalyst was reactivated by the calcination at 500 °C for 6 h.

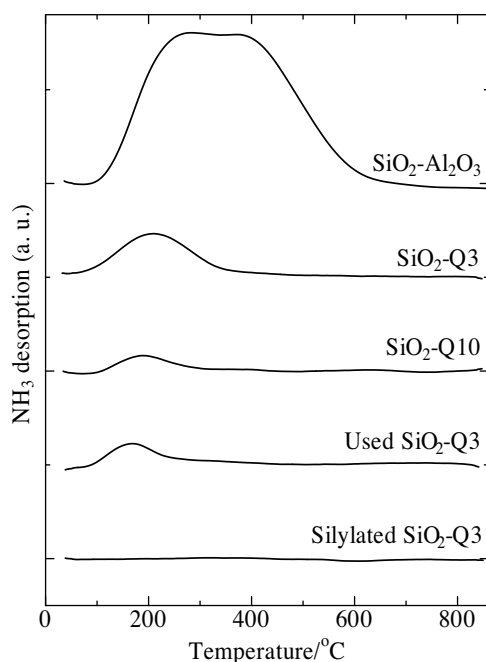
**Table 4**  
Hydration of ALs to LA over SiO<sub>2</sub>-Q3.<sup>a</sup>

ALs feed rate/g h <sup>-1</sup>	H <sub>2</sub> O feed rate/g h <sup>-1</sup>	ALs conversion <sup>b</sup> / mol%	LA selectivity <sup>b</sup> / mol%	LA yield <sup>b</sup> /mol%	K <sub>p</sub> <sup>c</sup> /atm <sup>-1</sup>	1/K <sub>p</sub> <sup>c</sup> /atm
1.3	1.3	60.6	82.4	49.9	2.9	0.34

<sup>a</sup> Reaction conditions: reaction temperature, 275 °C; N<sub>2</sub> gas flow rate, 30 cm<sup>3</sup> min<sup>-1</sup>; catalyst weight, 4 g.

<sup>b</sup> Averaged activity in the initial 3 h.

<sup>c</sup> K<sub>p</sub><sup>c</sup>, pressure equilibrium constant of ALs hydration to LA.



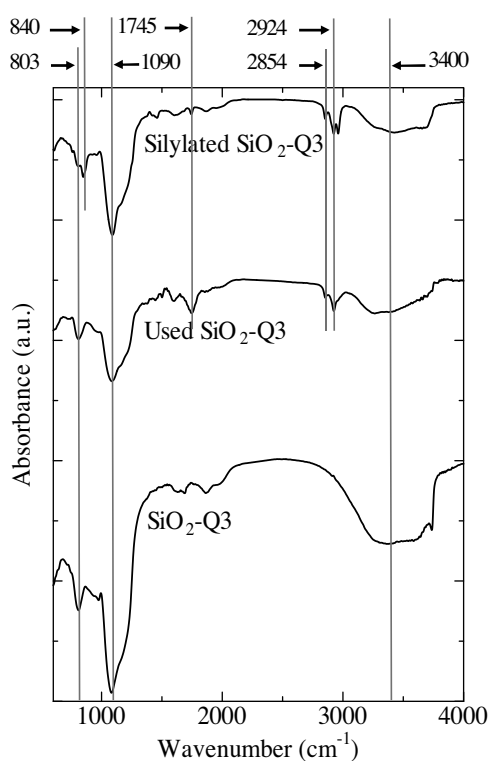
**Fig. 6.** NH<sub>3</sub>-TPD profiles of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-Q3, SiO<sub>2</sub>-Q10, used SiO<sub>2</sub>-Q3 and silylated SiO<sub>2</sub>-Q3.

The reaction conditions for the used SiO<sub>2</sub>-Q3 were as follows: reactant, pure LA; reaction temperature, 275 °C; W/F<sub>LA</sub>, 0.8 h; N<sub>2</sub> gas flow rate, 30 cm<sup>3</sup> min<sup>-1</sup>; reaction time, 10 h.

time on stream over a pure SiO<sub>2</sub>-Q3 and a silylated SiO<sub>2</sub>-Q3 in the lactonization of LA to ALs. The silylated SiO<sub>2</sub>-Q3 gave a much lower initial conversion of LA than that of as-received SiO<sub>2</sub>-Q3, whereas it increased along with the time on stream up to 4 h. At a time on stream of 4 h, the silylated SiO<sub>2</sub>-Q3 showed a conversion close to that over the as-received SiO<sub>2</sub>-Q3, and then it decreased with increasing the time on stream. The selectivity to ALs was stable at ca. 98% over both silylated SiO<sub>2</sub>-Q3 and as-received SiO<sub>2</sub>-Q3 at 275 °C. On the other hand, silicon-contained compounds, such as trimethyl silanol and hexamethyl disiloxane, were detected in the reaction effluents during the reaction when the silylated SiO<sub>2</sub>-Q3 was used as a catalyst. The amount of silicon-contained compounds decreased with increasing the time on stream, as shown in Fig. 5.

### 3.6. Characterization of the catalysts

Fig. 6 shows the NH<sub>3</sub>-TPD profiles of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-Q3 and SiO<sub>2</sub>-Q10 samples. SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> showed two desorption peaks at



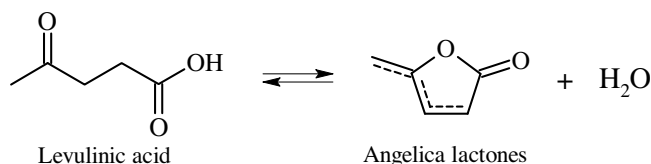
**Fig. 7.** DRIFT spectra of SiO<sub>2</sub>-Q3, used SiO<sub>2</sub>-Q3 and silylated SiO<sub>2</sub>-Q3.

The reaction conditions for the used SiO<sub>2</sub>-Q3 were as follows: reactant, pure LA; reaction temperature, 275 °C; W/F<sub>LA</sub>, 0.8 h; N<sub>2</sub> gas flow rate, 30 cm<sup>3</sup> min<sup>-1</sup>; reaction time, 10 h.

283 and 373 °C. SiO<sub>2</sub>-Q3, SiO<sub>2</sub>-Q10 and the used SiO<sub>2</sub>-Q3 showed desorption peaks at 211, 188 and 167 °C, respectively, whereas no peak was observed in the profile of the silylated SiO<sub>2</sub>-Q3. The acid amount of SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-Q3, SiO<sub>2</sub>-Q10 and the used SiO<sub>2</sub>-Q3 were 524.8, 92.2, 19.0 and 27.3 μmol g<sup>-1</sup>, respectively. The order of the acid strength were SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> > SiO<sub>2</sub>-Q3 > SiO<sub>2</sub>-Q10 > used SiO<sub>2</sub>-Q3 > silylated SiO<sub>2</sub>-Q3.

Fig. 7 shows the DRIFT spectra of as-received SiO<sub>2</sub>-Q3, used SiO<sub>2</sub>-Q3 and silylated SiO<sub>2</sub>-Q3. The peak at 1090 cm<sup>-1</sup>, which was assigned to the symmetric vibration of Si-O-Si [27,28], was observed in all the silica catalysts. The peak at 840 cm<sup>-1</sup>, which was attributed to the deformation vibration of Si-CH<sub>3</sub> [28], was only observed in the spectra of silylated SiO<sub>2</sub>-Q3. This indicates that the silanol group is exchanged with a silyl group through the silylation of SiO<sub>2</sub>-Q3, and that trimethylsilyl groups are successfully intro-





**Scheme 2.** Equilibrium between LA and ALs with water.

duced on the catalyst surface. In the spectra of the silylated SiO<sub>2</sub>-Q3 and used SiO<sub>2</sub>-Q3, the peaks assigned to the stretching vibration of C–H in CH<sub>2</sub> and CH<sub>3</sub> were observed at 2854 and 2924 cm<sup>-1</sup>, respectively [29]. The peak at 1745 in the spectra of the used SiO<sub>2</sub>-Q3 was attributed to the stretching vibration of a C=O group [30]. The existence of CH<sub>2</sub>, CH<sub>3</sub> and C=O in the used SiO<sub>2</sub>-Q3 clarified the formation of carbonaceous compounds on catalytic surface during the reaction. The peak observed at 803 cm<sup>-1</sup>, which is attributed to the asymmetric vibration of Si–OH [27,28], and the broad peak observed at 3400 cm<sup>-1</sup>, which is assigned to hydrogen bonded –OH groups [27], could be observed in all the catalysts, while the as-received SiO<sub>2</sub>-Q3 showed the highest intensity.

## 4. Discussion

### 4.1. Effect of catalyst properties on the formation of ALs

As shown in Table 1, the catalytic activity of the tested catalysts is much different. Although the residual products besides ALs were unidentified, they are probably the oligomers of ALs because it has been known that oligomerization of ALs easily proceeds over a base catalyst or a catalyst with strong acidity [20,21]. ZrO<sub>2</sub> and γ-Al<sub>2</sub>O<sub>3</sub> are widely used as acid–base catalysts [29,31,32], and we have also confirmed their acid–base properties by NH<sub>3</sub>- and CO<sub>2</sub>-TPD analysis in our previous study [33]. Thus, it is reasonable that the base sites in ZrO<sub>2</sub> and γ-Al<sub>2</sub>O<sub>3</sub> catalyze the further oligomerization of ALs, and that results in the low selectivity to ALs. The MFI and HY zeolites have been used for catalyzing the dehydration of 1,2-propanediol to propanal [34] and the cyclodehydration of diethylene glycol to 1,4-dioxane [29], respectively, and the oligomerization of propanal and diethylene glycol occurs in the reactions because of their strong acidity. In this study, MFI and HY zeolites show relatively low ALs selectivities, which is also proposed to attribute to the further oligomerization of ALs over the strong acid sites in zeolites. Because of the low surface area of TiO<sub>2</sub>, it shows the lowest activity for LA conversion.

It has been reported that the lactonization of LA to ALs can be efficiently catalyzed by sulfuric acid, phosphoric acid under reaction distillation conditions [3], which indicates that Brønsted acid is effective for the reaction. SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> are known as solid Brønsted acid catalysts, which show the relatively high activity. Among the tested SiO<sub>2</sub> catalysts, SiO<sub>2</sub>-Q3 has the highest surface areas, which means that it has the largest amount of active sites among the SiO<sub>2</sub> catalysts. Thus, SiO<sub>2</sub>-Q3 is more active than the other silicas, SiO<sub>2</sub>-Q6 and Q10. SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> reduced the selectivity to ALs because of the oligomerization of ALs (Fig. 1), whereas it also gives a higher ALs yield than that of SiO<sub>2</sub>-Q3 with high surface area (Table 1). In contrast to strong acidic SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>-Q3 can be used at large W/F<sub>LA</sub> values without obvious decrease in ALs selectivity (Fig. 1). This would be attributed to the weak acidity of SiO<sub>2</sub>-Q3 (Fig. 6), which accelerates no further oligomerization of ALs. Thus, a weak acidic SiO<sub>2</sub> catalyst would be suitable in such a vapor-phase reaction, because the selectivity and the stability of a catalyst are highly required especially in an industrial application.

### 4.2. Study on the reaction equilibrium of the LA lactonization

In the reaction results shown in Fig. 1b, in which the conversion of LA keeps at a constant value at high W/F<sub>LA</sub> values. Thus, it is suggested that the lactonization of LA to ALs and water is an equilibrium reaction (Scheme 2). Decreasing the water vapor pressure in the reaction system is proved to be effective for shifting the equilibrium from LA to ALs (Table 2 and Fig. 3), which is consistent with Le Chatelier's principle. In order to confirm the reaction equilibrium in the conversion of LA to ALs and water, we calculated the pressure equilibrium constant,  $K_p$ , in the reactions using aqueous LA solutions with different LA concentrations. The experimental  $K_p$  is estimated using the following equation:

$$K_p = \frac{P_{\text{ALs}} \times P_{\text{H}_2\text{O}}}{P_{\text{LA}}} \quad (3)$$

where  $P_x$  is the partial pressure of the reactant and products, and is calculated by the molar fraction of the reaction mixture. The calculation results are shown in the last column of Table 2 and Fig. 3. At 275 °C, the values of pressure equilibrium constant at different W/F<sub>LA</sub> are close to 0.2 atm, which indicates that the equilibrium was achieved in the reactions at a W/F<sub>LA</sub> of 3.6 h, and the pressure equilibrium constant is 0.2 atm in the lactonization of LA to ALs and water at 275 °C.

In order to further confirm the above-mentioned pressure equilibrium constant, we performed the reverse reaction, the hydration of ALs, at 275 °C and calculated its pressure equilibrium constant,  $K_p'$ . (Table 4). The  $K_p'$  is estimated using the following equation:

$$K_p' = \frac{P_{\text{LA}}}{P_{\text{ALs}} \times P_{\text{H}_2\text{O}}} \quad (4)$$

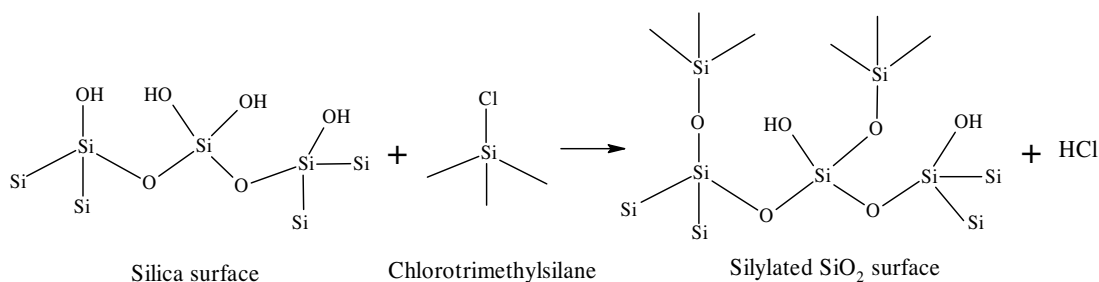
The reciprocal of  $K_p'$  is 0.34 atm, which is a little higher than 0.2 atm of  $K_p$ . The small difference is supposed to be attributed to the purity of the reactant. Nevertheless, this result demonstrates that the calculated  $K_p$  would be reliable.

For an equilibrium reaction, the equilibrium is dependent on the reaction temperature. Since the conversion increases with increasing the temperature (Fig. 2), the lactonization of LA to ALs is an endothermic reaction. However, the selectivity to ALs is low at high temperatures, which is because the oligomerization of ALs prefers high temperatures. Thus, an efficient production of ALs from LA cannot be achieved at high temperatures. On the other hand, based on Le Chatelier's principle, the equilibrium is also dependent upon the pressure in a molecule number–changed reaction. The conversion of LA to ALs and water is a reaction with increased molecule number, so that reduced pressure conditions would be effective for shifting the equilibrium from LA to ALs and H<sub>2</sub>O. Furthermore, a reduced pressure could induce the desorption of ALs from SiO<sub>2</sub> surface, and this would inhibit the further oligomerization of ALs. Therefore, reduced pressures promote the conversion of LA, and also improve the selectivity to ALs (Fig. 4).

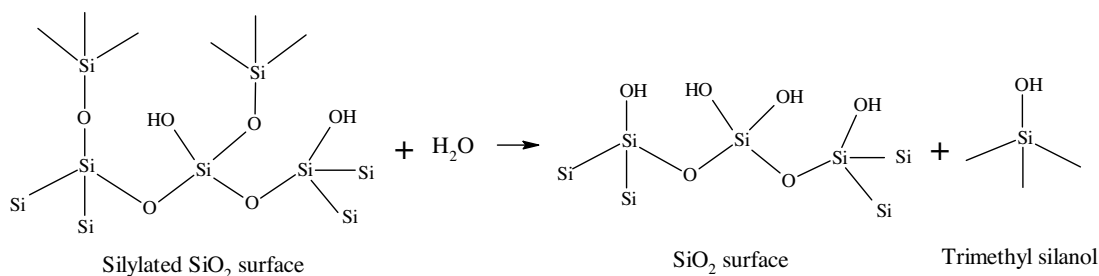
There is an essential issue for the separation of AL isomers. Although the maximum selectivity towards a particular compound is lower than 50%, separation of the ALs is not necessary in some applications of ALs, such as the hydrogenation of ALs to γ-valerolactone [15,19] and the conversion of ALs to hydrocarbons [20,21], because a mixture of ALs can be used as the reactant.

### 4.3. Mechanistic consideration of lactonization of LA to ALs over SiO<sub>2</sub>

SiO<sub>2</sub> has been usually used as a catalyst support and it also could be used as a catalyst in some reactions such as the dehydration of aldoximes to nitriles [35]. Additionally, silanol groups are generally considered to be the active sites in SiO<sub>2</sub> [35]. In order to confirm the active species for the lactonization of LA to ALs, the



**Scheme 3.** Silylation of the SiO<sub>2</sub> surface.



**Scheme 4.** Regeneration of the SiO<sub>2</sub> surface.

silylation of silanol of SiO<sub>2</sub>-Q3 with chlorotrimethylsilane was conducted. The silanol groups are expected to be partially exchanged by the trimethylsilyl groups through such an operation, as shown in Scheme 3, and the existence of trimethylsilyl groups in a silylated SiO<sub>2</sub>-Q3 is confirmed by DRIFT (Fig. 7). The disappearance of the NH<sub>3</sub>-desorption peak in the NH<sub>3</sub>-TPD profile of the silylated SiO<sub>2</sub>-Q3 also supports that the surface of the SiO<sub>2</sub>-Q3 is covered with trimethylsilyl groups (Fig. 6). The low initial conversion of LA over the silylated SiO<sub>2</sub>-Q3 indicates that lactonization of LA (Fig. 5) is inhibited by the trimethylsilyl groups on the SiO<sub>2</sub> surface, and the silanol groups are the active species for catalyzing the lactonization of LA. It is interesting that the conversion of LA increases along with the time on stream up to 4 h. Because the generation of silicon contained products are detected in the reaction effluent in each hour of the reaction, it is reasonable that the silylated SiO<sub>2</sub>-Q3 reacts with water, which is generated together with ALs from LA, and the silanol groups are regenerated during the reaction, as shown in Scheme 4. Thus, the increased conversion of LA is corresponded with the increasing amount of the regenerated silanol groups, which demonstrates again that the surface silanol groups of SiO<sub>2</sub> are the active species for the lactonization of LA to ALs.

The decrease in the conversion of LA at a time on stream from 4 to 5 h over a silylated SiO<sub>2</sub>-Q3 is considered to be caused by the catalytic deactivation (Fig. 5), which is also observed in the reaction over the as-received SiO<sub>2</sub>-Q3 at a low W/F<sub>LA</sub> of 0.4 h. Based on the TG and DRIFT analyses of the used SiO<sub>2</sub>-Q3 (Fig. 7), the deactivation is supposed to be caused by the accumulation of carbonaceous compounds during the reaction. Although the carbonaceous compounds were not identified, based on the absorption region of C=O, they are proposed to have lactone structures [30]. Comparing with the NH<sub>3</sub>-TPD profile of the as-received SiO<sub>2</sub>-Q3, the acid amount in the used SiO<sub>2</sub>-Q3 is small (Fig. 6), which is attributed to the poisoning of the silanol active sites by the carbonaceous compounds. In another word, the accumulation of carbonaceous compounds on catalyst surface results in the catalytic deactivation. On the other hand, the used catalysts can be regenerated by calcination without obvious decrease in the catalytic activity (Table 3).

In the previous studies, *pseudo*-LA was proposed to be the intermediate in the lactonization of LA to ALs over a Brønsted acid

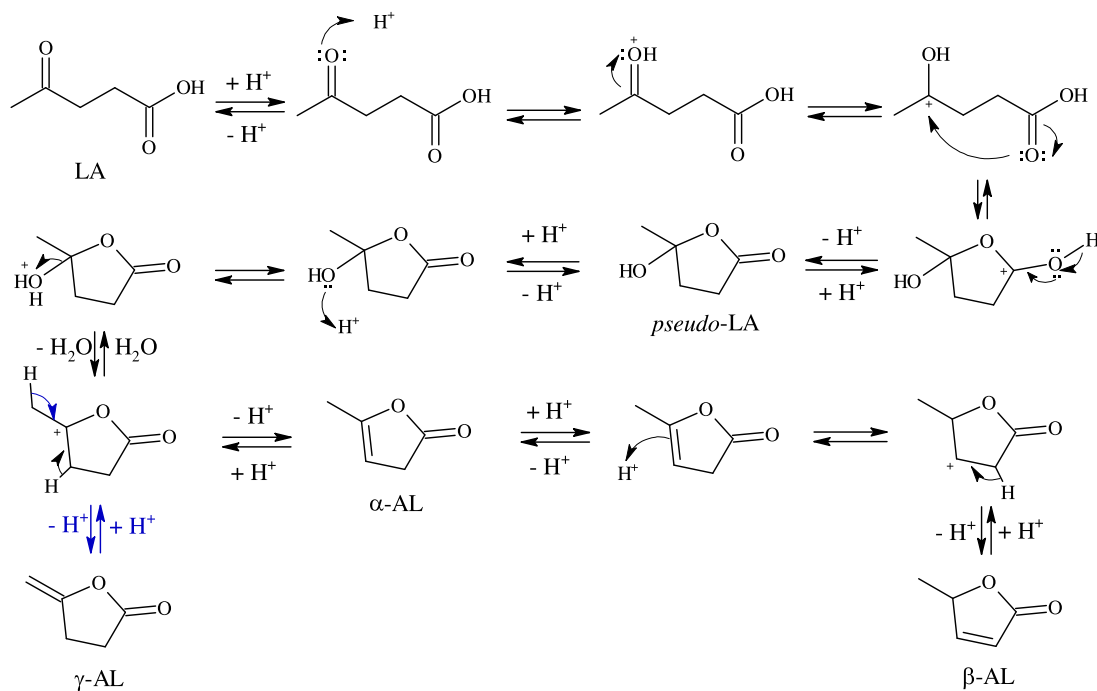
[36,37], whereas detailed formation routes were not discussed. We proposed a formation route of LA lactonization to ALs, as shown in Scheme 5. The reaction starts from the attacking of a proton to the carbonyl at position 4 of LA, which activates the carbon in the carbonyl. After that, cyclization proceeds through the connection of the carbon activated with the oxygen atom in the carbonyl of the carboxyl groups, and then a proton is released, followed by the formation of *pseudo*-LA. The intermediate, *pseudo*-LA, is easily activated by a proton, and it dehydrates to  $\alpha$ - and  $\gamma$ -AL through two different ways. The generated  $\alpha$ -AL further isomerizes to  $\beta$ -AL, which is also catalyzed by the Brønsted acid.

## 5. Conclusions

Vapor-phase lactonization of LA to ALs was performed in fixed-bed down-flow glass reactors over various solid catalysts. SiO<sub>2</sub>-Q3 showed the highest catalytic performance, especially at high W/F<sub>LA</sub> values. The weak acidity of SiO<sub>2</sub>, which is supposed to inhibit the further oligomerization of generated ALs, increases the selectivity to ALs. In the study of trimethylsilylation of surface silanol of SiO<sub>2</sub> catalyst, we proposed that the silanol groups of SiO<sub>2</sub> were the active species. Slight catalytic deactivation of SiO<sub>2</sub> was observed at a low W/F<sub>LA</sub> of 0.4 h, which was attributed to the coke accumulation on the catalyst surface, whereas the used catalyst can be regenerated by calcination at 500 °C without obvious decrease in the catalytic activity. Lactonization of LA to ALs and water is an equilibrium reaction, and the pressure equilibrium constant is calculated to be *ca.* 0.2 atm at 275 °C. Although high reaction temperatures can improve the conversion of LA, they decrease the selectivity to ALs. Therefore, the suitable temperature for lactonization of LA to AL is estimated to be 275 °C. In addition, reduced pressure conditions are efficient for shifting the equilibrium from LA to ALs, and an ALs yield of 87.5% with a LA conversion of 95.3% and an ALs selectivity of 91.8% was achieved over SiO<sub>2</sub>-Q3 at 275 °C.

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**Scheme 5.** Proposed reaction mechanism in the lactonization of LA to ALs.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcata.2016.07.025>.

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