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Catalysts for Vapor-Phase Dehydration of Ethylene Glycol and Their Application to Pyruvic Acid Synthesis

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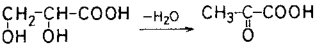
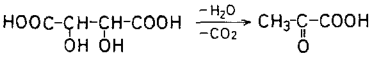
Vapor-phase dehydration of ethylene glycol over acidic catalysts such as η-Al_2O_3, SiO_2–MgO, $H_3PW_{12}O_{40}$, P_2O_5/Al_2O_3, $AlPO_4$, and $K_2S_2O_7/SiO_2$ has been examined as a probe reaction for attempted conversion of tartaric acid into pyruvic acid. The reaction was carried out by a conventional fixed-bed flow apparatus at 200–400°C with a space velocity of 1000 or 3600 h^{-1} for 10 vol% ethylene glycol in feed. η-Al_2O_3 gave 1,4-dioxane as a major detectable product at 200–250°C. The yield passed through a maximum (35%) at 280°C and then decreased with increasing temperature. Formation of the intramolecular dehydration product, acetaldehyde, was observed at above 250°C, showing a plateau of yield (55–60%) at higher temperatures. The lack of balance was presumably due to formation of linear polymers. Similar behavior was also observed for $H_3PW_{12}O_{40}$, but no dioxane was detected for SiO_2–MgO. Dioxane activity showed a shift to higher temperature for P_2O_5/Al_2O_3 and $AlPO_4$, and thus both dioxane and acetaldehyde were obtained in the same temperature region above 250°C. It is of interest to note that $AlPO_4$ prepared from sulfate showed high selectivity to acetaldehyde, while dioxane was the predominant product for $AlPO_4$ from nitrate. $K_2S_2O_7/SiO_2$ was another favorable catalyst for the intramolecular dehydration of glycol similar to $AlPO_4$ from sulfate, and revealed excellent activity for conversion of ethyl tartrate into ethyl pyruvate through dehydrative decarboxylation (yield 60% at 300°C with SV 500 h^{-1}). © 1991 Academic Press, Inc.

INTRODUCTION

Pyruvic acid has received increasing attention in recent years as a potential precursor for enzymatic conversion to L-amino acids (*1*). An established laboratory procedure for pyruvic acid synthesis, first described by Erlenmeyer (*2*) and recommended in (*3*), is the dehydrative distillation of glyceric acid (Eq. (1)) and/or tartaric acid (Eq. (2)) in the presence of an excess powder of potassium hydrogensulfate.


$$\underset{OH}{CH_2}-\underset{OH}{CH}-COOH \xrightarrow{-H_2O} CH_3-\underset{\overset{\|}{O}}{C}-COOH \qquad (1)$$


$$HOOC-\underset{OH}{CH}-\underset{OH}{CH}-COOH \xrightarrow[-CO_2]{-H_2O} CH_3-\underset{\overset{\|}{O}}{C}-COOH \qquad (2)$$

In the previous work (*4*), glyceric acid was obtained in high yield as the amide from acrylonitrile through epoxide intermediate and the subsequent hydration. It appeared of interest to convert glyceric acid continuously into pyruvic acid in a vapor-phase catalytic flow system. However, a preliminary attempt to dehydrate glyceric acid (Eq. (1)) over η-Al_2O_3 at 375°C resulted in decarboxylation, and unfortunately no pyruvic acid was obtained (*5*). Esterification of glyceric acid retards decarboxylation, and methyl pyruvate was obtained from methyl glycerate in 10–13% yield (*5*). The low yield of pyruvate suggests that the reaction involves a complex network of inter- and intramolecular dehydration, arising from the polyfunctional structure of the substrate, in addition to the unfavorable decarboxylation. Both for glycerate and tartrate, intramolecular dehydration might be presumed as a trigger for the pyruvic acid formation through enol carboxylate followed by the rapid isomerization to the keto ester. Thus,

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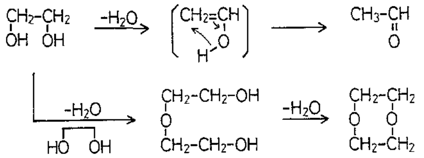
vapor-phase dehydration of ethylene glycol over acidic catalysts such as η-Al_2O_3, SiO_2–MgO, $H_3PW_{12}O_{40}$, P_2O_5/Al_2O_3, $AlPO_4$, and $K_2S_2O_7/SiO_2$ has been examined in the present work as a probe reaction in screening catalysts favorable for intramolecular dehydration of glycol species (Eq. (3)).[1] Among these catalysts potassium pyrosulfate on silica ($K_2S_2O_7/SiO_2$) showed excellent activity to afford ethyl pyruvate from ethyl tartrate.



(3)

(4)

EXPERIMENTAL

Apparatus and procedure. The reaction was carried out by a conventional fixed-bed flow apparatus. The catalyst was packed in a 8-mm i.d. glass tubing inserted in an electrically heated furnace. Ethylene glycol (10 mol%) was supplied by bubbling nitrogen through the saturator. Other substrates were supplied as the benzene solution by a Microfeeder (Type JP-S, Furue Science Co., Tokyo). The effluent gas was scrubbed by an ice-cooled ethanol or water to analyze by gas chromatography.

Materials. Acetaldehyde, benzene, crotonaldehyde, 1,4-dioxane, diethylene glycol, ethylene glycol, pyruvic acid, tartaric acid (Wako Pure Chemicals), diethyl tartrate, ethyl pyruvate, glyceric acid (Tokyo Kasei), and methyl pyruvate (Aldrich) were obtained commercially and used without further purifications. The preparation recipes and properties of η-Al_2O_3 (*7*), SiO_2–MgO (*7*), $H_3PW_{12}O_{40} \cdot 24\ H_2O$ (*8*), $AlPO_4$–N (*9*), $AlPO_4$–S (*9*), P_2O_5–Al_2O_3 (*10*), and $K_2S_2O_7/SiO_2$ are given in Table 1.

Analysis. Monitoring of the reaction was made with GC (Hitachi 163-FID for organic species and Yanako G-2800-TCD for CO_2). Pyruvic acid was analyzed being converted to ethyl pyruvate (*5*). Column packings used were as follows: 15% PEG 4000/Uniport B for acetaldehyde, crotonaldehyde, ethanol, and dioxane (100°C), Gaskropack 54 for dioxane, ethylene glycol, and diethylene glycol (220°C) and ethyl tartrate (250°C), 10% PEG 4000/Flusin T for ethyl pyruvate (140°C), and Unibeads C for CO_2 (100°C), methane, ethane, ethylene, propane, and acetylene (150°C). NMR spectra were measured by a Hitachi R-24 Spectrometer; chemical shifts are expressed in the unit δ. Mass spectra were measured with a Shimazu QP1000 Spectrometer.

RESULTS AND DISCUSSION

Dehydration of Ethylene Glycol

η-Alumina. Al_2O_3 is one of the most typical dehydration catalysts and has been investigated in detail (*11–15*). The intermolecular dehydration of an alcohol over γ- or η-Al_2O_3 occurs at a lower temperature to give an ether, while the intramolecular dehydration to afford an olefin is often predominant at a higher temperature (*11, 12*). The yield of ether shows a maximum at 250–260°C for ethanol (*12*). The decrease in ether with increase in ethylene at higher temperatures seems to reflect the thermodynamic nature, but the product pattern in practice is strongly dependent on the sort of catalyst. Thus the predominant product over Al_2O_3 (*12*) is ether at 250°C, while the equilibrium constants for the dehydration of ethanol to ethylene ($K_p = 57$) (*15*) and to ether ($K_p = 2.5$) (*14*) thermodynamically suggest ethylene in preference to ether even at a low temperature of 250°C.

A similar product pattern was also observed for dehydration of ethylene glycol over η-Al_2O_3, as shown in Fig. 1(a). Dioxane was obtained at 200–250°C as a major detectable product, and the yield passed through a maximum (ca. 35%) at 280°C and then decreased with increasing tempera-

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[1] Ethylene formation through ether was proved to be minor in ethanol dehydration (*6*). Similarly acetaldehyde through cleavage of dioxane was presumed to be negligible in the present work.

TABLE 1

Preparation Recipes and Properties of Catalysts Employed

Catalyst	Procedure	Calcination		Surface area (m^2/g)	Bulk density (g/cm^3)	Ref.
		Temp. (°C)	Time (h)			
η-Al_2O_3[a]	—	500	5 (air)	196	0.57_1	(*7*)
SiO_2–MgO	SiO_2 sol[b] was coagulated with MgO; 25 wt% MgO	500	5 (air)	254	0.54_5	(*7*)
$H_3PW_{12}O_{40}$	24-hydrate[c]			3.2	1.13	(*8*)
$AlPO_4$–N	$Al(NO)_3)_3$ 9 H_2O + H_3PO_4 + 3 NH_4OH	500	5 (N_2)	—	0.28_4	(*9*)
$AlPO_4$–S	$Al_2(SO_4)_3$ 20 H_2O + 2 H_3PO_4 + 6 NH_4OH	500	5 (air)	8.7	0.26_3	(*9*)
P_2O_5/Al_2O_3	η-Al_2O_3[a] was impregnated with 85% H_3PO_4; 10 mol% P_2O_5	500	5 (N_2)	6.0	0.87_3	(*10*)
$K_2S_2O_7/SiO_2$	SiO_2[d] (4.31 g) + 2.77 g $KHSO_4$/10 ml H_2O, evaporated the water at 80°C, and then calcined; 2.6_4 mmol $K_2S_2O_7$/g SiO_2	300	1 (N_2)	—	0.67_3	

[a] Sumitomo Chemical Co., Osaka.

[b] Snowtex N; Nissan Chemical Co., Tokyo.

[c] Wako Pure Chemicals, Tokyo.

[d] Silbead MS: Mizusawa Industrial Chemicals, Tokyo; calcined at 500°C for 5 h in air.

ture. The formation of intramolecular dehydration product, acetaldehyde, was observed above 250°C, showing a plateau of the yield (55–60%) at higher temperatures.

As reported in the liquid-phase dehydration of diethylene glycol in the presence of Al_2O_3 (*16*), dioxane was formed also in the vapor-phase through intermolecular dehydration of ethylene glycol to diethylene glycol followed by the intramolecular dehydration. However, no diethylene glycol was detected, presumably due to intermolecular dehydration to linear oligomers of ethylene glycol. Mass spectra of the mixture of the effluent at 200°C revealed that fragment peaks were detected at *m*/*e* 44 and 149. Those peaks correspond to the fragment peaks, $CH_2{=}CH{-}OH^+$ and $HOCH_2(CH_2OCH_2)_2CH_2O^+$, from polyethylene glycol. Thus a variation of the intermolecular dehydration mode might occur at lower temperatures. At a higher temperature, the formation of acetaldehyde became predominant in place of that of dioxane. Crotonalde-

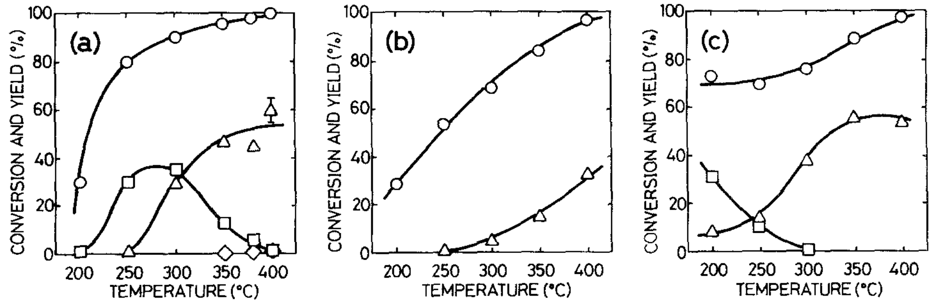

FIG. 1. Vapor-phase dehydration of ethylene glycol over acidic catalysts. 10% Ethylene glycol/N_2, SV = 3600 h^{-1}. (a) η-Al_2O_3; (b) SiO_2–MgO; (c), $H_3PW_{12}O_{40}$. ○, Ethylene glycol; △, acetaldehyde; □, dioxane; ◇, crotonaldehyde.

hyde, formed through an aldol condensation of acetaldehyde, was observed in a low yield. Above 350°C, an oily mist with a peculiar odor smoking through the ethanol-scrubber was observed in the effluent of the reactor. The reaction was carried out at 400°C to examine the lack of balance at high temperatures. Acetaldehyde was obtained in 60% yield with 2% dioxane and 5% crotonaldehyde without degeneration of activity during 9 h on-stream. Scrubbing with water, ethanol was detected in a low yield (ca. 2%). The analysis of the effluent gas revealed the formation of methane, ethane, ethylene, and propane in 0.21, 0.19, 3.8, and 0.07%, respectively. These products imply the cracking of ethylene glycol oligomers occured in parallel with the dehydration to acetaldehyde. Acethylene, which could be formed by the loss of two moles of water from ethylene glycol, was not detected at all. Attempted trapping of high boiling products resulted in 212 mg of brown oil for 4 h, which was only 5.3% based on the ethylene glycol supplied. The NMR spectra of the oil gave complex signals between 1 and 4 ppm, suggesting that an aldol condensation of more than three molecules of acetaldehyde occured. We did not carry out further isolation and identification of the oil. We guess the remainder of high boilers could be found in the oily mist with a peculiar odor. Unfortunately, the mist did not dissolve in ethanol, THF, or water. Another attempt to trap the mist directly at -20°C employing 3-mm i.d. × 2-m glass-tubing connected to the reactor exit gave ca. 900 mg of water with a trace of oil for 4 h on-stream. The mist seemed to be a polymer of acetaldehyde, because the yield of trapped water was at least 76% based on the ethylene glycol converted with a loss of one mole of water, which was relatively smaller than the sum of the yield (69%) of dehydration products, acetaldehyde (60%), dioxane (2%), ethanol (2%), and crotonaldehyde (5%).

Silica–magnesia. SiO_2–MgO prepared by the coagulation of colloidal silica with magnesia powder adsorbed pyridine and acetic acid at 300°C, indicating both acidic and basic sites (*7*), and was reported to be more active than other alkaline earth silicates in the vapor-phase dehydration of 1-butanol (*17*). Although the conversion of ethylene glycol in the dehydration on SiO_2–MgO was as high as 97% at 400°C, acetaldehyde was the only detectable product with 32% yield as shown in Fig. 1(b). A recent review (*18*) indicates that vapor-phase dehydration of ethylene glycol on acidic catalysts is known to predominantly afford dioxane rather than acetaldehyde, but no dioxane was detected for the present SiO_2–MgO, which turned black due to carbon deposit. The lack of balance due to carbonization suggests the formation of polymeric products through intermolecular dehydration.

12-Tungstophosphoric acid. Heteropoly acids are active for the conversion of methanol to hydrocarbons through dimethyl ether (*8, 19*). As shown in Fig. 1(c), ethylene glycol reacted on $H_3PW_{12}O_{40}$ with a high conversion over 70%, half of which gave dioxane, at temperatures below 200°C. With increasing temperature, the yield of dioxane decreased in the place of increasing acetaldehyde, of which yield was as high as 56% at 350°C. A trace of crotonaldehyde was also detected at high temperatures, but not diethylene glycol. Ethylene glycol is not readily dehydrated to acetaldehyde by an acidic catalyst (*18, 20*), but rather readily to dioxane, while many studies have been made on the enzymatic conversion to acetaldehyde (*21*). It seems worthwhile to mention that the present work provides an example for the formation of acetaldehyde by the vapor-phase dehydration of ethylene glycol on the strongly acidic $H_3PW_{12}O_{40}$.

Aluminum phosphate. $AlPO_4$ is an equimolar compound of Al_2O_3 and P_2O_5, and the dehydration behavior of alcohols over $AlPO_4$ is known to be dependent on the preparation procedure (*9, 22*). We carried out the dehydration of ethylene glycol on three types aluminum phosphate catalysts, P_2O_5/Al_2O_3, $AlPO_4$–S, and $AlPO_4$–N. At first, the dehydration of the diol on

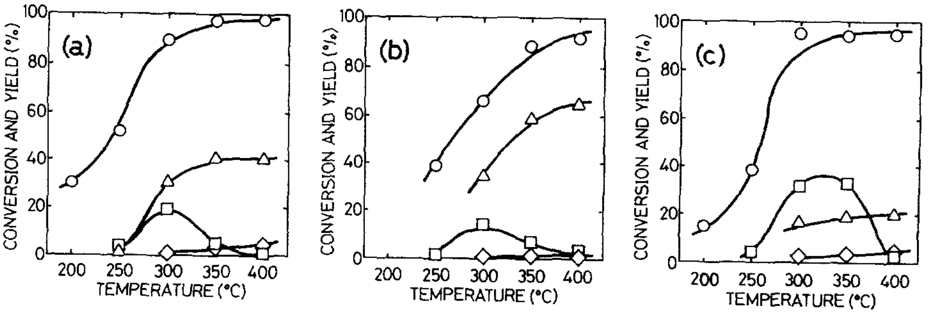

FIG. 2. Vapor-phase dehydration of ethylene glycol over aluminum phosphate catalysts. 10% Ethylene glycol/N_2, SV = 1000 h^{-1}. (a) P_2O_5/Al_2O_3; (b) $AlPO_4$–S; (c) $AlPO_4$–N. Symbols are the same as those in Fig. 1.

P_2O_5/Al_2O_3 was examined in order to compare the reaction behavior with that on η-Al_2O_3. As shown in Fig. 2(a), conversion of ethylene glycol and yield of acetaldehyde were almost similar to those on η-Al_2O_3, but somewhat different for dioxane. The maximum yield of dioxane (19%) was observed at around 300°C in contrast with that of η-Al_2O_3 (ca. 35% at 250–300°C). The temperature regions for the formation of acetaldehyde and dioxane on P_2O_5/Al_2O_3 were overlapped almost completely. Selective intramolecular dehydration of diols on the present catalyst seems to occur at a relatively higher temperature. Next, the dehydration on $AlPO_4$–S and $AlPO_4$–N was examined (Fig. 2(b) and 2(c), respectively). It was reported that dehydration of 1-butanol on $AlPO_4$–S showed predominant formation of intramolecular dehydration product, butene, in contrast with that on $AlPO_4$–N, where intermolecular dehydration occured favorably to give dibutyl ether (*9*, *22*). The conversion of ethylene glycol on $AlPO_4$ was relatively lower than that of η-Al_2O_3 and P_2O_5/Al_2O_3, but acetaldehyde was formed selectively in high yield (64% at 400°C). In contrast, dioxane was the major product on $AlPO_4$–N. These dehydration behaviors of the diol on $AlPO_4$–S and $AlPO_4$–N corresponded to those of monoalcohols (*9*, *22*). $AlPO_4$–N treated with dilute ammonium sulfate behaves similarly to $AlPO_4$–S (*9*) and it was suggested that the SO_4^{2-} ion in $AlPO_4$–S enhanced the intramolecular dehydration of alcohols (*22*).

Silica-supported potassium pyrosulfate. Potassium pyrosulfate is the dehydrated dimer form of potassium hydrogen-sulfate (*23*), which was reported to be effective for dehydrative decarboxylation of tartaric acid to pyruvic acid at 220–225°C in liquid-phase (*3*, *24*). Since pure $KHSO_4$ melts at a lower temperature of 197°C (*23*), a supported catalyst was prepared by impregnating silica gel with aqueous $KHSO_4$ to adapt for vapor-phase fixed-bed flow operations. Potassium pyrosulfate $K_2S_2O_7$ might be the active species at the reaction temperature (300°C). As shown in Fig. 3, the intramolecular dehydra-

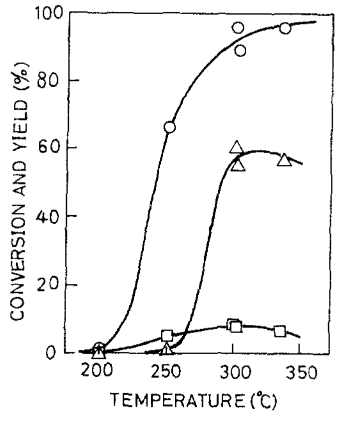

FIG. 3. Vapor-phase dehydration of ethylene glycol over $K_2S_2O_7/SiO_2$. 10% Ethylene glycol/N_2, SV = 1000 h^{-1}. Symbols are the same as those in Fig. 1.

tion of ethylene glycol to acetaldehyde was observed selectively at a lower temperature (300°C) in a high yield of 60%. Formation of dioxane was very small as anticipated (max. yield, 9% at 300°C), and $K_2S_2O_7/SiO_2$ was expected to be the most favorable catalyst for the application to pyruvic acid synthesis.

Dehydrative Decarboxylation of Ethyl Tartrate

The current technology for the synthesis of pyruvic acid is still based on the dehydrative decarboxylation of tartaric acid (Eq. (2)). The route provides pyruvic acid in good yield (50–60%) (*3*), but potassium hydrogensulfate powder should be used in a large excess per batch (*3, 24*). As an extension of the results for vapor-phase dehydration of ethylene glycol over various catalysts, pyruvic acid was expected to be obtained in the fixed-bed flow system.

Figure 4 compares the results in the attempted synthesis of pyruvic acid over η-Al_2O_3 (a) and $K_2S_2O_7/SiO_2$ (b) in the vapor phase, where ethyl tartrate was employed as the reactant to avoid the decomposition of free acids (*5*). The dehydration of ethyl tartrate on η-Al_2O_3 was observed at 350°C without formation of any trace of pyruvate with high conversion of the tartrate over 90%, approaching a steady state after 3.5 h on-stream as shown in Fig. 4(a). Another candidate, $AlPO_4$–S, which was a favorable catalyst for the intramolecular dehydration of ethylene glycol, was again disappointing in the pyruvate synthesis.

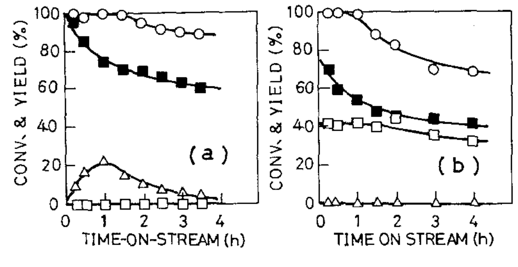

FIG. 4. Attempted conversion of ethyl tartrate to pyruvate. 5% Ethyl tartrate/benzene. (a) η-Al_2O_3, SV = 3600 h^{-1}, 350°C; (b) $K_2S_2O_7/SiO_2$, SV = 1000 h^{-1}, 300°C. ○, Ethyl tartrate; □, ethyl pyruvate; ■, CO_2, two moles based on tartrate; △, acetaldehyde.

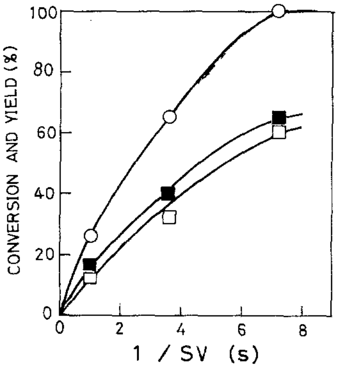

FIG. 5. Effect of the reciprocal space velocity on dehydrative decarboxylation of ethyl tartrate over $K_2S_2O_7/SiO_2$ at 300°C. ○, Conversion of ethyl tartrate; □, yield of ethyl pyruvate; ■, CO_2, two moles based on tartrate.

In contrast, ethyl pyruvate was obtained in a high yield of 40% on $K_2S_2O_7/SiO_2$ at 300°C with a space velocity of 1000 h^{-1}, as shown in Fig. 4(b). After the initial 2 h on-stream, the catalyst was domesticated to show a stable activity capable for continuous operation. Within 1.8 h on-stream, the cumulative amount of ethyl pyruvate obtained in the illustrative run given in Fig. 4(b) exceeded the stoichiometric requirement based on the amount of $K_2S_2O_7$ actually supported on silica. Thus the $K_2S_2O_7$ was not acting as a stoichiometric dehydrating reagent, but was a catalyst evidently regenerated *in situ*. With decreasing space velocity, the yield of ethyl pyruvate increased up to as high as 60% at SV 500 h^{-1} (Fig. 5), which corresponded to that reported in the batch system (*2, 3, 24*). The advantage of running the reaction in a flow system with a catalyst over the batch operation using an excess of the potassium hydrogensulfate has been approved, and $K_2S_2O_7/SiO_2$ appears to be a promising catalyst for pyruvic acid synthesis from the tartrate.

CONCLUSION

Among various acidic catalysts, $K_2S_2O_7/SiO_2$ revealed excellent activity for intramolecular dehydration of ethylene glycol to yield 60% acetaldehyde with 9% dioxane at 300°C, and was applied for the conversion of ethyl tartrate into the pyruvate. Thus, ethyl pyruvate was obtained in a good yield of 60% at 300°C with SV 500 h^{-1} over $K_2S_2O_7/SiO_2$. Potassium hydrogensulfate ($KHSO_4$), which melts at a lower temperature of around 200°C, was adapted in the present work for the vapor-phase fixed-bed flow operation as a silica-supported pyrosulfate catalyst.

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