Catalytic Conversion of Diethyl Tartrate into Pyruvate over Silica-Supported Potassium Disulfate

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Potassium hydrogensulfate ($KHSO_4$), which melts at a lower temperature of 197 °C, was adapted for vapor-phase fixed-bed flow operations as a silica-supported potassium disulfate ($K_2S_2O_7/SiO_2$) to afford 60% ethyl pyruvate continuously from the tartrate at 300 °C. The catalyst was effective for the intramolecular dehydration of glycol moieties, much less active for hydrolysis of esters, and capable of converting enol- to keto-form for the intermediate oxalacetate in favor of pyruvate. A TGA analysis revealed that $KHSO_4$ was converted to $K_2S_2O_7$ at 300 °C, this was in consistent with the XRD analysis.

Pyruvic acid has received increasing attention in recent years as being a potential precursor for α-cyanoacrylate adhesives and the enzymatic conversion to L-amino acids, as well as an excellent solvent for a photoresist in optoelectronics processing. An established laboratory procedure[1,2] for pyruvic acid synthesis is the dehydrative decarboxylation by the batch distillation of tartaric acid in the presence of potassium hydrogensulfate powder. It appeared to be of interest to apply a catalytic approach for the synthesis of pyruvic acid, which was thus obtained in rather good yield both in the liquid[3] and vapor[4] phases as reported in previous papers. Potassium hydrogensulfate ($KHSO_4$) melts at a lower temperature of 197 °C,[5] and was adapted for vapor-phase fixed-bed operations as a silica-supported potassium disulfate catalyst ($K_2S_2O_7/SiO_2$) prepared by calcination of $KHSO_4/SiO_2$ to afford 60% ethyl pyruvate (**1**) continuously from diethyl tartrate (**2**) at 300 °C.

Attempts were made in the present work to elucidate the unique properties of disulfate as a catalyst for pyruvic acid synthesis. The results of comparative reaction studies concerning the stability of ethyl pyruvate on η-Al_2O_3 and $K_2S_2O_7/SiO_2$, the conversion of diethyl oxalacetate (**3**) on $K_2S_2O_7/SiO_2$ in favor of pyruvate with quantitative analysis of the keto–enol isomers based on NMR measurements, and the measurement of XRD and TGA for $KHSO_4$–$K_2S_2O_7$–H_2O system near to the reaction conditions, are described.

Experimental

The reaction was carried out using a conventional fixed-bed flow apparatus at 200—400 °C with a space velocity (SV) of 500—7200 h^{-1}. Substrates (3 or 5 mol%) were supplied as the benzene or toluene solution by a Microfeeder (Furue Type JP-S). Monitoring of the reaction was made with GC (Hitachi 163-FID for organic species and Yanako G-2800-TCD for CO_2 and ethylene).[4] A thermogravimetric analysis (TGA) was made using a Shimadzu DTG-40 or RMB-50V. Powder X-ray diffraction (XRD) was measured by a Rigaku CN-2011. The NMR spectra was measured using a Hitachi R-24 Spectrometer in a $CDCl_3$ solution; chemical shifts are expressed in the unit δ. $K_2S_2O_7/SiO_2$ and η-Al_2O_3 were prepared according to a method described in the literature,[4] respectively. Methyl glycerate (**4**) was obtained by the esterification of the acid with methanol solution of $BF_3\cdot(C_2H_5)_2O$, and then purified by distillation under reduced pressure (bp 93—95 °C/2.1 Torr, lit,[6] 119—120 °C/14 Torr) [1 Torr=133.322 Pa]. Diethyl oxalacetate (**3**) was prepared by the reaction of sodium salts with HCl, and then distilled under reduced pressure (bp 71 °C/0.8 Torr, lit,[7] 131—132 °C/24 Torr). Elemental analysis of **3** and **4** showed pertinent figures, respectively. Other materials were obtained commercially and used without further purification.

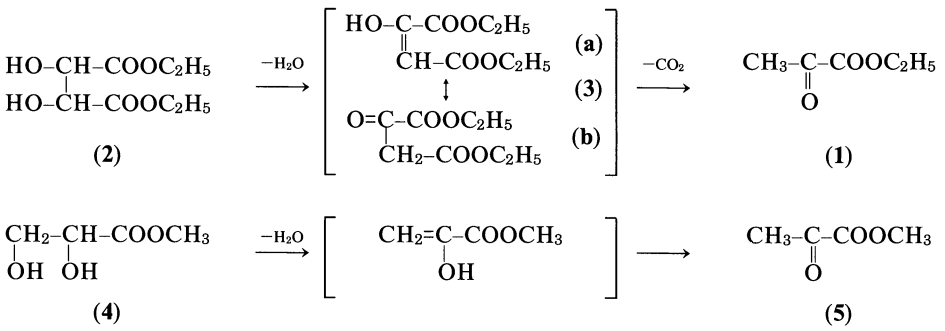
Results and Discussion

As shown in a previous paper,[4] η-Al_2O_3 and $K_2S_2O_7/SiO_2$ have revealed activity that is favorable for the intramolecular dehydration of ethylene glycol. It was expected that pyruvate could be obtained from glycols **2** and **4** on both catalysts.

However, **1** could not be detected on η-Al_2O_3 at 350 °C with SV=3600 h^{-1} to afford predominantly CO_2 with a high conversion of **2** over 90%. Figure 1(a) shows that **1** was easily hydrolyzed on η-Al_2O_3 in the presence of water vapor in the feed, signifying that **1** could not be obtained in the attempted conversion of **2** to **1** on η-Al_2O_3 due to the hydrolysis of the resulting ester followed by the decarboxylation of the free acid. A small amount of pyruvates (**5** and **1**) was obtained in yields of 13 and 2% from **4** and **2** on η-Al_2O_3, respectively, with a high space velocity of 7200 h^{-1} at 375 °C. $K_2S_2O_7/SiO_2$ was much less active for hydrolysis of pyruvate than η-Al_2O_3 (Fig. 1(b)), and the yields of pyruvates were improved up to 50% from **4** and 60% from **2** on $K_2S_2O_7/SiO_2$ at 300 °C with SV=500 h^{-1}. Presumably, disulfate was converted into hydrogensulfate in the presence of H_2O produced through the dehydration of the glycols **2** and **4**,

$$K_2S_2O_7 + H_2O \rightleftarrows 2KHSO_4,$$

leading to the unique activity of $K_2S_2O_7/SiO_2$ for pyruvic acid synthesis.



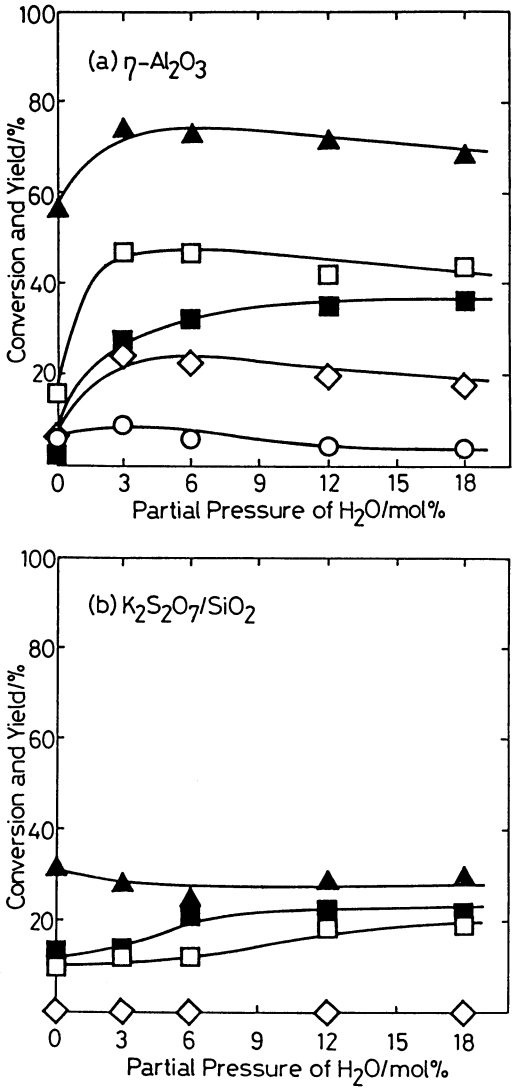


Fig. 1. Effect of the partial pressure of H_2O on the hydrolysis of ethyl pyruvate on (a) η-Al_2O_3 and (b) $K_2S_2O_7/SiO_2$ at 300 °C with SV=1000 h^{-1}. Feed: 3 mol% (toluene solution) diluted with N_2. ▲: Conversion of ethyl pyruvate, ■: yield of ethanol, ◇: yield of acetaldehyde, ○: yield of ethylene, and □: yield of CO_2.

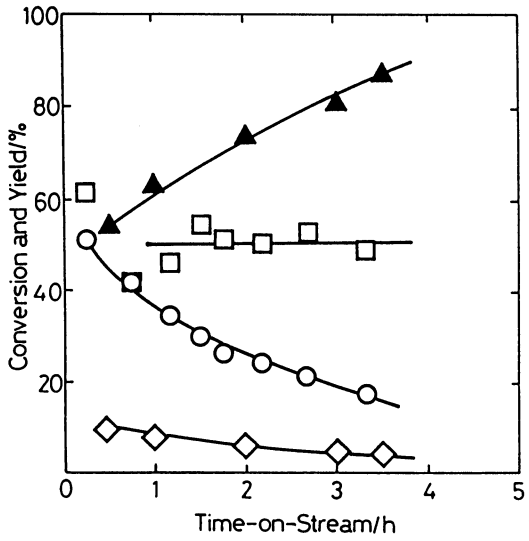


Fig. 2. Vapor-phase decarboxylation of diethyl oxalacetate on $K_2S_2O_7/SiO_2$ at 300 °C with SV=500 h^{-1}. Feed: 3 mol% diethyl oxalacetate (benzene solution) +3 mol% H_2O diluted with N_2. Symbols are same as those in Fig. 1. Yield of CO_2 is based on two moles decarboxylation of diethyl oxalacetate.

Diethyl tartrate (**2**) is a substituted glycol, thus having two hydroxyl groups; however, it dehydrated to a single intermediate, oxalacetate (**3**), due to the symmetric structure of **2**. However, the resulting **3** exists in two forms,[7] enol- (**3a**) or koto-form (**3b**), each of which can be distinguished together with ^1H NMR at the singlet CH proton signal of **3a** (δ=5.94) or singlet CH_2 proton signal of **3b** (δ=3.76), respectively. When a rather keto-rich **3** with **3a**/**3b**=1.8 was supplied in the presence of water vapor on $K_2S_2O_7/SiO_2$ at 300 °C with SV=500 h^{-1}, the yield of **1** immediately after the reaction started was 50%, as shown in Fig. 2, corresponding to the yield of CO_2 for decarboxylation of one -COOH of **3**. With increasing time-on-stream, the yield of **1** increased up to 90% with a decrease in C_2H_4 yield, while the yield of CO_2 was almost constant. The hydrolysis of $-CH_2-COOC_2H_5$ moiety of **3b** followed by the decarboxylation in favor of pyruvate would proceed predominantly on $K_2S_2O_7/SiO_2$. Employing an enol-rich **3** with **3a**/**3b** =4.4 in another run, the yield of **1** decreased to 50% after 4 h-on-stream. Since the ratio of **3a**/**3b** increased to 2.8 with more than 80% recovery of **3** when **3** with **3a**/**3b** =1.8 was supplied with H_2O in the absence of the catalyst under the same conditions as above, the catalyst

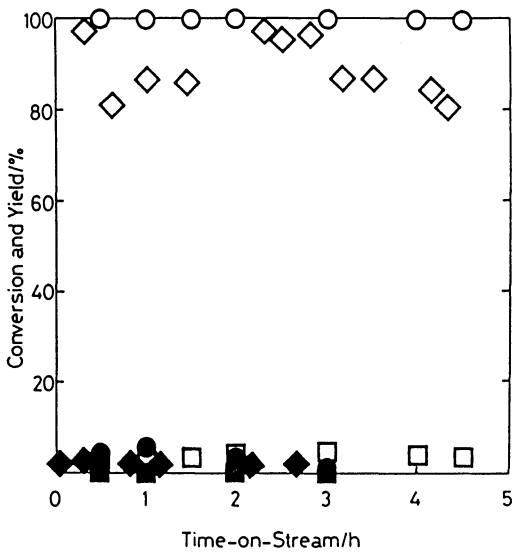


Fig. 3. Vapor-phase dehydration of ethanol on fresh (open symbols) and used (closed symbols) $K_2S_2O_7/SiO_2$ at 300 °C with SV=500 h^{-1}. Feed: mol% ethanol (benzene solution) +5 mol% H_2O diluted with N_2. ○: Conversion of ethanol, ◇: yield of ethylene, and □: yield of diethyl ether.

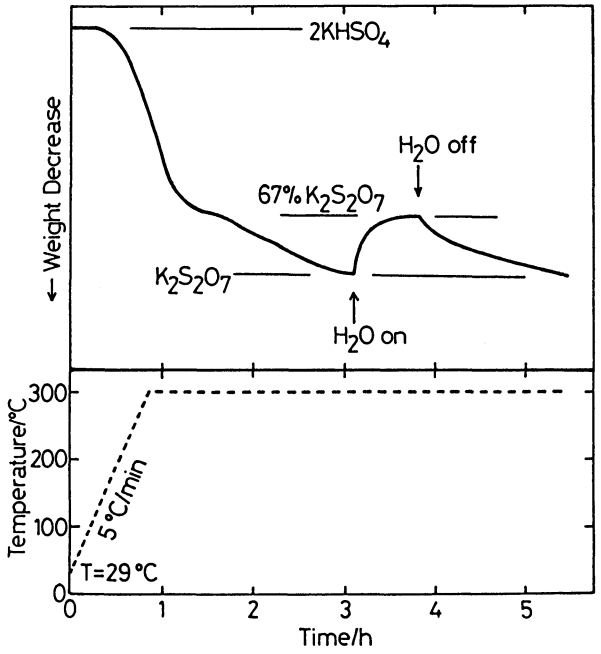


Fig. 4. Thermogravimetric analysis for $2KHSO_4 \rightleftarrows K_2S_2O_7+H_2O$.

is effective to convert **3a** to **3b**. Figure 2 shows that the catalytic properties of $K_2S_2O_7/SiO_2$ changed during time-on-stream. Ethanol was dehydrated with great ease on the fresh catalyst to afford C_2H_4 selectively, while the used $K_2S_2O_7/SiO_2$ was completely deactivated for ethanol dehydration as shown in Fig. 3. It is, however, of interest that the glycol moieties of **2** was dehydrated on the used $K_2S_2O_7/SiO_2$ to yield **1** in 40%.

The catalyst, $K_2S_2O_7/SiO_2$, was prepared by impregnating SiO_2 gel with aqueous $KHSO_4$, which is dehydrated to form $K_2S_2O_7$ at a high temperature. The TGA analysis given in Fig. 4 shows that the weight of the $KHSO_4$ specimen decreased toward the $K_2S_2O_7$ level through the dehydration at 300 °C, which was the same temperature as the typical reaction conditions employed in the present work. Potassium disulfate thus formed quickly trapped H_2O when supplied 3% moist nitrogen, as shown in Fig. 4. The weight increase showed a plateau at a composition of 67% $K_2S_2O_7$ without coming back to the $KHSO_4$ level, and again slowly dehydrated to $K_2S_2O_7$ under dry nitrogen. The value of 67% $K_2S_2O_7$ at 300 °C is in good agreement with that given by Mellor[8] for $KHSO_4$–$K_2S_2O_7$–H_2O system, suggesting that $K_2S_2O_7$ is supported by SiO_2 gel in the pore as a thin film of the molten salt of 67% $K_2S_2O_7$+33% $KHSO_4$ under reaction conditions. Powder X-ray analysis provided evidence for the formation of $K_2S_2O_7$[9] upon heating $KHSO_4$[10] at 300 °C, where the starting $KHSO_4$ was not detected in the XRD pattern.

In conclusion, ethyl pyruvate was obtained by the vapor-phase dehydrative decarboxylation of diethyl tartrate on $K_2S_2O_7/SiO_2$. The catalyst domesticated to steady-state activity within a few hours on-stream, and decomposed the intermediate oxalacetate through the keto-form in favor of pyruvate. TGA analysis revealed that the catalyst consisted of 67% $K_2S_2O_7$ and 33% $KHSO_4$ in the reaction conditions and was supported by SiO_2 gel in the pore as a thin film of the molten salt.

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