August, 1992] © *1992 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn.,* ***65****, 2083—2085 (1992)* 2083

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

Shigeru SUGIYAMA,* Sadao FUKUNAGA, Katsuhiro KAWASHIRO,
and Hiromu HAYASHI
Department of Chemical Science and Technology, Faculty of Engineering,
The University of Tokushima,
Minamijosanjima, Tokushima 770

(Received February 15, 1992)

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.

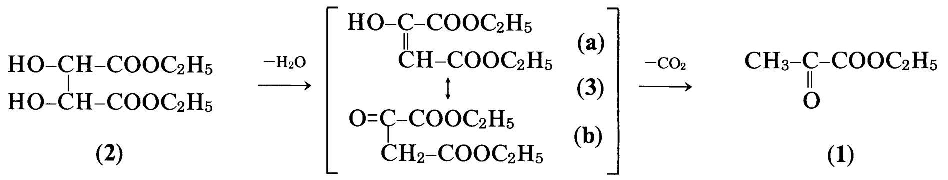
Results and Discussion

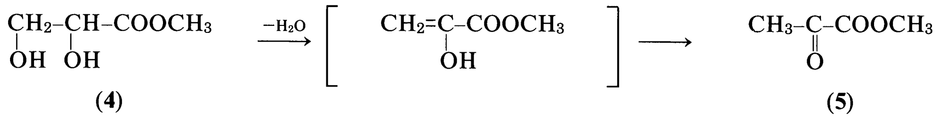
As shown in a previous paper,[4] η-Al_2O_3 and $K_2S_2O_7/SiO_2$ have revealed activity that is favorable for the intramolecular dehydration of ethylene glycol. It was expected that pyruvate could be obtained from glycols **2** and **4** on both catalysts.

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.





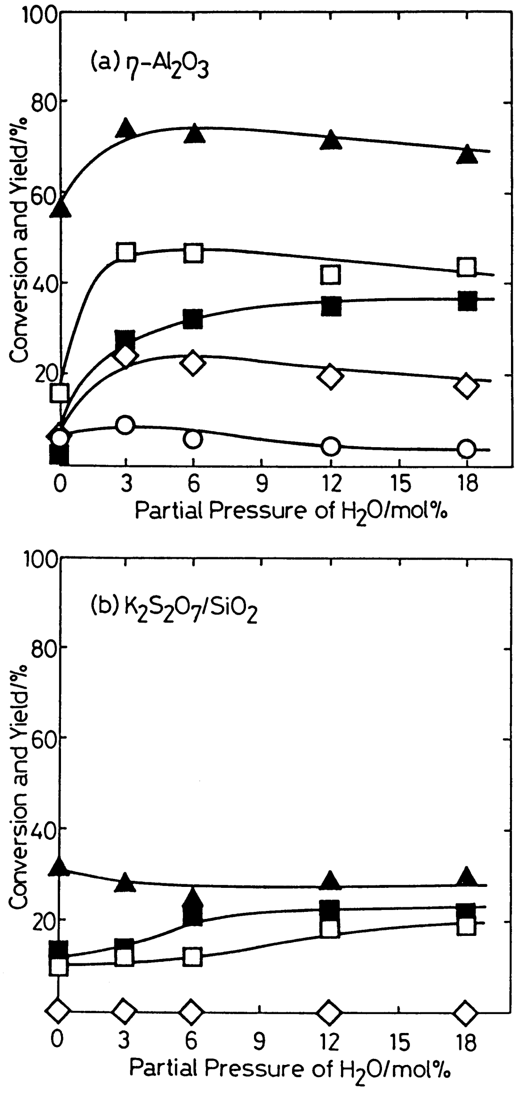


Fig. 1. Effect of the partial pressure of H_2O on the hydrolysis of ethyl pyruvate on (a) η-Al_2O_3 and (b) $K_2S_2O_7/SiO_2$ at 300 °C with SV=1000 h^{-1}. Feed: 3 mol% (toluene solution) diluted with N_2. ▲: Conversion of ethyl pyruvate, ■: yield of ethanol, ◇: yield of acetaldehyde, ○: yield of ethylene,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

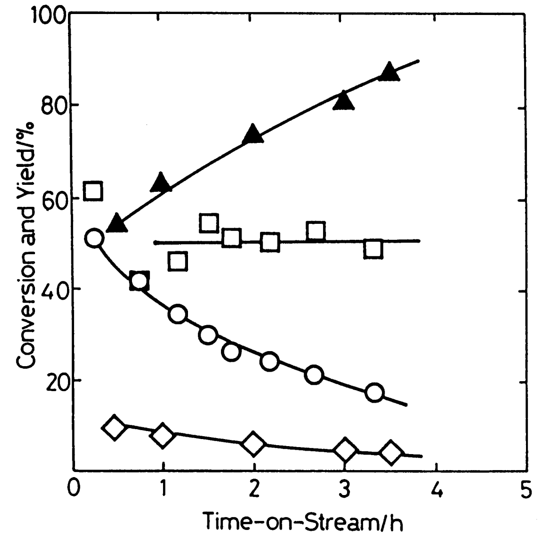


Fig. 2. Vapor-phase decarboxylation of diethyl oxalacetate on $K_2S_2O_7/SiO_2$ at 300 °C with SV=500 h^{-1}. Feed: 3 mol% diethyl oxalacetate (benzene solution) +3 mol% H_2O diluted with N_2. Symbols are same as those in Fig. 1. Yield of CO_2 is based on two moles decarboxylation of diethyl oxalacetate.

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 ^{1}H 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

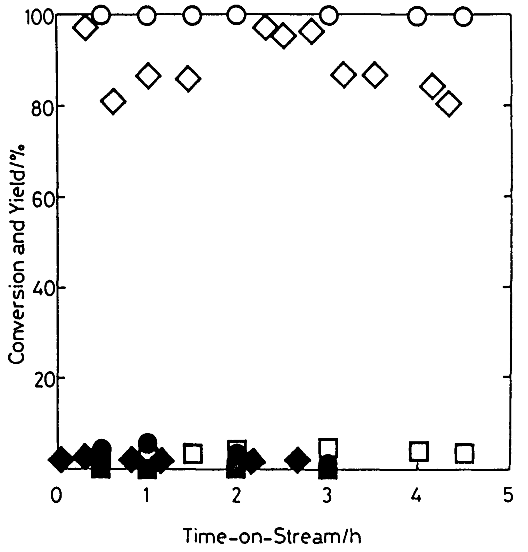


Fig. 3. Vapor-phase dehydration of ethanol on fresh (open symbols) and used (closed symbols) $K_2S_2O_7/SiO_2$ at 300 °C with SV=500 h^{-1}. Feed: mol% ethanol (benzene solution) +5 mol% H_2O diluted with N_2. ○: Conversion of ethanol, ◇: yield of ethylene, and □: yield of diethyl ether.

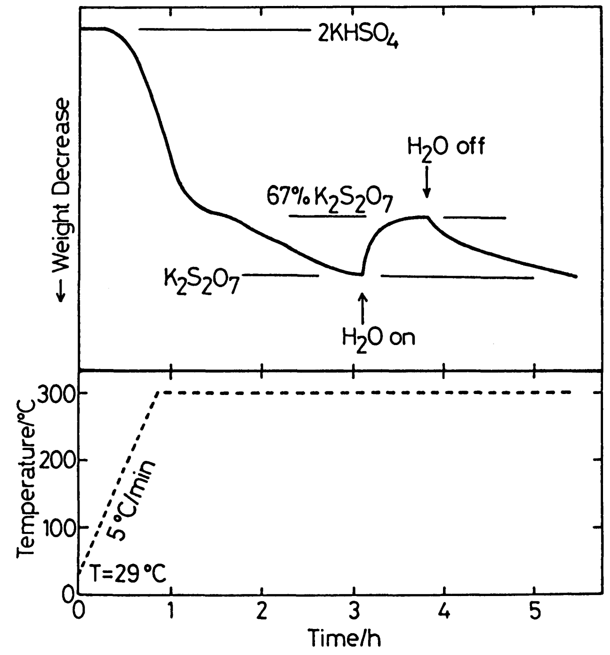


Fig. 4. Thermogravimetric analysis for $2KHSO_4 \rightleftarrows K_2S_2O_7+H_2O$.

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.

The authors thank The Ministry of Education, Science and Culture for a Grant-in-Aid for Scientific Research No. 03650679 to H. H.

References

1) E. Erlenmeyer, *Ber. Dtsch. Chem. Ges.*, **14**, 320 (1881).
2) J. W. Howard and W. A. Fraser, "Organic Synthesis," ed by H. Gilman, Wiley, New York (1945), Coll. Vol. 1, p. 475.
3) T. Tsujino, S. Ohigashi, S. Sugiyama, K. Kawashiro, and H. Hayashi, *J. Mol. Catal.*, **71**, 25 (1992).
4) S. Sugiyama, S. Fukunaga, K. Ito, S. Ohigashi, and H. Hayashi, *J. Catal.*, **129**, 12 (1991).
5) "The Merck Index—An Encyclopedia of Chemical and Drugs," 8th ed, ed by P. G. Stecher, Merck, Rahway, NJ (1968).
6) "Lange's Handbook of Chemistry," 11th ed, ed by J. A. Deam, McGraw-Hill, New York (1973), Chap. 7.
7) T. Yamashita and O. Manabe, *Nippon Kagaku Kaishi*, **(1990)** 890.
8) J. W. Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green and Co., London (1930) Vol. 10, p. 444.
9) ASTM, "X-ray Powder Data File," **1**-0717.
10) ASTM, "X-ray Powder Data File," **11**-649.