In Situ-Generated Supported Potassium Lactate: Stable Catalysis for Vapor-Phase Dehydration of Lactic Acid to Acrylic Acid

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

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

Supporting Information

ABSTRACT: We have studied unsupported, silica gel- and amorphous silica–alumina-supported catalysts derived from K salts for the vapor-phase dehydration of lactic acid (LA) to acrylic acid (AA). A catalytic study shows that the supported catalysts improve the activity and selectivity for the production of AA and decrease the selectivity for the production of propionic acid (PA). The silica–alumina-supported catalysts remain fairly stable in the catalytic performance during 90 h of reaction. The IR spectroscopic characterization combined with the catalytic study demonstrates that potassium lactate (C\textsubscript{3}H\textsubscript{5}KO\textsubscript{3}) in situ generated from LA and a K salt is an important reaction intermediate for the production of AA and the catalytic stability is associated with the chemical stability of C\textsubscript{3}H\textsubscript{5}KO\textsubscript{3} and the activity for the regeneration of C\textsubscript{3}H\textsubscript{5}KO\textsubscript{3} in the catalytic cycle. On silica–alumina, C\textsubscript{3}H\textsubscript{5}KO\textsubscript{3} is well stabilized and smoothly regenerated during the reaction, leading to the good catalytic stability. This work suggests for the first time that lactate salt acts as the true catalytic active species for the dehydration of LA to AA. We also propose a predominant reaction pathway for the vapor-phase dehydration of LA to AA with K salt catalyst systems.

1. INTRODUCTION

Acrylic acid (AA) and its derivatives are very versatile monomers for many industrial and commodity chemicals such as absorbents, detergents, dispersants, and flocculants. Due to a complicated propene oxidative process currently used in the industry, which is nonrenewable, the development of new processes producing sustainable AA from biomass derivatives has attracted much research interest. One of the promising biomass derivatives is lactic acid (LA), which is inexpensively available from biomass (e.g., starch) fermentation. AA can be produced from either liquid- or vapor-phase catalytic dehydration of LA:

\[
\text{C}_2\text{H}_4(\text{OH})\text{COOH} \rightarrow \text{C}_2\text{H}_3\text{COOH} + \text{H}_2\text{O} \quad (1)
\]

The liquid-phase catalytic formation of AA from LA was first reported by Odell et al. in 1985. At 150–250 °C and atmospheric pressure or below in the presence of group VIII metal complexes such as [PH(P\textsubscript{Et\textsubscript{3}})\textsubscript{3}]\textsuperscript{+}, PtCl\textsubscript{2}(P\textsubscript{Ph\textsubscript{3}})\textsubscript{2}, IrH\textsubscript{2}(CO)(P\textsubscript{Ph\textsubscript{3}})\textsubscript{2}, and Ni(CO)\textsubscript{2}(P\textsubscript{Ph\textsubscript{3}})\textsubscript{2} in aqueous solutions, hydrothermal reactions of LA produced \(\beta\)-hydroxypropanoic acid, pyruvic acid, acetic acid (HAc), acetaldehyde (CH\textsubscript{3}CHO), acetone, and ethanol (EtOH). Under optimal conditions, an AA yield of only 3.4% was obtained. Later on, the liquid-phase catalytic dehydration of LA to AA was investigated by Mok et al. and further by Lira and McCrackin. The reaction was reportedly operated in supercritical water at 320–400 °C and 310–340 bar. With an initial LA concentration of 0.1 M and residence time of ~30 s, the conversion of LA generally increased together with the yields of CH\textsubscript{3}CHO and CO as the solution acidity increased. In the presence of H\textsubscript{2}SO\textsubscript{4} as a precatalyst, the conversion of LA was 57–100% with the production of CH\textsubscript{3}CHO and CO/CO\textsubscript{2} as the predominant products. With the presence of NaOH instead of the acid as a precatalyst, the conversion of LA decreased to 23–41% with an increase in the yields of AA and propionic acid (PA). The yields of AA and PA reached a maximum (13 and 27%, respectively) when a small amount of NaOH was added. When Na\textsubscript{2}HPO\textsubscript{4} and NaOH were used as precatalysts with an initial LA concentration of 0.4 M and residence time of ~70 s, the yields of AA were found to be 15 and 6.8%, respectively. While the poor catalytic performance of these liquid-phase catalyst systems for the dehydration of LA to AA was shown, the nature of the catalytic active species was not discussed in the earlier studies. Nor the follow-up of the liquid-phase catalytic dehydration of LA to AA has been reported.

The first patent application on the vapor-phase catalytic dehydration of LA and alkyl lactates to AA and acrylates was filed by Holmen et al. in 1958. Higher AA yields of 42–68% were achieved from aqueous 10–50% solutions of LA over sulfate, phosphate, and mixed inorganic salts at 400–425 °C and atmospheric pressure. Evidently, the vapor-phase catalytic reaction displays an incomparable advantage over the liquid-phase catalytic reaction in the production of AA. Since then,
the catalytic process of vapor-phase dehydration of LA to AA has been attracting considerable interest of catalytic investigators for the sake of not only high efficiency but also green chemical manufacture. In this area, the selective catalyst systems reported for the production of AA include sulfate salts, phosphate salts, mixed inorganic salts, phosphate salt-containing materials, and modified zeolites. Alkali- and alkali-earth-metal phosphates and alkali-metal-modified zeolites were reported to be prominent catalyst systems for dehydration of LA to AA. Likely, the catalytic performance for the vapor-phase LA conversion promoted investigators to shed light on the LA reaction mechanism and catalytic active species on various catalyst systems. Miller and co-workers earlier studied the vapor-phase LA conversion mechanism on catalyst surfaces by means of IR, NMR, and GC/MS analyses of surface species apart from catalytic testing and kinetics. They discovered that low temperatures (<320 °C) and elevated pressures favor 2,3-pentanedione (2,3-PD) formation, whereas high temperatures and low pressures benefit AA and CH3CHO production. They sought to characterize the catalytic active species starting with various supported Na salts such as NaOH, NaN03, Na2SiO3, Na3PO4, Na2HPO4, sodium lactate (C3H5NaO3), and NaNO3 was confirmed by recent surface IR results of Sun et al. who studied the vapor-phase dehydration of LA to 2,3-PD on amorphous silica-Al2O3(36). The aqueous 10% C3H5KO3 solution was dried at 110 °C overnight followed by calcination at 540 °C in air for 5 h. C3H5KO3/SiO2 and C3H5KO3/Al2O3(36) were prepared by incipient wetting impregnation. The molar ratio of added K or Na to Si was 1.8:36. The impregnated samples except C3H5KO3/SiO2 and C3H5KO3/Al2O3(36) were dried at 110 °C overnight followed by calcination at 540 °C in air for 5 h to give the H-form SiO2-Al2O3(36), denoted as H-SiO2-Al2O3(36). The aqueous 10% C3H5KO3 solution was synthesized by reaction of an aqueous LA solution with equimolar KOH at 22 °C for 17 h. The aqueous solutions of 10% C3H5KO3 and 10% C3H5KO3 were prepared in a similar manner.

2. EXPERIMENTAL SECTION

The aqueous 90% LA solution was supplied by VWR Chemicals. AA (99%), PA (99%), and hydroxyacetone (HA, 95%) were obtained from Alfa Aesar. The 2,3-PD (97%), HAc (99%), EtOH (99.5%), NaNO3 (99.9%), KNO3 (99.9%), K2CO3 (99%), KOH (99.99%), and silica gel (SiO2, grade 15) were purchased from Sigma-Aldrich. SiO2 was employed without further treatment. The amorphous Na-form SiO2-Al2O3 was prepared according to the patent literature, which was stored after drying at 110 °C overnight. SiO2-Al2O3(23), SiO2-Al2O3(36), SiO2-Al2O3(77), and SiO2-Al2O3(138) stand for amorphous SiO2-Al2O3 (Si/Al = 23:1 molar ratio), SiO2-Al2O3 (Si/Al = 36:1 molar ratio), SiO2-Al2O3 (Si/Al = 77:1 molar ratio), and SiO2-Al2O3 (Si/Al = 138:1 molar ratio), respectively. The NH4-form SiO2-Al2O3 was obtained by ion-exchanging SiO2-Al2O3 with aqueous solutions of 0.5 M NH4NO3 at 80 °C for 17 h. After filtration and washing with deionized water, the ion-exchanged sample was dried at 110 °C overnight followed by calcination at 540 °C in air for 5 h to give the H-form SiO2-Al2O3(36), denoted as H-SiO2-Al2O3(36). The aqueous 10% C3H5KO3 solution was synthesized by reaction of an aqueous LA solution with equimolar KOH at 22 °C for 17 h. The aqueous solutions of 10% C3H5KO3 and 10% C3H5KO3 were prepared in a similar manner.

The supported Na and K salt precatalysts studied in this work such as KNO3/SiO2, KOH/SiO2, C3H5KO3/SiO2, NaNO3/SiO2-Al2O3(36), KNO3/SiO2-Al2O3(36), KOH/SiO2-Al2O3(36), K2CO3/SiO2-Al2O3(36), and C3H5KO3/SiO2-Al2O3(36) were prepared by incipient wetting impregnation. The molar ratio of added K or Na to Si was 1.8:36. The impregnated samples except C3H5KO3/SiO2 and C3H5KO3/SiO2-Al2O3(36) were dried at 110 °C overnight followed by calcination at 540 °C in air for 5 h. C3H5KO3/SiO2 and C3H5KO3/SiO2-Al2O3(36) were dried under vacuum (10−2 mmHg) at 22 °C overnight. The physical properties of SiO2, SiO2-Al2O3, and the supported precatalysts were determined by N2 adsorption–desorption (see the Supporting Information).

The vapor-phase dehydration reaction of LA was conducted at 350 °C under atmospheric pressure in a vertical, down-flow fixed-bed reactor. The reactor body consisted of a stainless steel tube (59 cm long, 1.2 cm o.d., and 0.85 cm i.d.), which was mounted in a cylindrical electric furnace (45 cm long). The catalyst bed was sandwiched in the middle of the reactor with quartz wool. A bed of glass beads (~1 g) was placed above the catalyst bed. Prior to the reaction, the powder of each supported precatalyst was subjected to pelleting at a
压力为40 kN，随后通过筛分得到400–600 μm的颗粒。0.50 g的前催化剂被装入反应器并随后在载体气体N2+He（N2:He = 1:5体积比）中进行流量为30 mL min⁻¹的反应。0.50 g的LA溶液在350 °C下进行了1 h的反应时间。在反应结果中，气相产品被冷阱捕捉在出口的反应器中，温度保持在350 °C。反应混合物中的CH₃CHO和气相产物被冷阱捕获并冷凝在冷阱处。

3.1. 前催化剂筛选

3.1.1. 前催化剂筛选

由于前催化剂对AA的选择性在蒸汽相裂解中的影响，我们实验研究了在所用催化剂条件下，我们通过公式推测得到的前催化剂的筛选结果。17 实验中，蒸汽相裂解的反应路径为LA到AA。KNO₃/SiO₂-Al₂O₃(36)在400 °C的温度下进行了1 h的反应。我们通过催化条件使用的限制，可以排除前催化剂的外部传质的影响。18 我们通过前催化剂的筛选来确定每一个催化剂在蒸汽相裂解中选择AA的能力。

3.2. 结果和讨论

3.2.1. 前催化剂筛选

我们开始了一个定期筛选不同催化剂系统在蒸汽相裂解的LA在350 °C下反应的实验。为了理解每个组件在前催化剂中的影响，我们使用了Weisz–Prater准则来验证蒸汽相传质扩散对400–600 μm颗粒的影响。28 我们的研究显示了 β ≈ 0.08，因此 Nₜₐₖ > 0.3，可以排除内部蒸汽相传质扩散的影响。29

蒸汽相传质扩散在LA到AA的蒸汽相裂解中被研究通过发射光谱光谱仪（BIO-RAD FTS 3000 MX FT-IR）测定。催化剂样品是与KBr在催化剂/KBr (1:50质量比)中装入片材，然后装入20–80 mg的流量为40 kN的反应器中。在加温前，反应器中的N₂流量为30 mL min⁻¹，数据在5 h后测定。28 我们通过ICP-OES在Varian Vista-MPX CCD同时ICP-OES光谱仪测定Si、Al、Na和K的性能。30

表1. 不同催化剂体系在蒸汽相裂解LA在350 °C时的选择性能

| 前催化剂         | 转化率 (%) | AA产率 (%) | AA | PA | 2,3-PD | HAc | HA | EtOH | 其他产品 |
|------------------|------------|-----------|----|----|--------|-----|----|------|----------|
| Nil              | 8.5        | 2.9       | 34 | 29 | 0.70   | 3.1 | 24 | 0.61 | 8.6      |
| SiO₂             | 57         | 7.4       | 13 | 1.8 | 0      | 0.51 | 1.5 | 0.10 | 83       |
| SiO₂-Al₂O₃(23)   | 99         | 9.9       | 10 | 0.70 | 0     | 0.11 | 0.11 | 0   | 89       |
| SiO₂-Al₂O₃(36)   | 85         | 26        | 30 | 4.1 | 2.2   | 0.16 | 0.14 | 2.1  | 61       |
| H₂SIO₂-Al₂O₃(36) | 97         | 6.8       | 7.0 | 1.5 | 0     | 0.32 | 0.03 | 0.01 | 91       |
| K₂CO₃           | 74         | 26        | 34 | 8.4 | 1.4   | 2.8  | 0.97 | 1.7  | 51       |
| K₂CO₃/SiO₂-Al₂O₃(36) | 85     | 33        | 39 | 7.5 | 2.1   | 2.5  | 2.1  | 2.1  | 45       |
| KOH             | 73         | 27        | 37 | 9.5 | 2.8   | 5.2  | 1.7  | 5.2  | 39       |
| KOH/SiO₂        | 90         | 34        | 38 | 3.7 | 3.9   | 2.0  | 3.0  | 1.3  | 48       |
| KOH/SiO₂-Al₂O₃(36) | 87     | 30        | 34 | 4.7 | 2.9   | 1.5  | 3.6  | 0.80 | 53       |
| KNO₃             | 67         | 23        | 35 | 12  | 1.1   | 4.6  | 2.2  | 1.6  | 44       |
| KNO₃/Al₂O₃      | 45         | 12        | 27 | 15  | 1.1   | 2.3  | 1.0  | 1.2  | 52       |
| KNO₃/SiO₂       | 90         | 35        | 39 | 5.5 | 2.0   | 2.1  | 2.1  | 1.5  | 47       |
| KNO₃/SiO₂-Al₂O₃(36) | 51     | 18        | 36 | 21  | 1.8   | 4.4  | 1.0  | 2.0  | 34       |
| C₃H₅KO₃/SiO₂-Al₂O₃(36) | 77     | 24        | 31 | 11  | 2.8   | 2.5  | 1.5  | 1.7  | 50       |
| C₃H₅KO₃/SiO₂-Al₂O₃(36) | 97     | 42        | 43 | 4.1 | 3.3   | 1.0  | 1.2  | 1.2  | 46       |
| C₃H₅KO₃/SiO₂-Al₂O₃(36) | 97     | 47        | 48 | 5.8 | 3.3   | 2.0  | 3.9  | 0.74 | 36       |
| NaNO₃           | 60         | 15        | 25 | 16  | 2.6   | 4.8  | 2.0  | 4.1  | 46       |
| NaNO₃/SiO₂-Al₂O₃(36) | 89     | 33        | 37 | 5.7 | 2.7   | 2.2  | 2.8  | 1.1  | 49       |

*a*0.50 g的前催化剂，20%的LA溶液，WHSV_LA = 0.46 h⁻¹，载体气体流量= 30 mL min⁻¹，数据在5 h后测定。b*数据在28 h后测定。
dehydration of LA. Table 1 presents the comparative catalytic results over the supports, unsupported and supported K and Na salts, after 5 h of reaction in vapor-phase dehydration of LA at 350 °C. The aqueous 20% LA solution had a pH value of ~2. A blank test with no precatalyst added indicated that the reaction already proceeds to a small extent with this acidic reactant solution. When the acid precatalyst SiO2, with almost no weak acid sites (see the Supporting Information) was used for the reaction, the conversion of LA was greatly enhanced from 8.5 to 57% with the concomitant increase in the yield of AA from 2.9 to 7.4%. When another acid precatalyst SiO2-Al2O3(36) with weak acid sites (see the Supporting Information) was employed for the reaction, the LA conversion and AA yield were continuously increased to 85 and 26%, respectively. However, further increasing the weak acidity (amount of weak acid sites) of the precatalyst diminished the AA yield to 9.9% although increasing the LA conversion to 99% by using SiO2-Al2O3(23) as a precatalyst. Such reaction results with varying precatalyst acidities suggest that a medium solid weak acidity benefits the catalytic production of AA from the vapor-phase dehydration of LA.

When the vapor-phase dehydration was run using unsupported base K2CO3 or KOH as a solid precatalyst, the LA conversion and AA yield ascended to ~74 and ~27%, respectively. This seems to be in agreement with the previous argument that solid base sites likewise effectively catalyze the vapor-phase dehydration of LA to AA as solid acid sites do. The use of the stronger base KOH instead of K2CO3 did not alter the LA conversion and AA yield significantly, seemingly indicating no influence of further increased base strength on the catalytic activity. On this basis, when either K2CO3/SiO2-Al2O3(36) or KOH/SiO2-Al2O3(36) was used as a precatalyst, the catalytic activity for the production of AA was only slightly higher than that over SiO2-Al2O3(36). It was recently asserted that concerted catalysis by weak acid and base sites is remarkably favorable for the vapor-phase dehydration of LA to AA. The scenario noted here does not appear to support the acid–base concerted effect on the reaction.

The catalytic results with the unsupported and supported K bases observed here are hardly elucidated by the acid–base properties of the precatalysts. At this point, we recalled the surface chemistry of Na salts occurring on silica during the vapor-phase conversion of LA to 2,3-PD and AA reported previously. Under LA vapor at 150−300 °C, an Na salt like NaOH or NaNO3 is able to completely transform to C3H5NaO3 on the surface with the evolution of its conjugate acid like H2O or HNO3. The resulting C3H5NaO3 is deemed to be the actual catalyst toward the vapor-phase dehydration of LA to 2,3-PD and AA. We anticipated that K2CO3, KOH, and KNO3 on SiO2 and SiO2-Al2O3(36) would behave in a close way under LA vapor at 350 °C to generate the supported C3H5KO3. On the other hand, we noticed a tremendous effect of K or Na salt on the enhancement of AA yield from LA in our work shown in Table 1. The use of an unsupported K or Na salt increased the AA yield to 13−27% from 2.9% relative to the catalyst-free system. The incorporation of K salt to SiO2 led to an increase in AA yield from 7.4 to ~35%. The alkali-metal-free H-SiO2-Al2O3(36) precatalyst brought about a huge AA yield drop to 6.8% while producing a high LA conversion of 97%. The AA yield fell by 74% as compared with that over Na-containing SiO2-Al2O3(36). These results promoted us to contemplate the possible unique role of K+ or Na+-derived lactate salt in the catalytic process. The unsupported K or Na salt systems exhibited much better catalytic performance toward the production of AA than the K- or Na-free systems. This led us to reason that the catalytic reaction over a K or Na salt system proceeds predominantly via a pathway with the lactate salt intermediate.

In turn, we worked on KNO3 and C3H5KO3 supported on SiO2 and on SiO2-Al2O3(36) for the catalytic reaction. As shown in Table 1, the use of unsupported KNO3 as a precatalyst led to similar results to those over either unsupported K2CO3 or KOH, as expected, likely due to the in situ formation of C3H5KO3 under the reaction conditions in all the three cases. The SiO2- or SiO2-Al2O3(36)-supported K salts resulted in markedly increased LA conversion and AA yield. This may primarily result from the high dispersion of K salts on the supports, which creates more available active sites. These supported K salts indeed transform to C3H5KO3 under the reaction conditions, as confirmed by an IR study (as shown later). The catalytic behavior over these supported K salts is on the whole consistent with that over the supported C3H5KO3. The lower LA conversion and AA yield over the supported C3H5KO3 may be explained by the partial decomposition of C3H5KO3 during the preparation of the supported C3H5KO3 (as shown by an IR study later). KNO3 appears to be a better precursor of the supported C3H5KO3 than K2CO3 or KOH for the production of AA. The fact that the AA yield is considerably improved over KNO3/SiO2-Al2O3(36) or NaNO3/SiO2-Al2O3(36) as compared with that over H-SiO2-Al2O3(36) further postulates that a lactate salt-involved reaction pathway is predominant for the production of AA over a K or Na salt system. In addition, SiO2-Al2O3(36) scarcely displays a notable advantage of support over SiO2 in the production of AA in a short term reaction (5 h).

It is known that K possesses more effective promotion than other alkali metals in alkali-metal-modified zeolites on the catalytic dehydration of LA-AA. In the present work, the K-containing systems show the prevailing catalytic performance in terms of LA conversion and selectivity to AA over the Na-containing systems, as seen in Table 1 and Figure 3. We thus chose KNO3 as the central catalyst precursor to study the catalytic properties and roles of supported lactate salt in the vapor-phase dehydration of LA to AA. We assume that the advantageous catalytic performance arises from the intrinsic higher activity and selectivity of C3H5KO3 for the production of AA regardless of the influence of K on the acidity of SiO2-Al2O3(36). In fact, the addition of a K salt (nitrate, hydroxide, and carbonate) to SiO2-Al2O3(36) merely diminishes the solid acidity slightly (see the Supporting Information). K+ is supposed to transform to C3H5KO3 under the reaction conditions with acidic LA and at 350 °C. The intrinsic activities and selectivities of C3H5KO3 and C3H5NaO3 for the production of AA are represented by the AA yields and selectivities to AA over unsupported KNO3 and NaN O3, respectively. The higher activity and selectivity of C3H5KO3 can be reflected in the AA yield ratio of 1.5 and the selectivity to AA ratio of 1.4 over the unsupported KNO3 and NaN O3. The differences in the AA yield and selectivity to AA between KNO3/SiO2-Al2O3(36) and NaN O3/SiO2-Al2O3(36) have ratios of 1.3 and 1.2, respectively, which appears to result from the intrinsic activities and selectivities to AA of C3H5KO3 and C3H5NaO3 rather than the modification of solid acidity with K. Besides, the high selectivities to other products found either with the K-free SiO2-Al2O3(36) (49−61%) or K-
containing SiO$_2$-Al$_2$O$_3$ (45–53%) are reasonably an indication that some side reactions like oligomerization occur on the strong acid sites of these catalyst systems. The data of the close selectivities to other products show that the addition of K to SiO$_2$-Al$_2$O$_3$ does not deactivate the strong acid sites of SiO$_2$-Al$_2$O$_3$.

We meanwhile looked into the effect of WHSV$_{\text{LA}}$ on the catalytic properties of the KNO$_3$-derived supported catalysts in the vapor-phase dehydration of LA. According to previous investigations, the variation of selectivity to product with WHSV$_{\text{LA}}$ or residence time in the vapor-phase dehydration of LA depends on the catalyst system used. No common trend is conclusive. Given a WHSV$_{\text{LA}}$ value or residence time, the selectivity virtually varies as functions of both temperature and reaction time. Gunter et al. who used Na$_3$PO$_4$/SiO$_2$-Al$_2$O$_3$ with a high Al$_2$O$_3$ content as a precatalyst observed that the selectivities to AA and 2,3-PD increased with increasing residence time at 280–300 °C. However, at 350 °C, both of them increased with increasing residence time up to 1–2 s and fell with further increasing residence time. Ghantani et al. reported that, at 375 °C over a calcium hydroxyapatite, the selectivities to AA and CH$_3$CHO ascends and declines, respectively, with decreasing WHSV$_{\text{LA}}$ (or with increasing residence time). From the experiments of Yan et al., the selectivities to AA was found to increase with decreasing WHSV$_{\text{LA}}$ (or with increasing residence time) up to 2.1–1.4 h$^{-1}$ and decline with further decreasing WHSV$_{\text{LA}}$ at 8 h of reaction at 360 °C over a calcium hydroxyapatite and over a Na and K-containing β zeolite. In our investigation, the WHSV$_{\text{LA}}$ was varied by adjusting both the precatalyst amount and LA solution feeding flow rate; the carrier gas flow rate being maintained at 30 mL min$^{-1}$.

Table 2. Variation of LA Conversion and Selectivity to Product with WHSV$_{\text{LA}}$ in Vapor-Phase Dehydration of LA at 350 °C$^d$

| precatalyst | precatalyst amount (g) | WHSV$_{\text{LA}}$ (h$^{-1}$) | conversion (%) | AA | PA | 2,3-PD | HAc | HA | EtOH | other products |
|-------------|------------------------|-------------------------------|----------------|----|----|--------|-----|----|------|----------------|
| KNO$_3$/SiO$_2$ | 0.10 | 2.3 | 60 | 24 | 10 | 1.2 | 0.66 | 0.25 | 0.27 | 64 |
|              | 0.30 | 0.77 | 70 | 30 | 7.3 | 1.6 | 1.9 | 1.7 | 0.60 | 57 |
|              | 0.50 | 0.46 | 90 | 39 | 5.5 | 2.8 | 2.0 | 2.1 | 1.5 | 47 |
| KNO$_3$/SiO$_2$ | 0.50 | 0.46 | 51 | 45 | 9.8 | 3.3 | 5.8 | 2.9 | 3.5 | 30 |
|              | 0.50 | 0.92 | 47 | 37 | 1.7 | 2.9 | 1.3 | 0.46 | 0.57 | 56 |
|              | 0.50 | 1.4 | 42 | 32 | 1.9 | 4.8 | 1.1 | 0.64 | 0.37 | 60 |
|              | 0.50 | 1.8 | 35 | 25 | 3.7 | 5.1 | 0.83 | 3.1 | 0 | 62 |
| KNO$_3$/SiO$_2$-Al$_2$O$_3$(36)$^b$ | 0.10 | 2.3 | 45 | 34 | 2.5 | 1.6 | 1.3 | 0 | 0.67 | 60 |
|              | 0.50 | 2.3 | 64 | 38 | 4.6 | 2.7 | 1.3 | 0 | 0.32 | 53 |
|              | 0.50 | 0.46 | 97 | 43 | 4.1 | 3.3 | 1.3 | 0 | 0 | 48 |
| KNO$_3$/SiO$_2$-Al$_2$O$_3$(36)$^c$ | 0.50 | 0.46 | 97 | 47 | 6.3 | 3.5 | 1.9 | 3.7 | 1.8 | 34 |
|              | 0.50 | 0.92 | 88 | 44 | 7.3 | 5.6 | 1.4 | 4.1 | 0.66 | 37 |
|              | 0.50 | 1.4 | 74 | 50 | 4.1 | 7.2 | 1.0 | 5.6 | 0.72 | 31 |
|              | 0.50 | 1.8 | 67 | 55 | 4.9 | 11 | 1.1 | 7.3 | 0.69 | 20 |

$^a$Aqueous 20% LA solution, carrier gas flow rate = 30 mL min$^{-1}$. $^b$Data taken at 5 h of reaction. $^c$Data taken at 24–30 h of reaction. $^d$Data taken at 47–53 h of reaction.

Figure 1. LA conversion and selectivity to AA as a function of reaction time in the vapor-phase dehydration of LA at 350 °C over (a) K$_2$CO$_3$, (b) KOH, and (c) KNO$_3$. 
WHSVLA (or with increasing residence time) over both catalyst systems. This variation trend is in accordance with what have been reported in the abovementioned papers. Our WHSVLA values and residence times fall in the ranges of below 2.1 h and below 2 s, respectively. At 22–28 h of reaction over KNO3/SiO2, the selectivity to AA increased, while the selectivity to 2,3-PD almost decreased with decreasing WHSVLA. At 47–53 h of reaction over KNO3/SiO2-Al2O3(36), the selectivity to AA almost decreased, while the selectivity to 2,3-PD decreased with decreasing WHSVLA.

From these results, low WHSVLA is favorable for the production of both AA and 2,3-PD in a short term reaction (5 h) at 350 °C over both catalyst systems. For a long term reaction at 350 °C over KNO3/SiO2, low WHSVLA is also beneficial for the production of AA. However, for a long term reaction at 350 °C over KNO3/SiO2-Al2O3(36), high WHSVLA is helpful for the production of both AA and 2,3-PD. These observed different trends may be attributed to different catalytic behavior leading to different reaction kinetics.

3.1.2. Catalytic Stability. The catalytic screening at 5 h of reaction reflects merely the essential catalytic properties rather than the overall situation including induction, deactivation, and decay of a catalyst system. To better realize the correlation between the catalytic performance and possible catalytic active species, we next tested the catalytic stability of various catalyst systems in the vapor-phase dehydration of LA to AA at 350 °C.

Figures 1–3 illustrate the comparative LA conversion and selectivity to AA as a function of reaction time at a WHSVLA value of 0.46 h−1 over the unsupported and supported catalyst systems. The unsupported K2CO3, KOH, and KNO3 behaved similarly in catalytic stability, comparable catalytic profiles being observed (Figure 1). Following an induction period, the LA conversion decreased quickly with reaction time, while the selectivity to AA fell slightly after ∼21 h. The LA conversion dropped from 67% at 5 h to 45% at 28 h over the unsupported KNO3, which gave rise to a simultaneous tremendous drop in AA yield from 23% at 5 h to 12% at 28 h. We inferred that the unsupported K salt catalyst systems deactivate susceptibly.
during the reaction, leading to a poor catalytic stability. Over KOH/SiO$_2$, KNO$_3$/SiO$_2$ and C$_3$H$_5$KO$_3$/SiO$_2$, the catalytic stability did not improve, although the selectivity to AA remained stable with reaction time (Figure 2). This hints that the use of SiO$_2$ does not stabilize the presumed catalytic active species but the selectivity to AA only. In contrast, the SiO$_2$-Al$_2$O$_3$(36) and SiO$_2$-Al$_2$O$_3$(36)-supported catalyst systems behaved in a distinct way. Following an induction period, the LA conversion was maintained fairly stable without apparent decrease, while the selectivity to AA increased slowly in all the cases (Figure 3). This suggests that the use of SiO$_2$-Al$_2$O$_3$(36) not only improves the stability of the presumed catalytic active species but also enhances the selectivity to AA. The production of large amounts of other products (Table 1) that easily induce coke formation essentially does not cause catalyst deactivation or poor catalytic stability either with the K-free SiO$_2$-Al$_2$O$_3$(36) or K-containing SiO$_2$-Al$_2$O$_3$(36). The addition of K to SiO$_2$-Al$_2$O$_3$(36) apparently has no impact on the catalytic stability.

On the basis of the above results, we extended the catalytic stability test of KNO$_3$/SiO$_2$-Al$_2$O$_3$(36) to the conditions of longer reaction time and higher WHSV$_{\text{LA}}$. At a WHSV$_{\text{LA}}$ value of 0.46 h$^{-1}$, a good catalytic stability was observed up to 97 h: the LA conversion slightly declined from 97% (5 h) to 92%, and the selectivity to AA slightly increased from 43% (5 h) to 51% with the concomitant low selectivity to PA and 2,3-PD (2.9 and 2.8% at 97 h, respectively), as shown in Figure 4. When using a WHSV$_{\text{LA}}$ value of 1.8 h$^{-1}$, a good catalytic stability was likewise obtained up to at least 90 h: the LA conversion of 78% at 5 h remained almost unchanged, and the selectivity to AA of 46% at 5 h decreased slowly to 40% with the concurrent low selectivity to PA and 2,3-PD (6.5 and 7.0% at 90 h, respectively), as shown in Figure 5. These catalytic stability data postulate that the presumed catalytic active species derived from the K salts during the vapor-phase dehydration of LA to AA is well stabilized on SiO$_2$-Al$_2$O$_3$(36).

3.2. IR Characterization of Catalyst Systems. 3.2.1. Surface Properties of Catalyst Systems. To confirm the presumed catalytic active species derived from the K salts in
the vapor-phase dehydration of LA to AA, a comparative IR study of various catalyst systems before and after the reaction was performed. As C$_3$H$_5$KO$_3$, LA, AA, and PA are involved as the major surface species on the catalyst systems during the reaction, the surface IR spectra in the 2500–900 cm$^{-1}$ region of these compounds in KBr wafers are given in Figure 6 for reference. The most noticeable spectral features are strong $\nu$C$\equiv$O stretching vibration bands at 1595 cm$^{-1}$ for C$_3$H$_5$KO$_3$ and at 1708–1732 cm$^{-1}$ for LA, AA, and PA. Other identifying spectral features include $\delta$OH deformation, $\delta$CH$_3$ deformation, $\delta$CH deformation, $\nu$CH$_3$ rocking, $\nu$C$\equiv$CH$_3$ stretching vibration, ($\delta$CH$_3$ + $\nu$CO) vibrational coupling, and ($\delta$OH + $\nu$CO) vibrational coupling bands for these compounds. The spectrum of the self-prepared C$_3$H$_5$KO$_3$ in KBr exhibited a set of bands at 1595(s), 1456(m), 1412(m), 1373(sh), 1354(m), 1310(w), 1121(m), 1088(w), and 1034(m) cm$^{-1}$. These bands are in accordance with those for C$_3$H$_5$NaO$_3$ in water in the literature.35 The IR spectra of LA, AA, and PA in KBr wafers are also consistent with those assigned for these compounds in the liquid form in the literature.35−37

In Figure 7, the surface IR spectra of SiO$_2$, KNO$_3$/SiO$_2$, C$_3$H$_5$KO$_3$/SiO$_2$, and KOH/SiO$_2$ in the 2500–1000 cm$^{-1}$ region are presented. On all the samples, there was a broad band around 1632 cm$^{-1}$ due to the $\delta$OH angular deformation of molecular H$_2$O adsorbed on SiO$_2$. On KNO$_3$/SiO$_2$, a sharp band present at 1385 cm$^{-1}$ is assigned to the degenerate $\nu_3$ ($\epsilon'$) antisymmetric stretching vibration of NO$_3^-$ (Figure 7b),38 while no band for NO$_2^-$ was visible. The IR observations are consistent with the TCD elemental analysis of N (see the Supporting Information), which assumes that most of the KNO$_3$ has decomposed to K$_2$O on SiO$_2$ straightly after calcination at 540 °C in air, likely due to the interaction between KNO$_3$ and SiO$_2$. On C$_3$H$_5$KO$_3$/SiO$_2$, six broad bands fell at 1722(sh), 1585(s), 1454(m), 1422(m), 1358(sh), and 1306(sh) cm$^{-1}$. This spectrum deviates from that of C$_3$H$_5$KO$_3$ in Figure 6a. The 1722 cm$^{-1}$ band may be due to small amounts of LA formed by light hydrolysis of C$_3$H$_5$KO$_3$ on the SiO$_2$ surface (as explained later). The presence of the lower wavenumber of $\nu$C$\equiv$O stretching vibration (1585 cm$^{-1}$) assumes the loss of the $\alpha$-OH group on the lactate salt.21 The spectral deviation may be caused by partial decomposition of C$_3$H$_5$KO$_3$ on SiO$_2$ during the preparation of C$_3$H$_5$KO$_3$/SiO$_2$. After deliberation and IR spectral analysis of some related compounds,36,39,40 we assume that C$_3$H$_5$KO$_3$ would dehydrate

Figure 6. IR spectra of (a) self-prepared C$_3$H$_5$KO$_3$, (b) LA, (c) AA, and (d) PA.

Figure 7. IR spectra of (a) SiO$_2$, (b) KNO$_3$/SiO$_2$, (c) C$_3$H$_5$KO$_3$/SiO$_2$, and (d) KOH/SiO$_2$. 
Figure 8. IR spectra of the following spent catalyst samples in ~28 h of the vapor-phase dehydration of LA at 350 °C: (a) KOH, (b) KNO3, (c) SiO2, (d) KNO3/SiO2, (e) C3H5KO3/SiO2, and (f) KOH/SiO2.

The results suggest that the reaction of KOH or KNO3 with LA eventually results in C3H3KO2 and C3H5KO2 in the solid phase under the reaction conditions. It is reasonably believed that C3H5KO3 is the primary product, which subsequently dehydrates to C3H3KO2 followed by hydrogenation to C3H5KO2 in part:

\[
\text{C}_2\text{H}_4(\text{OH})\text{COOK} + \text{K}^+ \rightarrow \text{C}_2\text{H}_4(\text{OH})\text{COOK}^+ + \text{H}^+ \quad (3)
\]

\[
\text{C}_2\text{H}_4(\text{OH})\text{COOK} \rightarrow \text{C}_2\text{H}_5\text{COOK} + \text{H}_2\text{O} \quad (4)
\]

\[
\text{C}_2\text{H}_5\text{COOK} + \text{H}_2 \rightarrow \text{C}_2\text{H}_5\text{COOK} \quad (5)
\]

When the steps of the C3H5KO2-to-AA and C3H3KO2-to-PA conversions are rate-limiting in the LA dehydration process, the spent catalyst sample will be present in the forms of C3H3KO2 and C3H5KO2. If C3H3KO2 and C3H5KO2 do not act as important reaction intermediates for the production of AA, then the slower steps will entirely impede the catalytic LA dehydration reaction (resulting in lower LA conversion, lower selectivity to AA, and higher selectivity to PA). We attribute the poor catalytic stability of the unsupported K salt systems for the production of AA to the slow C3H5KO2-to-AA conversion step that facilitates the formation of C3H3KO2 and PA. On the spent KNO3/SiO2, C3H5KO3/SiO2, and KOH/SiO2 catalyst samples, similar spectra to those of the spent KOH and KNO3 catalyst samples were obtained except an extra shoulder band at 1595 cm⁻¹. The 1595 cm⁻¹ band is characteristic of C3H5KO3. The results suggest that the spent SiO2-supported K salts contain C3H3KO2 as the minor form and C3H5KO3 as the major forms. Similar to the cases of the unsupported KOH and KNO3, the poor catalytic stability of the SiO2-supported K salt systems for the production of AA can be ascribed to the predominant formation of C3H3KO3 and C3H5KO2. In support of the IR observations of C3H3KO2 and C3H5KO2, the reaction data show lower activity to AA and higher selectivity to PA after 28 h of reaction over KNO3 and KNO3/SiO2, as seen in Table 1. In both cases, a higher selectivity ratio of 0.6 for the formation of PA and AA is produced. Our IR observations of C3H3KO2 and C3H5KO2 over the spent K salt catalyst samples are somewhat consistent with what was reported by Tam et al. on the severe decomposition of C3H3NaO3 on low-surface-area silica during the vapor-phase LA conversion at 350 °C.

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In Figure 9, the surface IR spectra in KBr wafers in the 2500–1000 cm\(^{-1}\) region of SiO\(_2\)-Al\(_2\)O\(_3\) (36), KNO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\) (36), C\(_3\)H\(_5\)KO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\) (36), KOH/SiO\(_2\)-Al\(_2\)O\(_3\) (36), and NaNO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\) (36) are given. On KNO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\) (36) or NaNO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\) (36), the observation of a narrow band at 1383 cm\(^{-1}\) is indicative of the existence of NO\(_3\)\(^-\) (Figure 9b,e).\(^{38}\) Meanwhile, no band for NO\(_2\)\(^-\) was present. The IR observations are likewise in accordance with the TCD elemental analysis of N (see the Supporting Information), which suggests that most of the KNO\(_3\) or NaNO\(_3\) has decomposed to K\(_2\)O on SiO\(_2\)-Al\(_2\)O\(_3\) (36) straightly after calcination at 540 °C in air, likely because of the interaction between KNO\(_3\) or NaNO\(_3\) and SiO\(_2\)-Al\(_2\)O\(_3\) (36). On C\(_3\)H\(_5\)KO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\) (36), six broad bands appeared at 1722 (sh), 1584 (s), 1456 (m), 1420 (m), 1366 (w), and 1310 (w) cm\(^{-1}\). This spectrum more or less deviates from that of C\(_3\)H\(_5\)KO\(_3\) in Figure 6a, closely resembling that of C\(_3\)H\(_5\)KO\(_3\)/SiO\(_2\) in Figure 7c. The 1722 cm\(^{-1}\) band may correspond to small amounts of LA formed presumably by light hydrolysis of C\(_3\)H\(_5\)KO\(_3\) on the SiO\(_2\)-Al\(_2\)O\(_3\) surface. The spectral deviation may likewise result from dehydration of C\(_3\)H\(_5\)KO\(_3\) to C\(_3\)H\(_3\)KO\(_2\) in part on SiO\(_2\)-Al\(_2\)O\(_3\) (36) during the drying process of C\(_3\)H\(_5\)KO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\) (36) under vacuum at 22 °C.

In Figure 10, the surface IR spectra in KBr wafers in the 2500–1000 cm\(^{-1}\) region of SiO\(_2\)-Al\(_2\)O\(_3\) (36), KNO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\) (36), C\(_3\)H\(_5\)KO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\) (36), KOH/SiO\(_2\)-Al\(_2\)O\(_3\) (36), K\(_2\)CO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\) (36), and NaNO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\) (36) are illustrated. Except the spent C\(_3\)H\(_5\)KO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\) (36) catalyst sample, all the spent catalyst samples had a close spectrum comprising broad bands around 1803 (w), 1701 (s), 1595 (vs), 1452 (s), 1412 (s), 1371 (s), and 1310 (sh) cm\(^{-1}\). The obvious bands at 1803, 1452, 1371, and 1310 cm\(^{-1}\) may belong to the features of crystalline AA. The 1701 cm\(^{-1}\) band may be a result of the overlap of the 1708 cm\(^{-1}\) band for dimeric AA and the 1680 cm\(^{-1}\) band for crystalline AA. Another band around 1630 cm\(^{-1}\) for crystalline AA may be located under the broad,
intense 1595 cm$^{-1}$ band. The bands at 1595 and 1412 cm$^{-1}$ are the major features characteristic of C$_3$H$_5$KO$_3$ or C$_3$H$_5$NaO$_3$ (Figure 6a). It is of interest to note that the latter two bands are able to remain with the spent catalyst samples after 28–54 h of reaction. This clearly accounts for that the K or Na salts transform to C$_3$H$_5$KO$_3$ or C$_3$H$_5$NaO$_3$ on SiO$_2$-Al$_2$O$_3$(36) under the reaction conditions and the resulting C$_3$H$_5$KO$_3$ or C$_3$H$_5$NaO$_3$ is well stabilized with the presence of SiO$_2$-Al$_2$O$_3$(36). Note that the SiO$_2$-Al$_2$O$_3$(36) used here contains some extra Na that should be converted to C$_3$H$_5$NaO$_3$ under the reaction conditions. At the same time, the stabilization of C$_3$H$_5$KO$_3$ or C$_3$H$_5$NaO$_3$ (the presence of the 1595 and 1412 cm$^{-1}$ bands) is accompanied by the absence of the 1402 cm$^{-1}$ band. Once the lactate salt converts to acrylate and propionate (the 1595 cm$^{-1}$ band shifts to 1562 cm$^{-1}$), the 1412 cm$^{-1}$ band will move to 1402 cm$^{-1}$ with other bands remaining substantially unchanged, as shown by comparing Figures 8 and 10. Hence, the presence of the 1402 cm$^{-1}$ band in Figure 8 may be associated to the formation of propionate. With the spent C$_3$H$_5$KO$_3$/SiO$_2$-Al$_2$O$_3$(36) catalyst sample, the initial bands at 1584 and 1420 cm$^{-1}$ (Figure 9c), which are presumably due to a mixture of C$_3$H$_5$KO$_3$ and C$_3$H$_5$KO$_2$, shift to 1570 and 1408 cm$^{-1}$ (Figure 10c). This implies that C$_3$H$_5$KO$_3$ converts to C$_3$H$_5$KO$_2$ and C$_3$H$_5$KO$_2$ in part during the reaction over C$_3$H$_5$KO$_3$/SiO$_2$-Al$_2$O$_3$(36). The C$_3$H$_5$KO$_2$ supported on SiO$_2$-Al$_2$O$_3$(36) seems less stable than the in situ-formed C$_3$H$_5$KO$_3$ on SiO$_2$-Al$_2$O$_3$(36) from the K or Na salts during the reaction.

We ascribe the good catalytic stability of the SiO$_2$-Al$_2$O$_3$(36)-supported K salt systems for the production of AA to the speedup of the C$_3$H$_5$KO$_3$-to-AA conversion step with the aid of SiO$_2$-Al$_2$O$_3$(36). Such a promotional effect results in the emergence of C$_3$H$_5$KO$_3$ in the spent catalyst samples. Once this step is accelerated, the C$_3$H$_5$KO$_3$-to-C$_3$H$_5$KO$_2$ conversion step may become rate-limiting so that the C$_3$H$_5$KO$_2$-to-C$_3$H$_5$KO$_3$ conversion might be restricted in the LA dehydration process. In such a case, the spent supported K salt is present in the form of the supported C$_3$H$_5$KO$_3$ that likely acts as the catalytic active species. The IR observations of the supported C$_3$H$_5$KO$_3$ are consistent with the reaction data over the supported K salt systems. In contrast to the cases with KNO$_3$ and KNO$_3$/SiO$_2$, the high activity to AA and lower selectivity to PA are produced after 28 h of reaction with KNO$_3$/SiO$_2$-Al$_2$O$_3$(36), as shown in Table 1. A much lower selectivity ratio of 0.1 for the production of PA and AA is obtained.

At this stage, the comparative IR analyses of our catalyst systems before and after the catalytic reaction have revealed that K or Na salts (nitrate, hydroxide, and carbonate) readily react with LA to produce C$_3$H$_5$KO$_3$ or C$_3$H$_5$NaO$_3$ during the vapor-phase dehydration of LA to AA at 350 °C and the in situ-formed C$_3$H$_5$KO$_3$ or C$_3$H$_5$NaO$_3$ is stable on SiO$_2$-Al$_2$O$_3$(36) under the catalytic conditions. By contrast, either the unsupported or SiO$_2$-supported lactate salt has been proven to be unstable under the catalytic conditions. The catalytic stability of our catalyst systems can gain support from the chemical stability of the lactate salt during the reaction. The good catalytic stability over C$_3$H$_5$KO$_3$/SiO$_2$-Al$_2$O$_3$(36) or C$_3$H$_5$NaO$_3$/SiO$_2$-Al$_2$O$_3$(36) may be associated to the good chemical stability of the lactate salt on SiO$_2$-Al$_2$O$_3$(36). The poor catalytic stability over C$_3$H$_5$KO$_3$ or C$_3$H$_5$KO$_3$/SiO$_2$ may be correlated with the poor chemical stability of C$_3$H$_5$KO$_3$ alone or on SiO$_2$. As such, the lactate salt can be regarded as the catalytic active species for the vapor-phase dehydration of LA to AA. In this aspect, C$_3$H$_5$NaO$_3$ supported on low-surface-area silica was once proposed to be the active catalyst and an intermediate for 2,3-PD formation from LA by Miller and co-workers. Unfortunately, the supported C$_3$H$_5$NaO$_3$ failed to resist against decomposition at reaction temperatures from 200 °C upward. To our knowledge, our present contribution includes for the first time the stabilization of lactate salt as the catalytic active species for conversion of LA.

3.2.2. Reactivity of LA, C$_3$H$_5$KO$_3$, C$_3$H$_5$KO$_2$, and C$_3$H$_5$KO$_2$.

From the correlation between the above catalytic and IR results, the stabilization of lactate salt plays a pivotal role in the catalytic stability of a K- or Na-containing system in the vapor-phase dehydration of LA to AA. The chemical stability of lactate salt determines the stability in the catalytic performance. During LA dehydration, the formation of surface lactate salt was proposed as the critical step in the catalytic reaction pathway resulting in 2,3-PD or AA by several groups. Moreover, it is well known that the vapor-phase catalytic conversion of lactates to AA proceeds selectively over various heterogeneous acid catalyst sys-
The thermal reactivity of C₃H₅KO₃ on SiO₂ illustrated in Figure 12 indicates the predominant polymerization of LA hydrolyzed from C₃H₅KO₃ over dehydration of C₃H₅KO₃ to C₃H₅KO₂, which is contrary to the IR results on the spent SiO₂-supported K salt catalyst samples in Figure 8. The cause may lie in the difference in water content between the two sample preparative ways, resulting in the difference in LA production. To reveal the effect of water content on the reaction outcome of C₃H₅KO₃ on SiO₂, we comparatively tracked the surface IR evolution during the thermal reaction of C₃H₅KO₃ in Figure 12.

The 1626 cm⁻¹ band markedly shifted toward higher wavenumbers as seen in Figure 11, the surface IR spectra taken in the 2500−1100 cm⁻¹ region during the thermal reaction of LA on SiO₂ under flowing N₂ are shown. A SiO₂ wafer was impregnated with a drop of diluted LA aqueous solution followed by treatment under flowing N₂ at 22 °C for 1.5 h. The resultant spectrum gave a set of broad bands at 1720(s), 1626(s), 1454(m), 1416(sh), 1381(m), and 1354(m) cm⁻¹. The bands at 1720, 1454, 1416, and 1381 cm⁻¹ are assignable to the adsorbed LA. The 1626 cm⁻¹ band is assigned to the adsorbed molecular H₂O. The bands at 1454, 1381, and 1354 cm⁻¹ together with the 1759 cm⁻¹ band probably hidden under the broad 1720 cm⁻¹ band are attributable to poly(LA). LA seems to polymerize susceptibly on the SiO₂ surface:

\[ nC₃H₅(OH)COOH \rightarrow [C₃H₅(OH)COOH]ₙ \]  
(6)

LA polymerization under an acidic condition has been previously reported. As the temperature increased, the center of the 1720 cm⁻¹ band markedly shifted toward higher wavenumbers as seen in Figure 11b,c. After 0.5 h of treatment at 350 °C, a strong 1759 cm⁻¹ band characteristic of poly(LA) was observed with the disappearance of the 1720 cm⁻¹ band. At the same time, other bands at 1450(m), 1404(sh), 1379(m), 1350(m), and 1314(m) cm⁻¹ were present, which are also attributed to poly(LA). Evidently, LA is fully transformed to poly(LA) upon heating LA/SiO₂ to 350 °C.

In Figure 12, the surface IR spectra collected in the 2500−1100 cm⁻¹ region during the thermal reaction of C₃H₅KO₃ on SiO₂ under flowing N₂ are shown. After a SiO₂ wafer was impregnated with a drop of diluted C₃H₅KO₃ aqueous solution and subsequently treated under flowing N₂ at 22 °C for 1.5 h, the resultant spectrum contained a set of bands at 1724(w), 1692(w), 1587(s), 1454(m), 1418(m), 1375 (w), 1350(m), 1312 (w), and 1298 (w) cm⁻¹. The bands at 1587, 1454, 1418, 1375, 1350, and 1312 cm⁻¹ are mostly due to the presence of C₃H₅KO₃. A slight shift of the main feature to 1587 cm⁻¹ may imply that light dehydration of C₃H₅KO₃ to C₃H₅KO₂ already takes place on SiO₂ at 22 °C. The 1724(w) cm⁻¹ band is assigned to small amounts of LA issued from light hydrolysis of C₃H₅KO₃ on SiO₂ at 22 °C:

\[ C₃H₅(OH)COOK + H₂O \rightarrow C₃H₅(OH)COOH + KOH \]  
(7)

The appearance of the bands at 1692(w) and 1298(w) cm⁻¹ assumes that AA is already formed in small amounts catalytically at 22 °C. When the temperature was raised to 100 °C, the latter two bands increased at the expense of the intensity of the 1587 cm⁻¹ band, which suggests that more AA is produced via C₃H₅KO₂. This appears to account for the role of an intermediate that we think C₃H₅KO₂ plays in the dehydration of LA to AA. It may be possible that the hydrolysis of C₃H₅KO₃ is strengthened to produce more LA, part of which reacts with C₃H₅KO₂ to give AA and C₃H₅KO₃:

\[ C₃H₅(OH)COOH + C₃H₅COOK \rightarrow C₃H₅COOH + C₃H₅(OH)COOK \]  
(8)

When the temperature reached 350 °C, the 1587 cm⁻¹ band dropped in intensity in favor of the growth of the main feature of poly(LA) at 1761 cm⁻¹. Poly(LA) is present as the major product in terms of the IR band intensity. This implies that LA polymerization is accelerated and dominates on SiO₂ at 350 °C, which triggers a greater equilibrium shift of C₃H₅KO₃ hydrolysis to LA. Based on the absence of the band of the adsorbed molecular H₂O, it is believed that the conversion of C₃H₅KO₃ to LA proceeds via hydrolysis on SiO₂, which consumes the adsorbed molecular H₂O.

To provide evident insights into the roles of LA, lactate, acrylate, and propionate salts in the catalytic pathway of dehydration of LA to AA, we monitored the chemical behavior of LA and C₃H₅KO₃ on SiO₂ and SiO₂-Al₂O₃(36) and the reactivities of LA with C₃H₅KO₂ and C₃H₅KO₃ on KBr and SiO₂-Al₂O₃(36) under flowing N₂ at different temperatures by transmission IR spectroscopy.

Figure 12. IR spectra of C₃H₅KO₃ or its derivatives on SiO₂ after treatments under flowing N₂ at (a) 22 °C for 1.5 h, (b) 100 °C for 0.5 h, and (c) 350 °C for 0.5 h.
the C$_3$H$_5$KO$_3$/SiO$_2$ precatalyst in a KBr wafer. After the drying treatment under vacuum at 22 °C, the water content in the C$_3$H$_5$KO$_3$/SiO$_2$ precatalyst is believed to be much lower. As a result, no bands of poly(LA) appeared in spite of the emergence of the signature bands of LA and AA at 1727 and 1687 cm$^{-1}$ during the thermal reaction, as shown in Figure 13. The signature band of C$_3$H$_5$KO$_3$ at 1594 cm$^{-1}$ was not retained until after a longer thermal reaction at 350 °C. Subsequently, the signature bands of C$_3$H$_3$KO$_2$ at 1630 and 1570 cm$^{-1}$ were predominantly present, which is consistent with the spectrum of the spent C$_3$H$_5$KO$_3$/SiO$_2$ catalyst sample (Figure 8e). During the thermal reaction, the presence of bands at 2375, 2356, and 2340 cm$^{-1}$ is attributed to the adsorption of CO$_2$ on SiO$_2$, which were produced from the catalytic dehydration of LA. As such, LA polymerization is facilitated by the presence of higher water content that ensures hydrolysis of C$_3$H$_5$KO$_3$ to LA on SiO$_2$. Poly(LA) production is limited in the vapor-phase dehydration of LA over K or Na salt catalyst systems.

In Figure 14, the surface IR spectra recorded in the 2500–1100 cm$^{-1}$ region during the thermal reaction of LA on SiO$_2$-Al$_2$O$_3$(36) under flowing N$_2$ are shown. A SiO$_2$-Al$_2$O$_3$(36) wafer was impregnated with a drop of diluted LA aqueous solution followed by treatment under flowing N$_2$ at 22 °C for 1.5 h. The resultant spectrum presented a set of bands at 1722(sh), 1618(s), 1593(s), 1474(m), 1454(m), 1422(m), 1377(sh), 1362(m), and 1314(w) cm$^{-1}$. The presence of the bands at 1593(s) cm$^{-1}$ as the main feature of C$_3$H$_5$NaO$_3$ and 1722(cm) as the principal feature of LA indicates that much of the LA converts to C$_3$H$_5$NaO$_3$ and H$^+$ by acting with surface Na$^+$ on the Na-containing SiO$_2$-Al$_2$O$_3$(36) at 22 °C:

$$C_2H_4(OH)COOH + Na^+ \rightarrow C_2H_4(OH)COONa + H^+$$

Upon heating to 100 °C, the 1722 cm$^{-1}$ band shifted to 1715 cm$^{-1}$ with the concomitant appearance of the 1296 cm$^{-1}$ band and diminution of the 1593 cm$^{-1}$ band intensity. This hints that AA is already formed via C$_3$H$_5$NaO$_3$ catalytically. Upon
heating to 350 °C, a feature of crystalline AA appeared at 1807 cm\(^{-1}\). The 1715 cm\(^{-1}\) band shifted to 1707 cm\(^{-1}\) with the concomitant increase of the 1296 cm\(^{-1}\) band intensity. Meanwhile, the 1593 and 1618 cm\(^{-1}\) bands disappeared, and a 1607 cm\(^{-1}\) band appeared instead. The 1607 cm\(^{-1}\) band is ascribed to C\(_3\)H\(_5\)NaO\(_3\), which may presumably result from the interaction between C\(_3\)H\(_5\)NaO\(_3\) and AA on SiO\(_2\)-Al\(_2\)O\(_3\)(36).

The results indicate that C\(_3\)H\(_5\)NaO\(_3\) issued from LA strongly converts to AA on SiO\(_2\)-Al\(_2\)O\(_3\)(36) at 350 °C. While the reaction was continued at 350 °C, the 1607 cm\(^{-1}\) band remained unchanged, accounting for the good chemical stability of C\(_3\)H\(_5\)NaO\(_3\) on SiO\(_2\)-Al\(_2\)O\(_3\)(36). However, it is uncertain from the IR results in Figure 14 whether C\(_3\)H\(_5\)NaO\(_3\), being a possible intermediate, is able to directly result in AA in the reaction pathway, independently of the participation of LA. We next thus followed the IR evolution of C\(_3\)H\(_5\)KO\(_3\) on SiO\(_2\)-Al\(_2\)O\(_3\)(36) at different temperatures starting with C\(_3\)H\(_5\)KO\(_3\). In Figure 15, the surface IR spectra measured in the 2500–1100 cm\(^{-1}\) region during the thermal reaction of C\(_3\)H\(_5\)KO\(_3\) on SiO\(_2\)-Al\(_2\)O\(_3\)(36) under flowing N\(_2\) are shown. After a SiO\(_2\)-Al\(_2\)O\(_3\)(36) wafer was impregnated with a drop of diluted C\(_3\)H\(_5\)KO\(_3\) aqueous solution and subsequently treated under flowing N\(_2\) at 22 °C for 1.5 h, the resultant spectrum consisted of a set of bands at 1730(w), 1593(vs), 1470(m), 1454(m), 1423(s), 1362(m), and 1314 (w) cm\(^{-1}\). The presence of the bands at 1730(w) cm\(^{-1}\) as the main feature of LA apart from 1593(vs) cm\(^{-1}\) as the principal feature of C\(_3\)H\(_5\)KO\(_3\) shows that part of the C\(_3\)H\(_5\)KO\(_3\) transforms to LA on SiO\(_2\)-Al\(_2\)O\(_3\)(36) at 22 °C. The absence of a visible band around 1618 cm\(^{-1}\) for the adsorbed molecular H\(_2\)O further assumes that the transformation of C\(_3\)H\(_5\)KO\(_3\) to LA occurs via hydrolysis on SiO\(_2\)-Al\(_2\)O\(_3\)(36). Increasing the temperature to 100 °C speeded up the formation of LA and produced AA simultaneously. As a matter of fact, the 1730 cm\(^{-1}\) band increased in intensity and shifted to 1722 cm\(^{-1}\), and a 1296 cm\(^{-1}\) band emerged at the
expense of the 1593 cm\(^{-1}\) band intensity. Upon heating to 350 °C, the 1593 cm\(^{-1}\) band intensity kept decreasing in favor of the shift of the 1722 cm\(^{-1}\) band to 1705 cm\(^{-1}\) and the increase of the 1296 cm\(^{-1}\) band intensity. Meanwhile, the relative band intensity of 1705 to 1722 cm\(^{-1}\) increased significantly. This significantly indicates that the production of AA involves the consumption of both C\(_3\)H\(_5\)KO\(_3\) and LA and C\(_3\)H\(_5\)KO\(_3\) acts as an intermediate to produce AA. As the heating was continued at 350 °C, the intensity of the existing bands declined progressively, likely due to the desorption of these compounds from the surface. There was no longer an increase in the intensity of the bands of LA and AA, which hints that there are no LA and AA produced from C\(_3\)H\(_5\)KO\(_3\) on the surface. There was no longer an increase in the intensity of the bands of LA and AA, which hints that there are no LA and AA produced from the surface. There was no longer an increase in the intensity of the bands of LA and AA, which hints that there are no LA and AA produced from the surface. There was no longer an increase in the intensity of the bands of LA and AA, which hints that there are no LA and AA produced from the surface. There was no longer an increase in the intensity of the bands of LA and AA, which hints that there are no LA and AA produced from the surface. There was no longer an increase in the intensity of the bands of LA and AA, which hints that there are no LA and AA produced from the surface.

As illustrated in Table 1 and Figures 1–3, the orders of both the AA yield and catalytic stability over the KNO\(_3\) systems at 350 °C are ranked as KNO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\)(36) > KNO\(_3\)/SiO\(_2\) > KNO\(_3\). As indicated in Figures 13 and 16 and Figure S4, the order of the chemical stability of the C\(_3\)H\(_5\)KO\(_3\) systems at 350 °C is ranked as C\(_3\)H\(_5\)KO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\)(36) > C\(_3\)H\(_5\)KO\(_3\)/SiO\(_2\) > C\(_3\)H\(_5\)KO\(_3\). This order is in accordance with the order of the IR band intensity of C\(_3\)H\(_5\)KO\(_3\) on the spent KNO\(_3\), KNO\(_3\)/SiO\(_2\), and KNO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\)(36) catalyst samples in Figures 8 and 10. The AA yield and catalytic stability over the KNO\(_3\) systems are indeed associated with the chemical stability of C\(_3\)H\(_5\)KO\(_3\) in these systems. A good chemical stability of C\(_3\)H\(_5\)KO\(_3\) as the possible catalytic active species can ensure a high and stable conversion of LA to AA.

At this stage, we hypothesize that C\(_3\)H\(_5\)KO\(_3\) would play the roles of important intermediate and catalytic active species in the vapor-phase dehydration of LA to AA. As stated above, the transition of C\(_3\)H\(_5\)KO\(_3\) to AA does not seem to proceed independently without the attendance of LA during the reaction process. Although initial C\(_3\)H\(_5\)KO\(_3\) as the true catalyst is easily formed from LA and a starting K salt, the regeneration of C\(_3\)H\(_5\)KO\(_3\) poses a challenge in the catalytic cycle. The good chemical stability of C\(_3\)H\(_5\)KO\(_3\) on SiO\(_2\)-Al\(_2\)O\(_3\)(36) illustrated in Figures 14–16 coincides with the IR spectra of the spent SiO\(_2\)-Al\(_2\)O\(_3\)(36)-supported K salt catalyst samples in Figure 10.

Herein, it is of interest to correlate the AA yield and catalytic stabilities over KNO\(_3\), KNO\(_3\)/SiO\(_2\), and KNO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\)(36) with the chemical stabilities of C\(_3\)H\(_5\)KO\(_3\), C\(_3\)H\(_3\)KO\(_2\)/SiO\(_2\), and C\(_3\)H\(_3\)KO\(_2\)/SiO\(_2\)-Al\(_2\)O\(_3\)(36) at 350 °C. As illustrated in Table 1 and Figures 1–3, the orders of both the AA yield and catalytic stability over the KNO\(_3\) systems at 350 °C are ranked as KNO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\)(36) > KNO\(_3\)/SiO\(_2\) > KNO\(_3\). As indicated in Figures 13 and 16 and Figure S4, the order of the chemical stability of the C\(_3\)H\(_5\)KO\(_3\) systems at 350 °C is ranked as C\(_3\)H\(_5\)KO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\)(36) > C\(_3\)H\(_5\)KO\(_3\)/SiO\(_2\) > C\(_3\)H\(_5\)KO\(_3\). This order is in accordance with the order of the IR band intensity of C\(_3\)H\(_5\)KO\(_3\) on the spent KNO\(_3\), KNO\(_3\)/SiO\(_2\), and KNO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\)(36) catalyst samples in Figures 8 and 10. The AA yield and catalytic stability over the KNO\(_3\) systems are indeed associated with the chemical stability of C\(_3\)H\(_5\)KO\(_3\) in these systems. A good chemical stability of C\(_3\)H\(_5\)KO\(_3\) as the possible catalytic active species can ensure a high and stable conversion of LA to AA.

Unlike in the case of C\(_3\)H\(_5\)KO\(_3\) on SiO\(_2\), no visible bands of poly(LA) are discerned during the thermal reaction of C\(_3\)H\(_5\)KO\(_3\) on SiO\(_2\)-Al\(_2\)O\(_3\)(36). Catalytic LA polymerization is negligible on SiO\(_2\)-Al\(_2\)O\(_3\)(36) under equivalent conditions. Similar behavior is observed during the thermal reaction of the as-prepared C\(_3\)H\(_5\)KO\(_3\)/SiO\(_2\)-Al\(_2\)O\(_3\)(36) precatalyst (Figure 16). The water content does not seem to affect the catalytic LA polymerization on SiO\(_2\)-Al\(_2\)O\(_3\)(36). During the thermal reaction, the observation of bands at 2364, 2349, and 2339 cm\(^{-1}\) is due to the adsorption of CO\(_2\) on SiO\(_2\)-Al\(_2\)O\(_3\)(36) which were produced from the catalytic dehydration of LA. The good chemical stability of C\(_3\)H\(_5\)KO\(_3\) on SiO\(_2\)-Al\(_2\)O\(_3\)(36) illustrated in Figures 14–16 coincides with the IR spectra of the spent SiO\(_2\)-Al\(_2\)O\(_3\)(36)-supported K salt catalyst samples in Figure 10.

Figure 17. IR spectra after the reaction of LA and C\(_3\)H\(_5\)KO\(_3\) on KBr under flowing N\(_2\) at (a) 22 °C for 3 min, (b) 22 °C for 50 min, (c) 100 °C for 0.5 h, (d) 200 °C for 0.5 h, (e) 300 °C for 0.5 h, and (f) 350 °C for 0.5 h.
examined the reactivities of LA with C₃H₃KO₂ and C₃H₅KO₂ on KBr and SiO₂-Al₂O₃ (36).

In Figure 17, the surface IR spectra observed in the 2500−900 cm⁻¹ region during the thermal reaction of LA and C₃H₃KO₂ on KBr under flowing N₂ are shown. A KBr wafer was impregnated with a drop of aqueous 10% C₃H₃KO₂ solution in air followed by removal of water under vacuum at 22 °C for 0.5 h. The resultant C₃H₃KO₂/KBr was impregnated with a drop of aqueous 10% LA solution and subsequently treated under flowing N₂ at 22 °C for 3 min. At this point, the signature shoulder band of C₃H₅KO₃ at 1591 cm⁻¹ appeared together with a band of AA at 983 cm⁻¹, indicating the easy formation of C₃H₅KO₃ and AA from LA and C₃H₃KO₂, as shown in Figure 17a. As the reaction was continued, the signature bands of C₃H₃KO₂ at 1636 and 1559 cm⁻¹ and LA at 1726 cm⁻¹ decreased in intensity in favor of the increase of the band intensity of C₃H₅KO₃. Meanwhile, the shift of the 1726 cm⁻¹ band to 1708 cm⁻¹ implies an increase in the production of AA during the reaction. At 200 °C, C₃H₃KO₂ almost vanished in favor of the formation of C₃H₅KO₃ (Figure 17d). The results demonstrate that the displacement of unsupported C₃H₃KO₂ with LA susceptibly takes place to generate C₃H₅KO₃ and release AA. When the temperature was further increased, the 1590 cm⁻¹ band shifted toward 1568 cm⁻¹ with the concurrent reappearance of the features of C₃H₃KO₂. This accounts for that the C₃H₅KO₃ produced from LA and C₃H₃KO₂ is prone to dehydrating to C₃H₃KO₂ at higher temperatures (≥300 °C), in agreement with the IR results on the spent unsupported K salt catalyst samples in Figure 8 and the thermal reactivity of C₃H₅KO₃ on KBr (see the Supporting Information).

Following the above reaction at 350 °C, the KBr-supported product wafer was allowed to further react with LA for testing the ability to further regenerate C₃H₅KO₃. The IR results are presented in Figure 18. After LA was added onto the wafer followed by treatment under flowing N₂ at 22 °C, the 1568

Figure 18. IR spectra after 0.5 h of reaction of LA with the KBr-supported species shown in Figure 17f under flowing N₂ at (a) 22 °C, (b) 100 °C, (c) 200 °C, (d) 300 °C, and (e) 350 °C.

Figure 19. IR spectra of the following treatments on KBr-supported spent KNO₃ in 28 h of the vapor-phase dehydration of LA at 350 °C: (a) under vacuum at 22 °C for 1 h, (b) under vacuum at 350 °C for 0.5 h, (c) with LA under flowing N₂ at 22 °C for 0.5 h, (d) with LA under flowing N₂ at 100 °C for 0.5 h, and (e) with LA under flowing N₂ at 200 °C for 0.5 h.
This indicates that C$_3$H$_5$KO$_3$ is regenerated only partly from the supported product. Increasing the temperature was unable to produce more C$_3$H$_5$KO$_3$. The dehydration of C$_3$H$_5$KO$_3$ to C$_3$H$_3$KO$_2$ was carried out again at higher temperatures (≥300 °C).

When a wafer of the KBr-supported spent KNO$_3$ catalyst sample in 28 h of the vapor-phase dehydration of LA at 350 °C was subjected to reacting with LA, the signature band of C$_3$H$_3$KO$_2$ at 1566 cm$^{-1}$ was able to shift to 1575 cm$^{-1}$ only, as shown in Figure 19. This hints that C$_3$H$_5$KO$_3$ is regenerated even more difficultly from the spent KNO$_3$ catalyst sample. This is also evidence that, with unsupported K salt catalyst systems, the ability to regenerate C$_3$H$_5$KO$_3$ weakens obviously as the catalytic cycle increases.

In Figure 20, the surface IR spectra recorded in the 2500–900 cm$^{-1}$ region during the thermal reaction of LA and C$_3$H$_5$KO$_3$ on KBr under flowing N$_2$ are shown. A KBr wafer was first impregnated with a drop of aqueous 10% C$_3$H$_5$KO$_2$ solution in air followed by removal of water under vacuum at 22 °C for 0.5 h. Upon impregnation of the resultant C$_3$H$_5$KO$_2$/KBr with a drop of aqueous 10% LA solution, the signature band of C$_3$H$_5$KO$_2$ at 1562 cm$^{-1}$ nearly vanished, while the signature band of C$_3$H$_5$KO$_3$ at 1590 cm$^{-1}$ appeared, as seen in Figure 20a. The result suggests the easy reaction of LA and C$_3$H$_5$KO$_2$ to produce C$_3$H$_5$KO$_3$ and PA:

$$\text{C}_2\text{H}_4(\text{OH})\text{COOH} + \text{C}_3\text{H}_5\text{COOK} \rightarrow \text{C}_2\text{H}_4\text{COOH} + \text{C}_2\text{H}_4(\text{OH})\text{COOK}$$

(10)

The absence of bands of PA may be due to the difficult adsorption of PA on the surface. The reaction was markedly accelerated when heated to 100 °C, the 1590 cm$^{-1}$ band of C$_3$H$_5$KO$_3$ growing at the expense of the 1716 cm$^{-1}$ band of LA and the 1562 and 1370 cm$^{-1}$ bands of C$_3$H$_5$KO$_2$, as shown in Figure 20c. When heated to 200 °C, a nearly pure spectrum of C$_3$H$_5$KO$_3$ was present. The simultaneous presence of a tiny band at 1760 cm$^{-1}$ is ascribed to the production of poly(LA) in trace amounts. As expected, raising the temperature to 350 °C led to the dehydration of C$_3$H$_5$KO$_3$ to C$_3$H$_3$KO$_2$, as shown by the spectral change between Figure 20d,e. It follows that the
reactivity of LA and C$_3$H$_5$KO$_2$ is similar to that between Figure 20d,e. It follows that the reactivity of LA and C$_3$H$_5$KO$_2$ is similar to that of LA and C$_3$H$_3$KO$_2$.

In Figure 21, the surface IR spectra observed in the 2500−1100 cm$^{-1}$ region during the thermal reaction of LA and C$_3$H$_3$KO$_2$ on SiO$_2$-Al$_2$O$_3$(36) under flowing N$_2$ are shown. A SiO$_2$-Al$_2$O$_3$(36) wafer was impregnated with a drop of aqueous 10% C$_3$H$_3$KO$_2$ solution followed by removal of water under vacuum at 22 °C for 0.5 h. The resultant C$_3$H$_3$KO$_2$/SiO$_2$-Al$_2$O$_3$(36) was impregnated with a drop of aqueous 10% LA solution and subsequently treated under flowing N$_2$ at 22 °C for 0.5 h. The obtained spectrum contained surface molecular H$_2$O and C$_3$H$_3$KO$_2$ at 1639(m), 1553(s), and 1364(m) cm$^{-1}$.

From this spectrum, LA has rather low reactivity with C$_3$H$_3$KO$_2$/SiO$_2$-Al$_2$O$_3$(36) at 22 °C. While the temperature was raised toward 350 °C, the bands of C$_3$H$_3$KO$_2$ at 1639 and
1364 cm⁻¹ gradually fell in intensity, whereas the bands of LA and C₃H₅KO₃ at 1725 and 1553 cm⁻¹ shifted to 1702 and 1612 cm⁻¹, respectively. We thus reason that the reactivity of LA with C₃H₅KO₂ and the surface Na⁺ to form C₃H₅KO₅, C₃H₅NaO₅, and AA increases with increasing temperature. After the temperature had reached 350 °C, the bands of both LA and C₃H₅KO₃ tremendously declined in intensity in favor of the emergence of bands of C₃H₅KO₃ and C₃H₅NaO₃ at 1612(s), 1455(m), and 1410(m) cm⁻¹. This hints that the displacement of LA with C₃H₅KO₃ to produce C₃H₅KO₄ and AA is favorable at 350 °C. The upward shift of the signature band of C₃H₅KO₃ and C₃H₅NaO₃ to 1612 cm⁻¹ may be due to the interaction between the lactate salt and AA on SiO₂-Al₂O₃(36). The fact that C₃H₅KO₃ and C₃H₅NaO₃ are stably retained on SiO₂-Al₂O₃(36) at 350 °C shows that C₃H₅KO₃ and C₃H₅NaO₃ dehydrate to C₃H₅KO₂ and C₃H₅NaO₂ on SiO₂-Al₂O₃(36) at 350 °C harder.

In Figure 22, the surface IR spectra observed in the 2500–1100 cm⁻¹ region during the thermal reaction of LA and C₃H₅KO₃ on SiO₂-Al₂O₃(36) under flowing N₂ are shown. A SiO₂-Al₂O₃(36) wafer was impregnated with a drop of aqueous 10% LA solution followed by removal of water under vacuum at 22 °C for 0.5 h. The resultant C₃H₅KO₃/SiO₂-Al₂O₃(36) was impregnated with a drop of aqueous 10% LA solution and displayed the features of LA at 1725(w) cm⁻¹ and lactate salts around 1615(sh) cm⁻¹ (subsequently treated under flowing N₂ at different temperatures). After 0.5 h of reaction at 22 °C, the upward shift of the signature band of C₃H₅KO₃ at 1561 cm⁻¹ already occurred, suggesting that LA and C₃H₅KO₃ already starts to transform to C₃H₅KO₂ and PA on SiO₂-Al₂O₃(36) at 22 °C. With increasing temperature, the band shift kept increasing up to 1604 cm⁻¹ at 350 °C. In the meantime, the signature band of LA at 1723 cm⁻¹ shifted to 1715 cm⁻¹, hinting the formation of small amounts of AA on the surface. The observations implicate that LA would catalytically react with C₃H₅KO₂ and the surface Na⁺ to form C₃H₅KO₅, C₃H₅NaO₅, PA, and AA on SiO₂-Al₂O₃(36) during this process. The existence of the signature band of C₃H₅KO₂ and C₃H₅NaO₃ at 1604 cm⁻¹ after 0.5 h of heating at 350 °C confirms the good chemical stability of C₃H₅KO₂ and C₃H₅NaO₃ on SiO₂-Al₂O₃(36) at 350 °C. The lack of bands of PA may likewise be due to the difficult adsorption of PA on the surface. The presence of the 1604 cm⁻¹ band further assumes that the interaction between the lactate salt and AA on SiO₂-Al₂O₃(36) would cause an upward shift of the main band of the lactate salt. It seems that C₃H₅KO₂ is more reactive with LA than C₃H₅KO₃ on SiO₂-Al₂O₃(36).

The good thermochemical stability of C₃H₅KO₃ issued from LA and C₃H₅KO₅ or C₃H₅KO₂ on SiO₂-Al₂O₃(36) stated above virtually reflects the strong ability to regenerate C₃H₅KO₃ from the supported K salt catalyst systems as the catalytic reaction proceeds. This matches with the IR results of the spent SiO₂-Al₂O₃(36)-supported K salt catalyst samples in Figure 10.

The combined catalytic and IR studies presented above have suggestively established the relationship among LA, C₃H₅KO₅, C₃H₅KO₃, AA, C₃H₅KO₂, and PA in the dehydration process of LA to AA and PA over the K salt (nitrate, hydroxide, and carbonate) catalyst systems. We propose a general reaction pathway for the vapor-phase dehydration of LA to AA with a K salt catalyst system, as depicted in Scheme 1. In a reaction from LA over a K salt catalyst system, on principle, the AA yield is dependent on the catalytic selectivities for both C₃H₅KO₃ dehydration and regeneration steps. Given a catalytic selectivity for the conversion of LA to AA, the catalytic stability is related to the ability of the catalyst system to regenerate C₃H₅KO₃ from LA and C₃H₅KO₃ or C₃H₅KO₂. In this work, the contrast in the catalytic stability over KNO₃, KNO₃/SiO₂, and KNO₃/SiO₂-Al₂O₃(36) is shown to reflect their distinct abilities to regenerate C₃H₅KO₃ from LA and C₃H₅KO₂ or C₃H₅KO₂ based on the IR results of the spent catalyst samples and the reactivity between LA and C₃H₅KO₃ or C₃H₅KO₂. The three KNO₃ catalyst systems give rise to LA conversion of 67–97% and selectivity to AA of 35–43% at an initial stage (5 h). However, only the KNO₃/SiO₂-Al₂O₃(36) system behaves well in the catalytic stability during the reaction on stream because of its strong ability to regenerate C₃H₅KO₃ from LA and C₃H₅KO₂ or C₃H₅KO₂. The cause leading to the difference in the activity of C₃H₅KO₃ regeneration from LA and C₃H₅KO₂ or C₃H₅KO₂ is not clear for the time being. The relevant factors may presumably involve the catalyst acid–base property, interaction between K salt and support, dispersion of K salt and catalyst coking, etc. An in-depth investigation is in progress. Since the production of AA requires the presence of C₃H₅KO₃, the ability of a K salt catalyst system to regenerate C₃H₅KO₃ from LA and C₃H₅KO₂ or C₃H₅KO₂ and the chemical stability of C₃H₅KO₂ under the catalytic conditions determine the catalytic performance stability of this system. The poor regeneration ability of C₃H₅KO₂ affects the reaction rate, LA conversion, and AA yield. Both easy decomposition of C₃H₅KO₂ and the consumption of LA via other pathways are responsible for low AA yields.

In the case with an unsupported or SiO₂-supported K salt as a precatalyst, the step of the C₃H₅KO₂-to-AA conversion with the regeneration of C₃H₅KO₃ via the displacement of C₃H₅KO₂ with LA proceeds more slowly than the C₃H₅KO₂-to-C₃H₅KO₂ conversion step via dehydration at 350 °C, as demonstrated by the IR observations (Figures 8 and 17–19). C₃H₅KO₂ could be more readily formed via C₃H₅KO₂ hydrogenation to give PA eventually. The steps of formation of AA and PA from C₃H₅KO₂ and C₃H₅KO₂, respectively, are believed to be rate-limiting. In the case with a SiO₂(36)-Al₂O₃-supported K salt as a precatalyst, the step of the C₃H₅KO₂-to-C₃H₅KO₂ conversion proceeds more slowly than the step of the C₃H₅KO₂-to-AA conversion with the regeneration of C₃H₅KO₂ at 350 °C, as shown by the IR results (Figures 10 and 21). The displacement of C₃H₅KO₂ with LA could go more rapidly, and the formation of C₃H₅KO₂ and PA could get suppressed. The C₃H₅KO₂-to-C₃H₅KO₂ conversion step is assumed to be rate-limiting. In both cases, C₃H₅KO₂ is suggested to be the true catalytic active species and an important intermediate for the vapor-phase dehydration of LA to AA.

4. CONCLUSIONS

K or Na salt catalyst systems (nitrate, hydroxide, and carbonate) enable the vapor-phase dehydration of LA to AA to proceed predominantly via a pathway with the lactate salt intermediate. The unsupported K salt systems give rise to LA conversion and selectivity to AA of ~70 and ~35%, respectively. The SiO₂-supported K salt systems exhibit increased LA conversion and decreased selectivity to PA and similar selectivity to AA. Nevertheless, these two types of systems are catalytically unstable and deactivate seriously in the reaction on stream. The SiO₂-Al₂O₃(36)-supported K salt...
systems display the fairly stable catalytic performance in 90 h of reaction, in which the LA conversion and selectivity to AA reach more than 75 and 40%, respectively, and the selectivity to PA remains <7.0% at a WHSVLA value of 1.8 h⁻¹.

The distinction in the catalytic stability consists in the distinction in the chemical stability of C₃H₅KO₃ and the activity for the regeneration of C₃H₅KO₃ from LA and C₃H₅KO₂ or C₃H₅KO₂ over the different catalyst systems. With the unsupported and SiO₂-supported K salt systems, the in situ-generated C₃H₅KO₃ readily transforms to C₃H₃KO₂. In all the three cases, C₃H₅KO₃ acts as important reaction intermediates for the production of AA, their formation affects the catalytic activity and selectivity. With the SiO₂-Al₂O₃(36)-supported K salt systems, the in situ-generated C₃H₅KO₃ readily transforms to C₃H₃KO₂, which is diagnostically regenerated from LA and C₃H₅KO₂ or C₃H₅KO₂. Since C₃H₅KO₂ and C₃H₅KO₂ are not important reaction intermediates for the production of AA, their formation affects the catalytic activity and selectivity. With the SiO₂-Al₂O₃(36)-supported K salt systems, the in situ-formed C₃H₅KO₃ is well stabilized under the reaction conditions. C₃H₅KO₂ is easily regenerated from LA and C₃H₅KO₂ or C₃H₅KO₂. In all of these cases, C₃H₅KO₃ acts as the catalytic active species and an important reaction intermediate for the production of AA.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b00745.

Physical properties of precatalysts, acidity of supports and supported precatalysts, reactivity of LA and C₃H₅KO₃ on KBr, elemental analysis by ICP, and elemental analysis of N by TCD (PDF)

**AUTHOR INFORMATION**

Corresponding Authors
* E-mail: huang_lin@ices.a-star.edu.sg. Fax: (+65)-6316-6182. (L.H.)
* E-mail: ias_cwang@njtech.edu.cn (C.W.).

ORCID
Lin Huang: 0000-0001-6062-0496
Lili Zhang: 0000-0002-9143-9320
Luwei Chen: 0000-0002-1042-2034

Present Address
†Present address: Institute of Advanced Synthesis, Nanjing Tech University, 30 Puzhu South Road, Nanjing 211816, China.

Notes
The authors declare no competing financial interest.

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