

Electronic supplementary information for

Stable catalysis of neutral silica-supported potassium lactate for vapour-phase dehydration of lactic acid to acrylic acid – Critical role of support

Lin Huang,* De Sheng Theng, Lili Zhang, Luwei Chen, Chuan Wang, Feng Gao and Armando Borgna

Process and Catalysis Research, Institute of Chemical and Engineering Sciences, Agency for Science, Technology and Research, 1 Pesek Road, Jurong Island, Singapore 627833, Singapore

Acid properties of catalyst systems and interaction between KNO_3 and silica

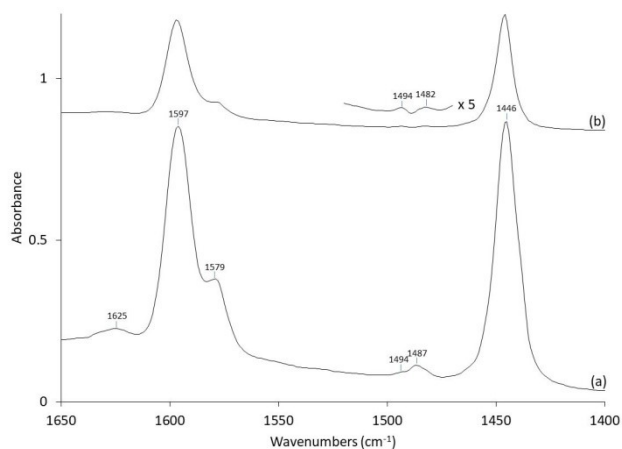


Fig. S1. Subtract IR spectra of pyridine adsorbed on SBA-15 (20 mg) at (a) 22 °C and (b) 100 °C.

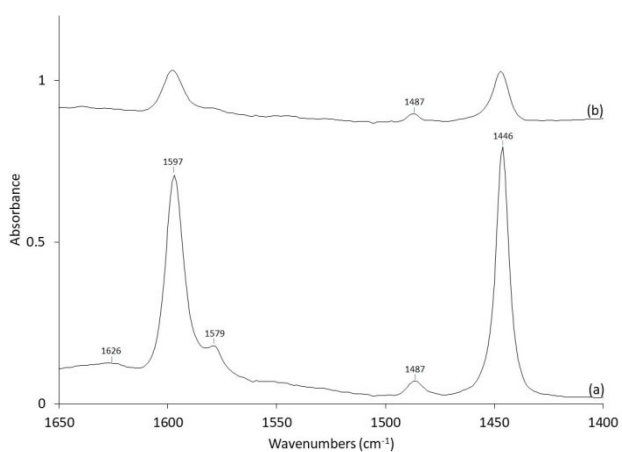


Fig. S2. Subtract IR spectra of pyridine adsorbed on AS300 (20 mg) at (a) 22 °C and (b) 100 °C.

Fig. S3 shows the comparative IR spectra in the 4000-1800 cm^{-1} region of S15, S15cal, AS300 and SBA-15 after 2 h of evacuation at 350 $^{\circ}\text{C}$. With an equivalent amount of sample wafer (40 mg), S15 had an obviously lower $\nu(\text{O-H})$ stretching vibration band intensity of isolated OH groups at 3746 cm^{-1} than AS300 or SBA-15. The emergence of less isolated OH groups may be associated with the formation of more Si ions of strained siloxane bridge (Si-O-Si) as Lewis acid sites.

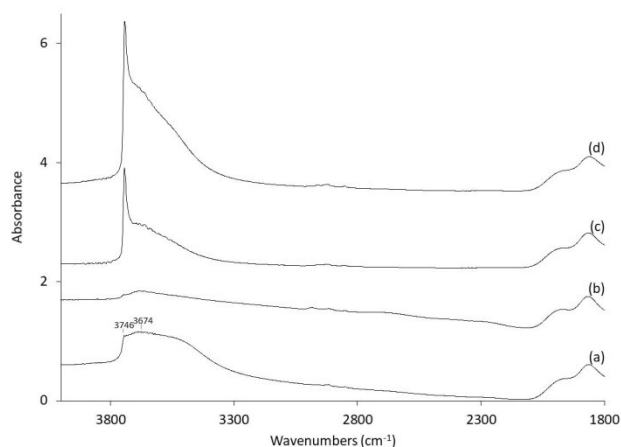


Fig. S3. IR spectra after evacuation (10^{-2} mmHg) at 350 $^{\circ}\text{C}$ of (a) S15, (b) S15cal, (c) AS300 and SBA-15.

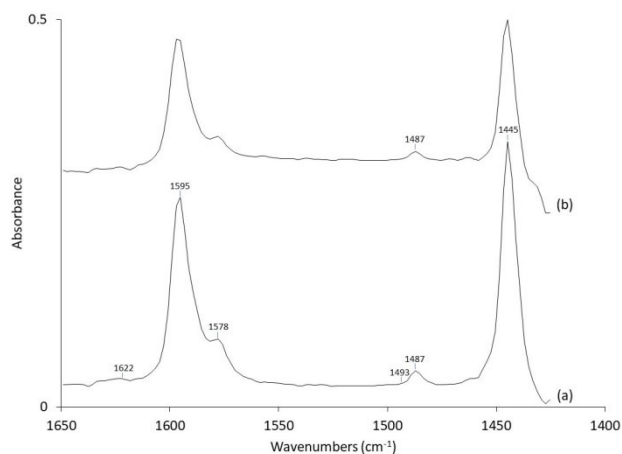


Fig. S4. Subtract IR spectra of pyridine adsorbed on $\text{KNO}_3/\text{S15}$ (40 mg) at (a) 22 $^{\circ}\text{C}$ and (b) 100 $^{\circ}\text{C}$.

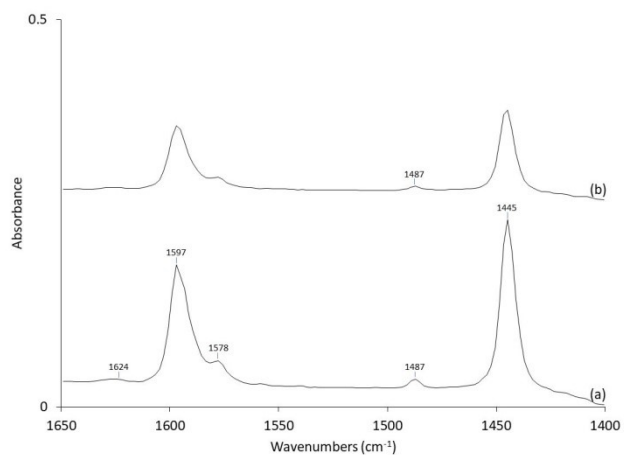


Fig. S5. Subtract IR spectra of pyridine adsorbed on KNO₃/SBA-15 (40 mg) at (a) 22 °C and (b) 100 °C.

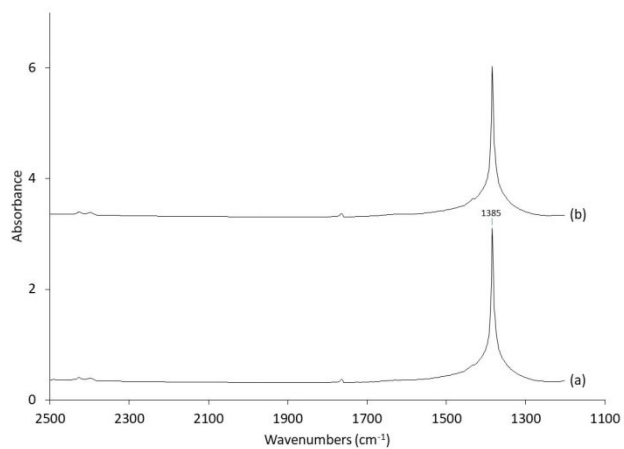


Fig. S6. IR spectra on KBr of KNO₃ after (a) drying at 110 °C and (b) calcination in air at 540 °C.

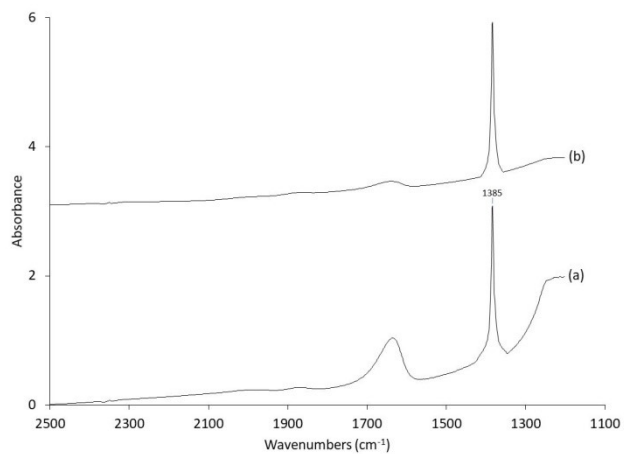


Fig. S7. IR spectra on KBr of KNO₃/AS300 after (a) drying at 110 °C and (b) calcination in air at 540 °C.

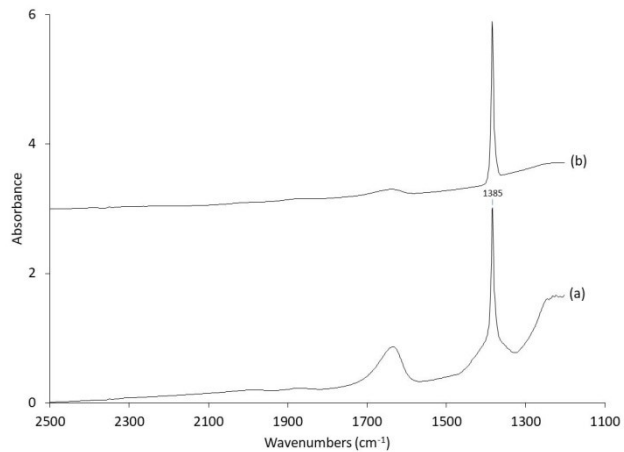


Fig. S8. IR spectra on KBr of KNO₃/S15cal after (a) drying at 110 °C and (b) calcination in air at 540 °C.

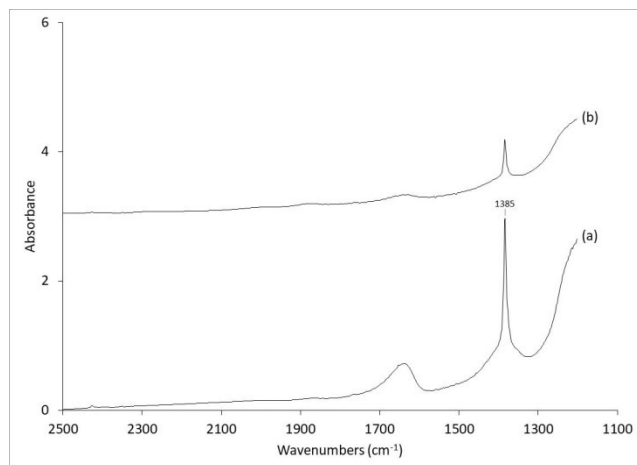


Fig. S9. IR spectra on KBr of KNO₃/S15 after (a) drying at 110 °C and (b) calcination in air at 540 °C.

Catalytic properties in vapour-phase dehydration of LA to AA

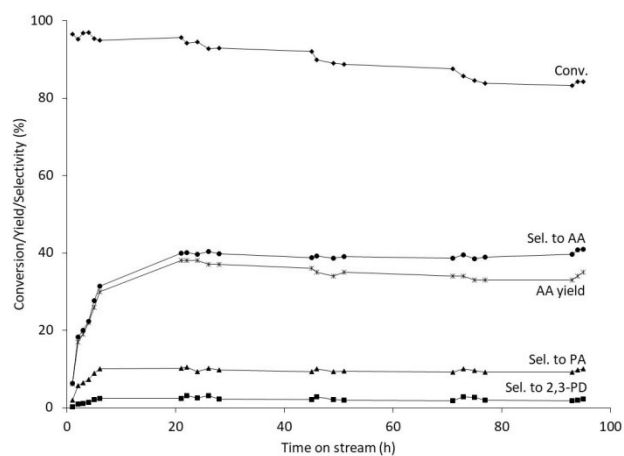


Fig. S10. LA conversion, AA yield and selectivities to chief products as a function of reaction time at a $WHSV_{LA}$ of 0.46 h^{-1} in vapour-phase dehydration of LA at $350 \text{ }^\circ\text{C}$ over $\text{KNO}_3/\text{S15cal}$.

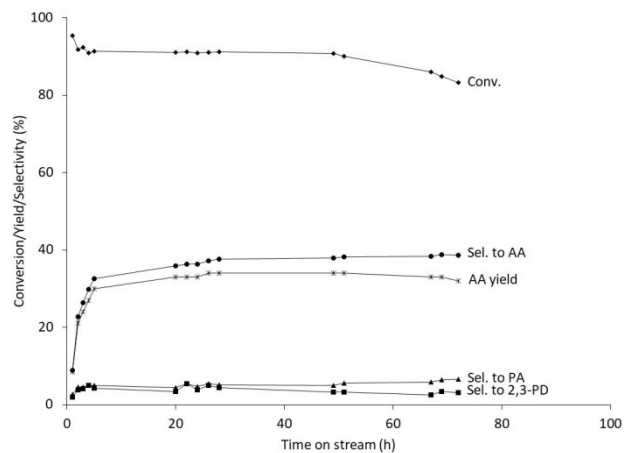


Fig. S11. LA conversion, AA yield and selectivities to chief products as a function of reaction time at a $WHSV_{LA}$ of 0.46 h^{-1} in vapour-phase dehydration of LA at $350 \text{ }^\circ\text{C}$ over $\text{KNO}_3/\text{AS300}$.

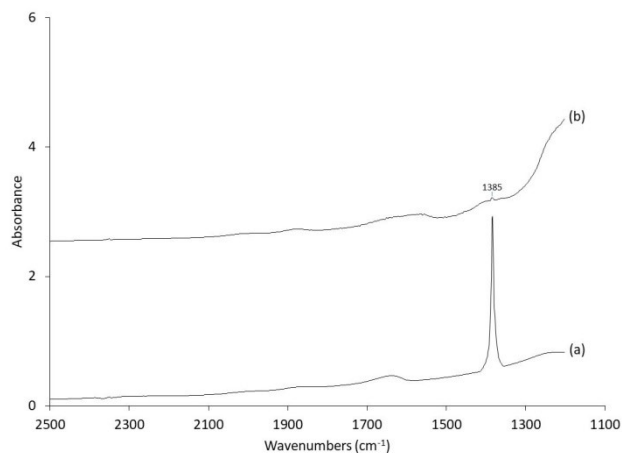


Fig. S12. IR spectra on KBr of $\text{KNO}_3/\text{AS300}$ (a) before and (b) after 5 h of vapour-phase dehydration of LA at 350 °C.

Table S1. Properties of silica-supported catalyst systems in vapour-phase dehydration of LA at 350 °C. ^a

Precatalyst	Cycle	Conversion (%)					Selectivity (%)														
		5 h	28 h	49 h	72 h	99 h	AA					PA					2,3-PD				
							5 h	28 h	50 h	72 h	99 h	5 h	28 h	50 h	72 h	99 h	5 h	28 h	50 h	72 h	99 h
$\text{KNO}_3/\text{AS300}$	1	91	91	91	83	33	38	38	39	5.0	5.2	5.0	6.6	4.3	4.4	3.3	3.2				
	2	93	94	93	87	34	39	40	40	4.9	5.0	5.0	6.5	4.3	4.4	3.4	3.4				
$\text{KNO}_3/\text{SBA-15}$	1	95	95	94	92	97	37	44	44	44	4.0	4.7	7.3	10	11	4.5	3.4	3.5	3.5	2.5	
	2	97	97	96	95	94	41	46	46	45	44	3.9	4.6	7.5	9.6	10	3.2	3.4	2.7	2.7	2.5
$\text{KNO}_3/\text{S15}$	1	81	51				30	27			16	21			1.5	1.6					
	2	63	39				28	26			20	24			1.5	1.5					

^a 0.50 g of precatalyst, 20 % LA aqueous solution, $\text{WHSV}_{\text{LA}} = 0.46 \text{ h}^{-1}$, carrier gas flow rate = 30 ml min^{-1} .

Reactivity on catalyst systems under dehydration conditions

Figs. S13 and S14 show the IR spectra in the 2500-900 cm^{-1} region of representative carboxyl group-containing compounds including LA, AA, PA, potassium lactate, potassium acrylate and potassium propionate on KBr, which were prepared from compound aqueous solutions followed by removal of water under vacuum at 22 °C. The IR spectra of these compounds on KBr are in agreement with the IR data of these compounds in water or on KBr reported in the literature.⁷⁶⁻⁸⁰ The presence of an additional band at 1731(w) cm^{-1} in the spectrum of potassium lactate is attributed to the formation of small amounts of LA from slight potassium lactate hydrolysis on KBr (Fig. S13(a)). The observation of an extra band at 1720(w) cm^{-1} in the spectrum of potassium acrylate is due to the production of small amounts of AA from slight potassium acrylate hydrolysis on KBr (Fig. S13(d)).

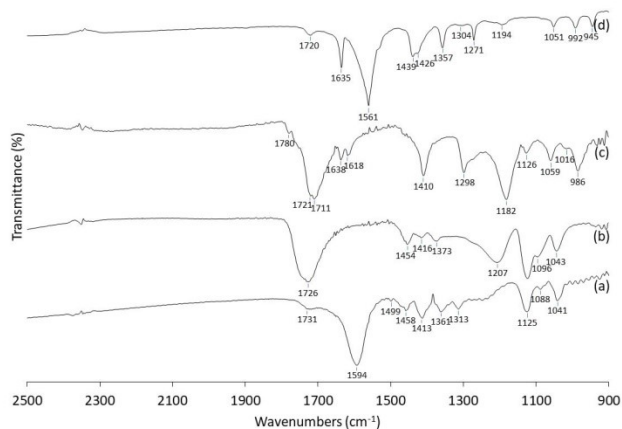


Fig. S13. IR spectra on KBr of (a) potassium lactate, (b) LA, (c) AA and (d) potassium acrylate.

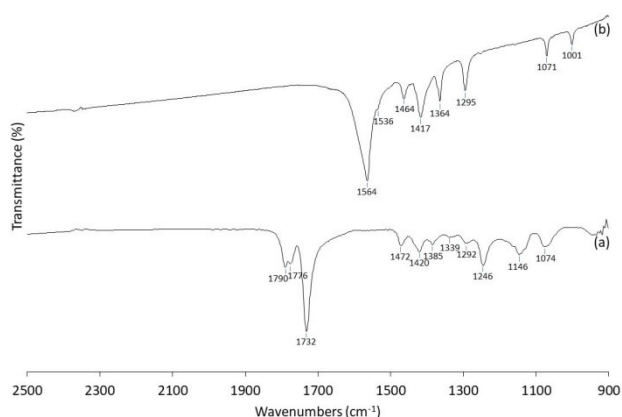


Fig. S14. IR spectra on KBr of (a) PA and (b) potassium propionate.

Fig. S15 shows the subtract surface IR spectra in the 2500-900 cm⁻¹ region during a thermal reaction of potassium lactate on KBr. In the IR experiment, a small drop of *ca.* 20 % potassium lactate aqueous solution was added onto a KBr wafer (80 mg) loaded in the IR cell followed by 0.5 h of evacuation at 22 °C. Potassium lactate is rather stable on KBr till at least 200 °C, as evidenced by the presence of bands at 1594(s), 1458(m), 1413(m), 1359(m), 1313(m), 1125(m), 1088(w), 1041(m) and 924(w) cm⁻¹.⁷⁸ Slight potassium lactate hydrolysis occurred at 22 °C, which gave rise to a principal band of LA at 1731(w) cm⁻¹.⁷⁸ When the temperature rose to 300 °C, the bands of potassium lactate at 1594, 1413 and 1353 cm⁻¹ shifted downwards to 1578, 1405 and 1364 cm⁻¹, respectively with the concomitant marked diminution of the bands of potassium lactate at 1458, 1125, 1088 and 1041 cm⁻¹. At the same time, a new band appeared at 1632(sh) cm⁻¹ and the band at 1308 cm⁻¹ remained unchanged in intensity.

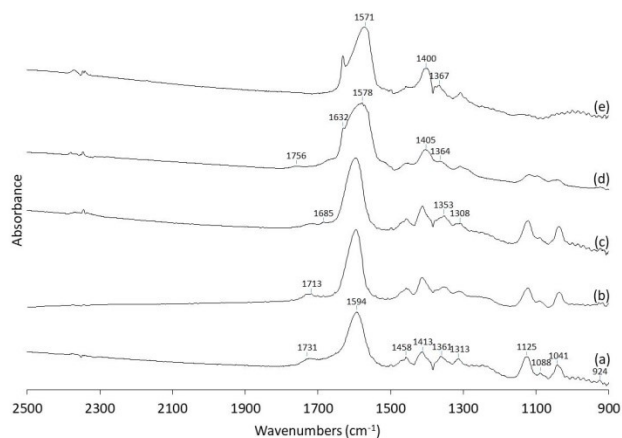


Fig. S15. Subtract surface IR spectra after 0.5 h of treatment of potassium lactate on KBr at (a) 22 °C, (b) 100 °C, (c) 200 °C, (d) 300 °C and (e) 350 °C.

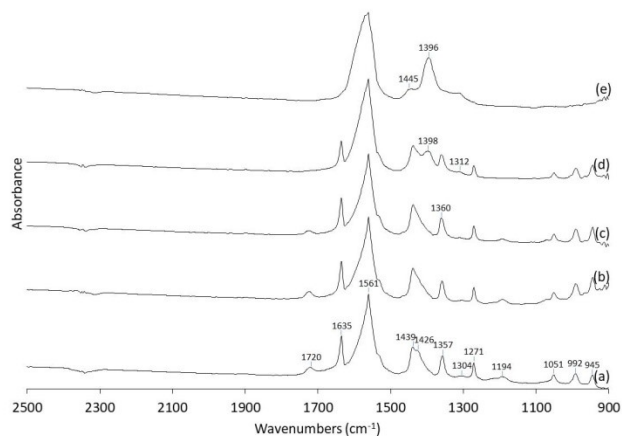


Fig. S16. Subtract surface IR spectra after 0.5 h of treatment of potassium acrylate on KBr at (a) 22 °C, (b) 100 °C, (c) 200 °C, (d) 300 °C and (e) 350 °C.

Upon heating at 350 °C, the bands of 1578, 1405 and 1364 cm^{-1} further shifted to 1571, 1400 and 1367 cm^{-1} , respectively while the bands of potassium lactate nearly disappeared. Besides, the bands at 1632 and 1308 cm^{-1} increased in intensity, and no bands of potassium acrylate were present. These results suggest that potassium lactate already dehydrates to potassium acrylate which subsequently polymerizes on KBr at 300 °C, the potassium lactate dehydration is almost complete and the potassium acrylate polymerization is complete at 350 °C. In Fig. S15(e), the bands at 1632(m), 1571(s), 1458(w), 1400(m), 1367(w) and 1308(w) cm^{-1} are assignable to poly(potassium acrylate).^{79,80} The bands at 1632(m), 1571(s) and 1400(m) cm^{-1} can be viewed as signature features of poly(potassium acrylate).^{79,80} During the whole thermal treatment process, negligible LA polymerization takes place on KBr, a band of poly(LA) at

1756(vw) cm^{-1} being observed at 300 $^{\circ}\text{C}$.

Potassium acrylate polymerization on KBr is demonstrated by our IR study of a thermal reaction of potassium acrylate on KBr. In the IR experiment, a small drop of *ca.* 10 % potassium acrylate aqueous solution was added onto a KBr wafer (80 mg) loaded in the IR cell followed by 0.5 h of evacuation at 22 $^{\circ}\text{C}$. As shown in Fig. S16, potassium acrylate is substantially stable on KBr till at least 200 $^{\circ}\text{C}$ without spectral change. The presence of an additional band at 1720(w) cm^{-1} at 22-200 $^{\circ}\text{C}$ may be attributed to the formation of small amounts of AA from slight potassium acrylate hydrolysis on KBr. At above 200 $^{\circ}\text{C}$, AA neutralization with KOH seems to dominate over potassium acrylate hydrolysis on KBr, the band at 1720 cm^{-1} gradually disappearing. Upon heating to 300 $^{\circ}\text{C}$, the bands of potassium acrylate at 1635, 1439, 1357, 1271, 1194, 1051, 992 and 945 cm^{-1} diminished in favour of growth of the bands at 1561 and 1312 cm^{-1} and emergence of a new band at 1398 cm^{-1} . This spectral evolution implies transition of potassium acrylate to poly(potassium acrylate).^{79,80} When heating to 350 $^{\circ}\text{C}$, the bands of potassium acrylate disappeared with the concomitant emergence of a new spectrum consisting of bands at 1635(sh), 1561(s), 1445(w), 1396(m), 1360(sh) and 1312(w) cm^{-1} as in Fig. S16(d). This new spectrum represents poly(potassium acrylate).^{79,80} Potassium acrylate is deemed to totally polymerize at 350 $^{\circ}\text{C}$ on KBr, judging from the resulting new spectrum that comprises no bands of potassium acrylate (Fig. S16(d)).

Fig. S17 shows the comparative IR spectra in the 2500-1100 cm^{-1} region of AA on KBr, potassium lactate on KBr and (AA + potassium lactate) on KBr after 0.5 h of thermal treatment at 200 $^{\circ}\text{C}$. In the IR experiments, AA/KBr or potassium lactate/KBr was made by addition of a small drop of 20 % AA or *ca.* 20 % potassium lactate aqueous solution onto a KBr wafer (80 mg) loaded in the IR cell followed by 0.5 h of evacuation at 22 $^{\circ}\text{C}$. (AA + potassium lactate)/KBr was obtained by addition of two small drops of a

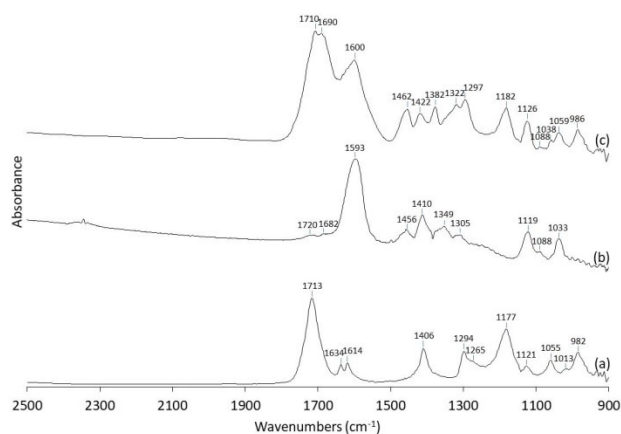


Fig. S17. IR spectra after 0.5 h of treatment at 200 $^{\circ}\text{C}$ of (a) AA on KBr, (b) potassium lactate on KBr and (c) (AA + potassium lactate) on KBr.

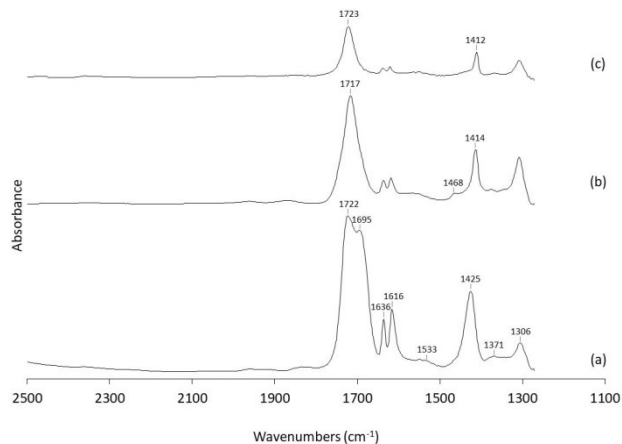


Fig. S18. Subtract surface IR spectra after 0.5 h of treatment of AA on AS300 at (a) 22 °C, (b) 100 °C and (c) 350 °C.

mixture of 20 % AA and *ca.* 20 % potassium lactate aqueous solutions onto a KBr wafer (80 mg) loaded in the IR cell followed by 0.5 h of evacuation at 22 °C.

As a result of intermolecular interaction between two kinds of organic compounds, IR bands in a binary system shift, narrow or broaden and even change their fundamental shape.^{82,84-86} By examining the spectra of AA and potassium lactate in Figs. S13 and S17, it is seen that either AA/AS300 or potassium lactate/AS300 is stable at 200 °C without spectral change. From the comparative spectra in Fig. S17, the spectrum of a mixture of AA and potassium lactate is not a simple additive of the spectra of AA and potassium lactate on KBr. An additional band appeared at 1690 cm^{-1} (Fig. S17(c)). It is believed that there is not any reaction between AA and potassium lactate on KBr at 200 °C. The appearance of the 1690 cm^{-1} band is presumably due to the intermolecular interaction between AA and potassium lactate on KBr.

Fig. S19 gives the surface IR spectra in the 2500-1300 cm^{-1} region during a thermal reaction of potassium lactate on AS300 under flowing N_2 at 22-350 °C. A small drop of *ca.* 20 % potassium lactate aqueous solution was added onto an AS300 wafer and subsequently evacuated at 22 °C. The resultant sample wafer was subjected to thermal treatment under flowing N_2 at 22-350 °C. At 22 °C, the surface spectrum exhibited new bands at 1719(m), 1700(sh), 1591(s), 1458(m), 1420(m), 1376(w), 1347(w) and 1318(sh) cm^{-1} . The band at 1719(m) cm^{-1} can be deconvoluted into two bands around 1730 and 1710 cm^{-1} that are assigned to LA and AA, respectively. The band at 1591(s) cm^{-1} can be regarded as a band overlapped of two bands around 1595 and 1560 cm^{-1} that are assigned to potassium lactate as the major species and potassium acrylate as the minor species, respectively. And the bands at 1458(m), 1376(w), 1347(w) and 1318 (sh) cm^{-1} can be viewed as overlapped ones of LA at 1458 and 1376(w) cm^{-1} and of potassium lactate at 1458, 1347(w) and 1318 (sh) cm^{-1} . This result implies that potassium lactate readily hydrolyzes to LA which then catalytically dehydrates to AA on AS300. The potassium acrylate may form

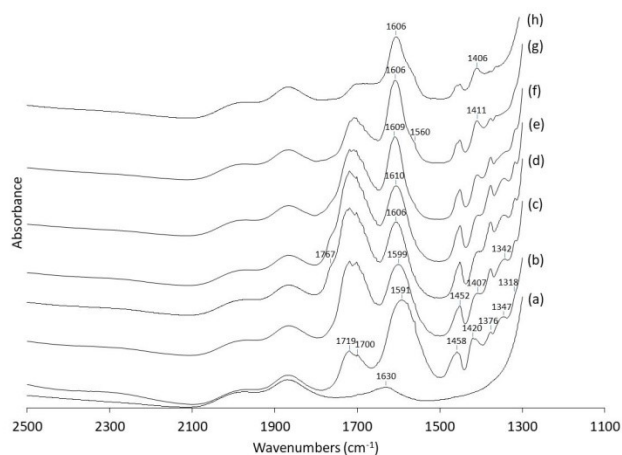


Fig. S19. Surface IR spectra before (a) and after reaction of potassium lactate on AS300 under flowing N_2 at (b) 22 °C for 0.5 h, (c) 100 °C for 0.5 h, (d) 200 °C for 0.5 h, (e) 300 °C for 0.5 h, (f) 350 °C for 0.5 h, (g) 350 °C for 3 h and (h) 350 °C for 8 h.

from AA neutralization with KOH issuing from potassium lactate hydrolysis. The band at 1700(sh) cm^{-1} is assumed to result from the intermolecular interaction between AA and potassium lactate. When the temperature rose to 100 °C, the intensity of the 1591 cm^{-1} band decreased in favour of intensity increase of the 1719, 1700 and 1376 cm^{-1} ones, which implies the domination of potassium lactate hydrolysis over other reactions such as LA neutralization with KOH, AA neutralization with KOH, potassium acrylate displacement with LA and LA polymerization. Meanwhile, the 1700 cm^{-1} band became more resolved, and the 1591 cm^{-1} band shifted upwards to 1599 cm^{-1} with the concurrent shift of other bands in position, which may be attributed to strengthened intermolecular interaction between AA and potassium lactate. At 200-300 °C, the relative intensity of the 1719, 1700 and 1376 cm^{-1} bands to the band of potassium lactate kept increasing together with further upward shift of the 1599 cm^{-1} band to 1610 cm^{-1} . This indicates that potassium lactate hydrolysis continues to dominate up to 300 °C and that the formation of more AA causes stronger upward shift of the band of potassium lactate. Besides, a new band appeared at 1767(sh) cm^{-1} probably as the dominant feature of poly(LA)⁸¹ at 200 °C, which confirms that LA negligibly polymerizes on AS300. After the temperature had reached 350 °C, the position of the 1610 cm^{-1} band shifted downward to 1606 cm^{-1} while the intensity of the 1719 and 1700 cm^{-1} bands progressively fell, further assuming the relation between the shift of the band of potassium lactate and the AA - potassium lactate intermolecular interaction. In the meantime, the band of potassium lactate grew at the expense of intensity of the band of LA at 1376 cm^{-1} within the first 3 h, assuming the domination of reactions relating to production of potassium lactate such as LA neutralization with KOH, AA neutralization with KOH, potassium acrylate displacement with LA over potassium lactate hydrolysis at 350 °C. After the first 3 h, a unique new band emerged at 1560(sh) cm^{-1} , which may be due to potassium acrylate produced from AA

neutralization with KOH. At the end of 8 h, the intensity of the band of potassium lactate decreased by *ca.* a quarter with the concurrent downward shift of 1411 cm^{-1} band to 1406 cm^{-1} while LA was heavily consumed. The 1560(sh) and 1406 cm^{-1} bands may mostly be attributed to poly(potassium acrylate) that may arise from AA neutralization with KOH followed by potassium acrylate polymerization. This further implies that potassium lactate hydrolysis prevails to cause the production of poly(potassium acrylate) on AS300 where there is a shortfall of LA. Probably due to the presence of little K^+ source with respect to the case of LA on $\text{KNO}_3/\text{AS300}$, it seems that little potassium acrylate is produced so that poly(potassium acrylate) is hardly produced in the case of potassium lactate on AS300. During 8 h of thermal treatment at 350 $^\circ\text{C}$, the band of the unreacted potassium lactate was substantially present in the spectrum (Fig. S19(h)), which confirms good stability of potassium lactate on AS300 at 350 $^\circ\text{C}$.

Fig. S20 presents the subtract surface IR spectra in the 2500-1300 cm^{-1} region during a thermal reaction of potassium acrylate on AS300. In the IR experiment, a small drop of *ca.* 10 % potassium acrylate aqueous solution was added onto an AS300 wafer (20 mg) loaded in the IR cell followed by 0.5 h of evacuation at 22 $^\circ\text{C}$. Potassium acrylate is basically stable on AS300 till at least 200 $^\circ\text{C}$ without spectral change. The presence of an extra band at 1713(w) cm^{-1} at 22-100 $^\circ\text{C}$ may be due to the production of small amounts of AA from slight potassium acrylate hydrolysis on AS300. At above 100 $^\circ\text{C}$, AA neutralization with KOH appears to dominate over potassium acrylate hydrolysis on AS300, the band at 1713 cm^{-1} disappearing at 200 $^\circ\text{C}$. When heating to 300 $^\circ\text{C}$, the relative intensity of the 1635, 1433 and 1361 cm^{-1} bands to the 1565 cm^{-1} band decreased with the concurrent appearance of a new 1406 cm^{-1} band. This spectral evolution suggests transition of potassium acrylate to poly(potassium acrylate).^{79,80} Upon heating to 350 $^\circ\text{C}$, potassium acrylate is believed to nearly totally polymerize on AS300, judging

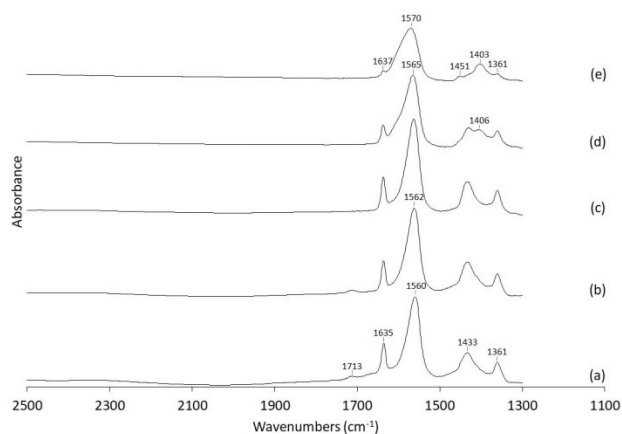


Fig. S20. Subtract surface IR spectra after 0.5 h of treatment of potassium acrylate on AS300 at (a) 22 $^\circ\text{C}$, (b) 100 $^\circ\text{C}$, (c) 200 $^\circ\text{C}$, (d) 300 $^\circ\text{C}$ and (e) 350 $^\circ\text{C}$.

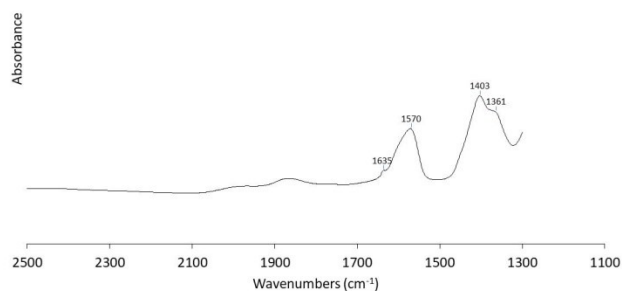


Fig. S21. Original surface IR spectrum after 0.5 h of treatment of potassium acrylate on AS300 at 350 °C (corresponding to Fig. S13(e)).

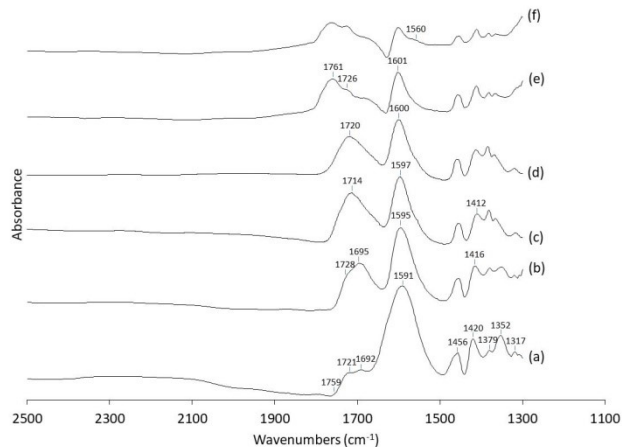


Fig. S22. Subtract surface IR spectra after reaction of potassium lactate on S15 under flowing N₂ at (a) 22 °C for 1.5 h, (b) 100 °C for 0.5 h, (c) 200 °C for 0.5 h, (d) 300 °C for 0.5 h, (e) 350 °C for 0.5 h and (f) 350 °C for 3 h.

from the resulting new spectrum that contains nearly no band of potassium acrylate at 1433 cm⁻¹. The resulting new spectrum consisted of bands at 1637(w), 1570(s), 1451(w), 1403(m) and 1361(w) cm⁻¹ as in Fig. S20(e), which can reasonably be assigned to poly(potassium acrylate) supported on AS300.^{79,80}

Fig. S21 illustrates the original surface IR spectrum corresponding to Fig. S20(e). The original spectrum exhibited relevant bands at 1635, 1570, 1403 and 1361 cm⁻¹. The positions of the corresponding bands indicated in Figs. S20(e) and S21 are much the same.

Fig. S22 presents the subtract surface IR spectra in the 2500-1300 cm⁻¹ region during a thermal reaction of potassium lactate on S15. At 22 °C, the surface spectrum showed bands at 1759(sh), 1721(w), 1692(w), 1591(s), 1456(m), 1420(m), 1379(w), 1352(m) and 1317(w) cm⁻¹, which indicate the occurrence

of potassium lactate hydrolysis, catalytic LA dehydration, AA neutralization with KOH and LA polymerization in the system. As the temperature rose up to 350 °C, the band intensity of potassium lactate gradually decreased. The band intensity of LA and AA remarkably increased at 100-200 °C and gradually decrease at 300-350 °C. Upon heating to 350 °C, the band intensity of poly(LA) steeply increased, prevailing over those of LA and AA. After the first 3 h, the band intensity of potassium lactate continued to decrease. And a unique new band at 1560(sh) cm^{-1} appeared, which is indicative of the formation of small amounts of potassium acrylate that presumably forms from AA neutralization with KOH. These results turn out that potassium lactate hydrolysis dominates in the system up to 300 °C, and potassium lactate hydrolysis and LA polymerization dominate in the system at 350 °C on the acidic S15. Probably due to the poor catalytic production of AA and the presence of little K^+ source which give rise to little potassium acrylate, poly(potassium acrylate) is not produced within a short term (3 h).

Fig. S23 shows the surface IR spectra in the 2500-1300 cm^{-1} region during a thermal reaction of LA on $\text{KNO}_3/\text{S15cal}$ under flowing N_2 at 22-350 °C. On $\text{KNO}_3/\text{S15cal}$, KNO_3 remains stable as well after calcination in air at 540 °C as described in this work. From our acidity data, $\text{KNO}_3/\text{S15cal}$ is neutral although S15cal is somewhat acidic. After addition of a diluted LA aqueous solution onto a $\text{KNO}_3/\text{S15cal}$ wafer followed by evacuation at 22 °C, the resultant sample wafer was subjected to thermal treatment under flowing N_2 at 22-350 °C. At 22 °C, the surface spectrum presented new bands at 1720(sh), 1639(s), 1587(s), 1455(m), 1413(m), 1376(sh), 1355(sh) and 1317(sh) cm^{-1} . The 1720(sh) cm^{-1} band may be regarded as an overlapped one of LA and AA. The 1639(s) cm^{-1} band may be due to the molecular water adsorbed on the Lewis acid sites of S15cal. The 1587(s) cm^{-1} band may be referred to as an overlapped one of potassium lactate and potassium acrylate. And the 1455(m), 1413(m), 1376(sh), 1355(sh) and

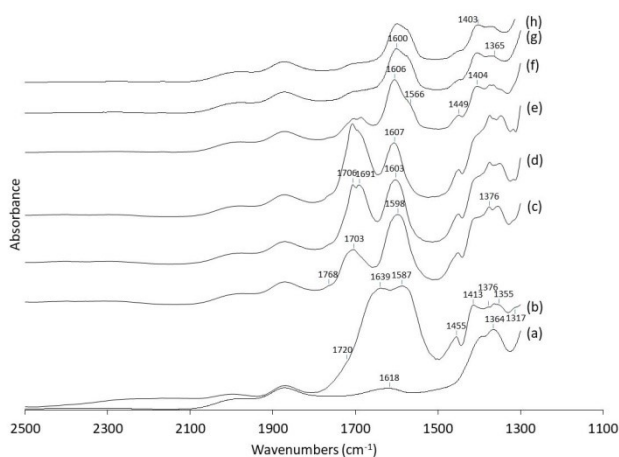


Fig. S23. Surface IR spectra before (a) and after reaction of LA on $\text{KNO}_3/\text{S15cal}$ under flowing N_2 at (b) 22 °C for 0.5 h, (c) 100 °C for 0.5 h, (d) 200 °C for 0.5 h, (e) 300 °C for 0.5 h, (f) 350 °C for 0.5 h, (g) 350 °C for 4 h and (h) 350 °C for 7 h.

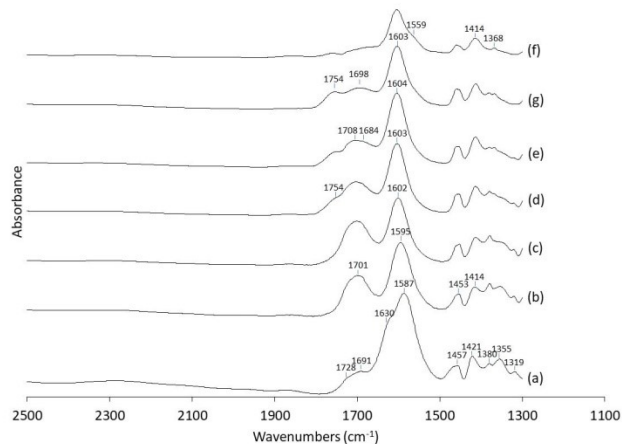


Fig. S24. Subtract surface IR spectra after reaction of potassium lactate on S15cal under flowing N₂ at (a) 22 °C for 0.5 h, (b) 100 °C for 0.5 h, (c) 200 °C for 0.5 h, (d) 300 °C for 0.5 h, (e) 350 °C for 0.5 h, (f) 350 °C for 4 h and (g) 350 °C for 7 h.

1317(sh) bands may be viewed as overlapped ones of LA at 1455 and 1376(sh) and of potassium lactate at 1455, 1413(m), 1355(sh) and 1317(sh). The emergence of this spectrum may implicate the occurrence of the following reactions on the neutral KNO₃/S15cal at 22 °C, similar to the case of LA on KNO₃/AS300: (1) KNO₃ displaces with LA to AA and potassium lactate; (2) LA catalytically dehydrates to AA over potassium lactate; and (3) KNO₃ displaces with AA to HNO₃ and potassium acrylate. When the temperature rose to 100 °C, the 1639(s) cm⁻¹ band disappeared because of desorption of the adsorbed molecular water. And two new bands appeared at 1768(sh) and 1703(m) cm⁻¹ apart from upward shift of the 1587(s) cm⁻¹ band to 1598(s) cm⁻¹. The bands at 1768(sh), 1703(m) and 1598(s) cm⁻¹ are attributed to poly(LA), AA and potassium lactate, respectively. The results are an indication that negligible LA polymerization takes place while potassium acrylate displacement with LA occurs at 100 °C. As the temperature rose to 300 °C, the band intensity of potassium lactate was noticed to gradually decline in favour of increase of the band intensity of LA at 1376 cm⁻¹ (from 100 °C), which assumes that potassium lactate hydrolysis dominates over all other reactions from 100 °C on KNO₃/S15cal, similar to the case of LA on KNO₃/AS300. Besides, the band position of potassium lactate shifted upwards from 1598 to 1607 cm⁻¹ with the concurrent splitting of the 1703 cm⁻¹ band into 1706 and 1691 cm⁻¹ ones, which again suggests strengthened intermolecular interaction between AA and potassium lactate. After the temperature had reached 350 °C, the band position of potassium lactate shifted downwards from 1607 to 1600 cm⁻¹ as AA desorbed from KNO₃/S15cal, in support of the assumption of the intermolecular interaction between AA and potassium lactate. Apparently because of fast LA consumption at 350 °C, the band intensity of potassium lactate continued to decline together with the appearance of two new bands at 1566(sh) and 1403(m) cm⁻¹ due to poly(potassium acrylate) (Fig. S20), which again suggests that where

there is a shortfall of LA, the occurrence of potassium lactate hydrolysis incurs a chance of potassium acrylate polymerization on silica. It is noteworthy that the band of the unreacted potassium lactate at 1600 cm^{-1} is retained after a prolonged thermal treatment (7 h) at $350\text{ }^{\circ}\text{C}$, hinting good stability of potassium lactate on $\text{KNO}_3/\text{S15cal}$ at the LA dehydration temperature.

Comparatively, Fig. S24 illustrates the subtract surface IR results in the $2500\text{-}1300\text{ cm}^{-1}$ region during a thermal reaction of potassium lactate on S15cal. It is verified that potassium lactate is likewise substantially stable on S15cal at $350\text{ }^{\circ}\text{C}$ despite that S15cal is slightly acidic, in contrast with the case of potassium lactate on S15. Except for the emergence of a little more poly(LA) at $300\text{-}350\text{ }^{\circ}\text{C}$ in the case of potassium lactate on S15cal probably due to the acidity of S15cal, potassium lactate on S15cal behaved consistently with potassium lactate on $\text{KNO}_3/\text{S15cal}$ and similarly to potassium lactate on AS300. In the case of potassium lactate on S15cal, no bands of poly(potassium acrylate) were observed despite that there was a shortfall of LA at $350\text{ }^{\circ}\text{C}$. This may be because the presence of little K^+ source results in the formation of little potassium acrylate and thus no chance of polymerization, compared to the case of LA on $\text{KNO}_3/\text{S16cal}$. More importantly, the IR spectrum of the spent $\text{KNO}_3/\text{Si15cal}$ catalyst sample in the long-term vapour-phase dehydration of LA to AA at $350\text{ }^{\circ}\text{C}$ presents bands of potassium lactate at $1601(\text{s})$, 1456 and $1416(\text{m})\text{ cm}^{-1}$ with no bands of poly(potassium acrylate) (Fig. 10(d)). This result illustrates that potassium lactate as the catalytic active species in-situ generated on $\text{KNO}_3/\text{S15cal}$ is stable during the long-term LA dehydration to AA and that AA neutralization with KOH, potassium acrylate displacement with LA and LA neutralization with KOH proceed efficiently to produce AA and potassium lactate under the catalytic conditions. All these spectral results are in accordance with the good catalytic stability of the neutral $\text{KNO}_3/\text{S15cal}$ system in vapour-phase dehydration of LA to AA, which again

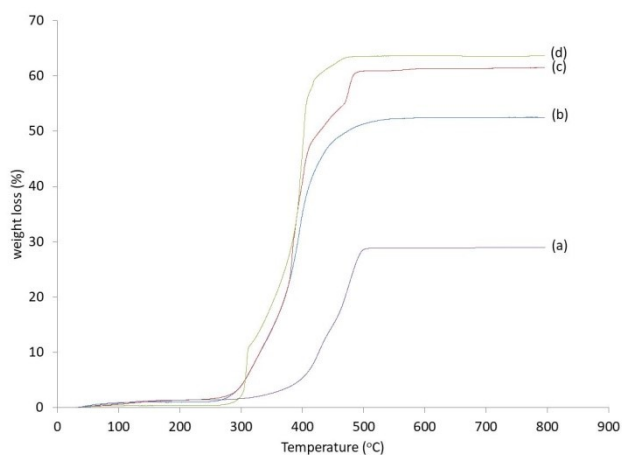


Fig. S25. TG profiles in air of the following spent catalyst samples in vapour-phase dehydration of LA at $350\text{ }^{\circ}\text{C}$: (a) $\text{KNO}_3/\text{S15}$ after 28 h, (b) $\text{KNO}_3/\text{AS300}$ after 72 h, (c) $\text{KNO}_3/\text{S15cal}$ after 97 h and (d) $\text{KNO}_3/\text{SBA-15}$ after 99 h.

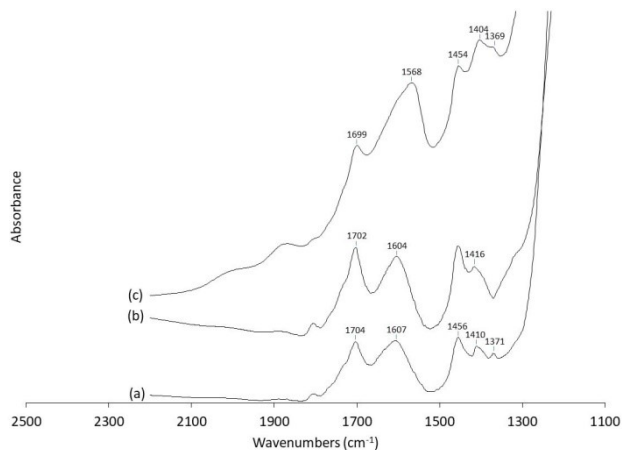


Fig. S26. IR spectra on KBr of the following spent recycled catalyst samples in vapour-phase dehydration of LA at 350 °C: (a) KNO₃/AS300 after 72 h, (b) KNO₃/SBA-15 after 99 h and (c) KNO₃/S15 after 28 h.

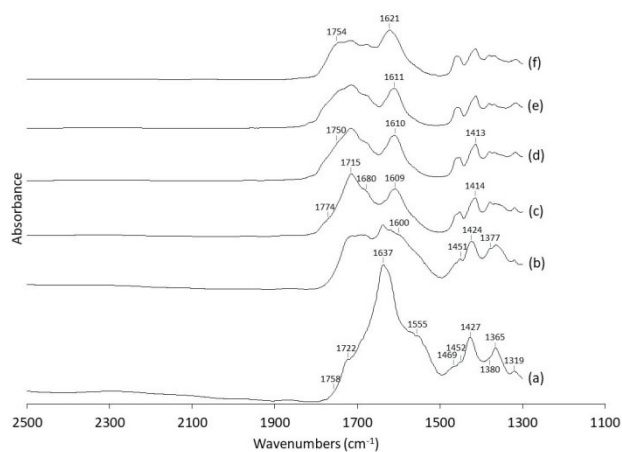
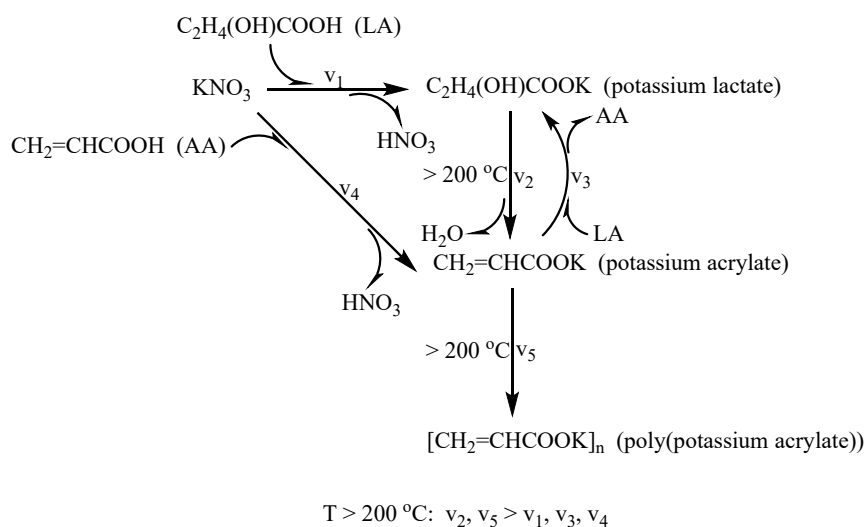


Fig. S27. Subtract surface IR spectra after reaction of LA and potassium acrylate on S15cal at (a) 22 °C for 0.5 h, (b) 100 °C for 0.5 h, (c) 200 °C for 0.5 h, (d) 300 °C for 0.5 h, (e) 350 °C for 0.5 h and (f) 350 °C for 4 h.

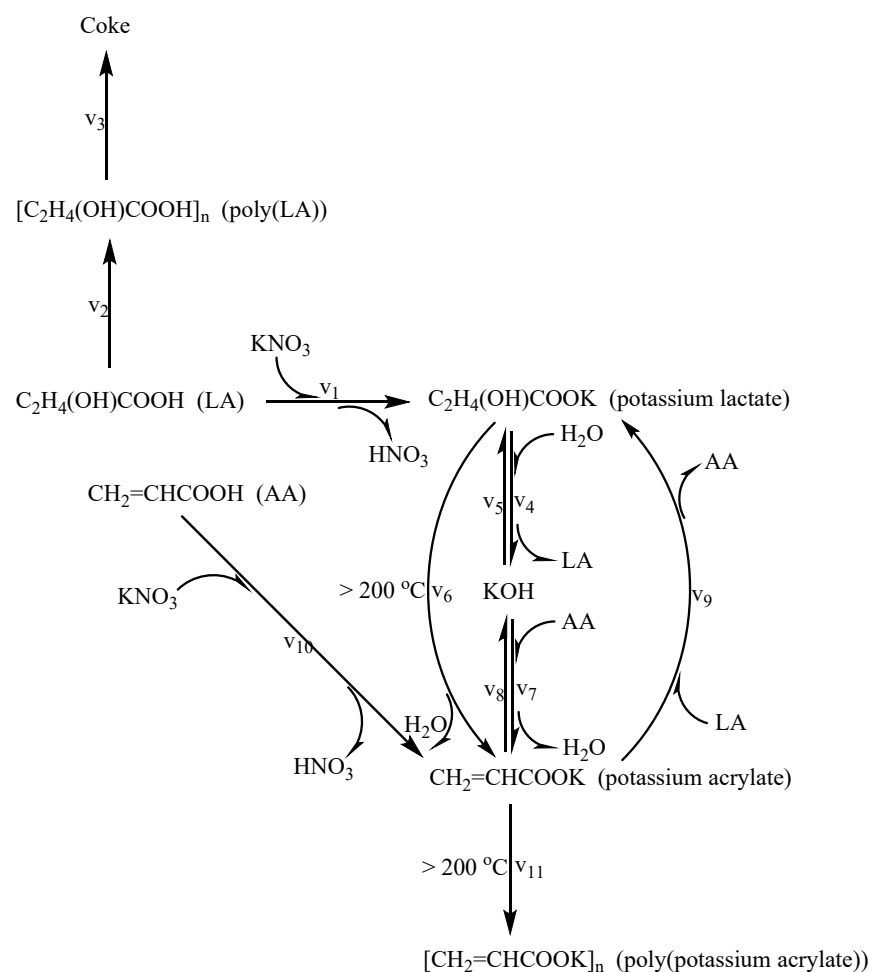
suggests that the interaction between potassium lactate and silica could stabilize potassium lactate and thus could ensure long-term catalytic performance of a neutral KNO₃/silica system in vapour-phase dehydration of LA to AA.

Fig. S27 gives the subtract surface IR spectra in the 2500-1300 cm⁻¹ region during a reaction between LA and potassium acrylate on S15cal in flowing N₂ at 22-350 °C. Onto an S15cal wafer a small drop of *ca.* 10 % potassium acrylate aqueous solution was added in air followed by evacuation at 22 °C. Onto the resultant sample wafer was added a small drop of 10 % LA aqueous solution in air followed by evacuation at 22 °C. The resulting surface spectrum presented bands at 1758(sh), 1722(sh), 1637(s), 1555(sh), 1469(sh), 1452(sh), 1427(m), 1380(sh), 1365(m) and 1319(w) cm⁻¹. The 1758(sh) cm⁻¹ band

may be due to poly(LA). The 1722(sh) and 1380(sh) cm^{-1} bands may be ascribed to LA. The 1637(s) cm^{-1} band may be assigned to the molecular water adsorbed on the Lewis acid sites of S15cal. The 1555(sh), 1427(m) and 1365 cm^{-1} bands may be due to potassium acrylate. The 1469(sh), 1365 and 1319(w) cm^{-1} bands may be attributed to potassium lactate. And the 1365(m) cm^{-1} band may be an overlapped one of LA, potassium acrylate and potassium lactate. The results indicate that potassium acrylate only partly displaces with LA to give potassium lactate on the acidic S15cal at 22 °C. This may be because of the competition of LA polymerization on the acidic S15cal. As the temperature rose to 200 °C, the adsorbed molecular water gradually desorbed, and the bands of potassium acrylate at 1555, 1427 and 1365 cm^{-1} gradually diminished in favour of emergence of the bands of potassium lactate at 1609 and 1414 cm^{-1} (Fig. S27(c)). The concurrent appearance of bands at 1715 and 1680 cm^{-1} supports the occurrence of the intermolecular interaction between AA and potassium lactate. In addition, a marked band at 1774(sh) cm^{-1} appeared, indicative of further formation of poly(LA). As the temperature rose up to 350 °C, the amount of poly(LA) produced increased as shown by the presence of bands at 1774-1750 cm^{-1} . And bands of potassium lactate at 1621 cm^{-1} and LA at 1377 cm^{-1} were well retained in intensity and no bands of poly(potassium acrylate) were present during 4 h of thermal treatment at 350 °C. This shows that despite that S15cal is somewhat acidic, the side reactions can be controlled while potassium lactate regeneration from potassium acrylate displacement with LA can proceed smoothly, which can secure the content and stability of potassium lactate as the catalytic active species. The spectral results are not only consistent with that of the spent $\text{KNO}_3/\text{S15cal}$ catalyst sample but also in accordance with the fact that the $\text{KNO}_3/\text{S15cal}$ system performs well in catalytic stability towards the long-term vapour-phase dehydration of LA to AA.



Scheme S1. Suggested chemistry of the unsupported KNO_3 under LA dehydration conditions.



$T = 22\text{-}200^\circ\text{C}$: $v_2, v_3, v_4 > v_1, v_5, v_7, v_9, v_{10}$

$T > 200^\circ\text{C}$: $v_2, v_3, v_4, v_{11} > v_1, v_5, v_6, v_7, v_9, v_{10}$

Scheme S2. Suggested chemistry of the acidic $\text{KNO}_3/\text{S15}$ under LA dehydration conditions.

Experimental

Table S2. Physical properties of silicas and precatalysts.

Sample ^a	BET surface area ^b (m ² g ⁻¹)	Pore volume ^b (ml g ⁻¹)	K content ^c (%)
S15 ^d	707	0.42	
KNO ₃ /S15	15.2	0.071	3.3
S15cal	591	0.34	
KNO ₃ /S15cal	4.10	0.053	3.1
AS300 ^d	295	1.5	
KNO ₃ /AS300	59.2	0.17	3.2
SBA-15 ^d	684	1.1	
KNO ₃ /SBA-15	81.2	0.45	3.3

^a Calcined in air at 540 °C for 5 h. ^b Measured by N₂ adsorption-desorption. ^c Determined by ICP-OES. ^d Uncalcined.