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Conversion of ethanol over calcium stannate catalyst under supercritical conditions

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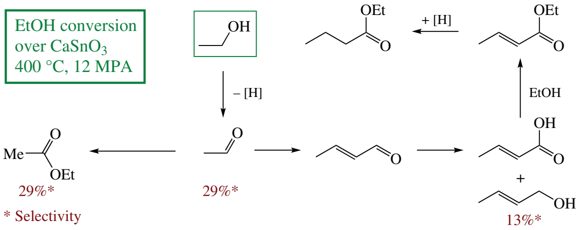
Ethanol over calcium stannate ($CaSnO_3$) catalyst under supercritical conditions (400 °C, 120 atm) is transformed mainly into ethanal, ethyl acetate and 2-buten-1-ol. The process is accompanied by crystallization of the amorphous catalyst.



Keywords: ethanol conversion, supercritical conditions, dehydrogenation, aldol condensation, Tishchenko reaction, borrowing hydrogen, calcium stannate, catalyst crystallization.

Owing to the possibility of synthesizing ethanol from renewable feedstocks,[1–3] studies are currently underway on the processes for ethanol conversion to obtain higher hydrocarbons, oxygenates and other valuable compounds[4] that can serve as platforms for organic synthesis and can be used as fuels.[5] During conversion ethanol undergoes dehydration to ethylene, dehydrogenation to ethanal, these products would be hydrogenated on the C=C and C=O bonds, oligomerization of the resulting olefins by condensation according to the Gerbe reaction[6,7] can occur along with formation of esters by the Tishchenko reaction.[8] Ethylene and propylene are obtained from ethanol in high olefin yields.[2] The synthesis of *n*-butanol from ethanol is of great interest[7,9,10] since it is used as a basis for synthesizing C_{4+} products.[10–12] The formation of *n*-butanol from ethanol occurs *via* the Gerbe reaction that involves a number of steps: (1) dehydrogenation of ethanol to afford ethanal; (2) aldol condensation of two ethanal molecules to give crotonaldehyde; and (3) hydrogenation of the unsaturated condensation products at C=O and C=C bonds. However, condensation of two alcohol molecules competes with the homo- and cross-condensations of alcohols and aldehydes,[13,14] which decreases the process selectivity. Studies on directional ethanol conversion by fitting the thermodynamic parameters of the process and on the condensation mechanism are continuing.[15]

We have shown previously[16–20] that stannates of alkaline earth metals are active in the aldol-crotonic condensation of acetone, in the conversion of 2-propanol,[21] and in acetone and 2-propanol[22] joint conversion under supercritical conditions. Basic metal oxides are known to be active in the conversion of ethanol to butanol at 300–450 °C.[23–26] It may be assumed that alkaline earth metal stannates possessing basic Brønsted properties would also be active as ethanol conversion catalysts.

It is known[27] that catalytic reactions under supercritical conditions have advantages over conventional conditions due to the following features: favorable mass- and heat-conductive properties allowing heterogeneous catalytic reactions to occur efficiently; lack of diffusion limitations due to the complete mutual miscibility of reagents; longer operation times of heterogeneous catalysts due to dissolution of coke precursors. Experiments on the aldol condensation of acetone on calcium and strontium stannates showed that the catalyst featured stable operation under supercritical conditions, in contrast to the gas-phase process.[16,17]

In this work, the conversion of ethanol at 400 °C and 120 atm was carried out on amorphous calcium stannate ($CaSnO_3$) as the catalyst. The latter was obtained by the calcination of $CaSn(OH)_6$ at 450 °C [$CaSn(OH)_6 \rightarrow CaSnO_3 + 3H_2O$]. Under the reaction conditions, ethanol would exist in the supercritical state ($T_c = 243.2$ °C, $p_c = 63$ atm).[28] Catalytic tests were carried out in a stainless steel flow-type tubular reactor (for details of catalyst synthesis and catalytic experiments, see Online Supplementary Materials).

The data of the catalytic experiments (ethanol conversion and products selectivity) are shown in Figure 1. The following compounds were obtained with the highest selectivity: ethyl acetate (29%), ethanal (29%) and 2-buten-1-ol (crotyl alcohol) (13%). Crotonaldehyde and ethyl butanoate were also formed with selectivities of 4–6%. The selectivities for other products were lower than 2%. Analysis of the compounds formed shows that the main direction of the reaction is dehydrogenation of ethanol to form ethanal, which further condenses to form crotonaldehyde and undergoes the Tishchenko reaction to give ethyl acetate. In the course of the Tishchenko reaction, ethanal first disproportionates into ethanol and acetic acid that further undergo esterification to give ethyl acetate. Up to the 210th min of the reaction, ethyl acetate is the predominant conversion product. Initially, the selectivity to ethanal is smaller than that to ethyl acetate, but after 210 min of the reaction, the selectivities to ethanal and ethyl acetate level off. In ref. 29, the conversion of ethanol to ethyl acetate over PdO/SiO_2 catalyst was performed. It was found that the selectivities to ethanal and ethyl acetate

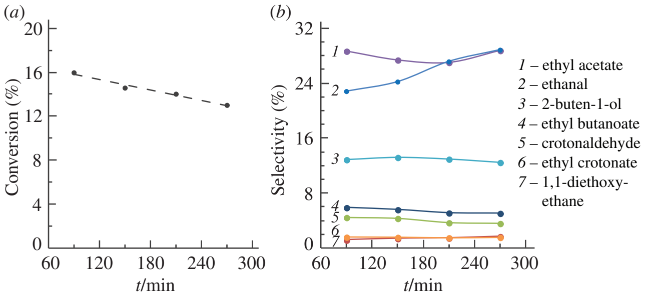


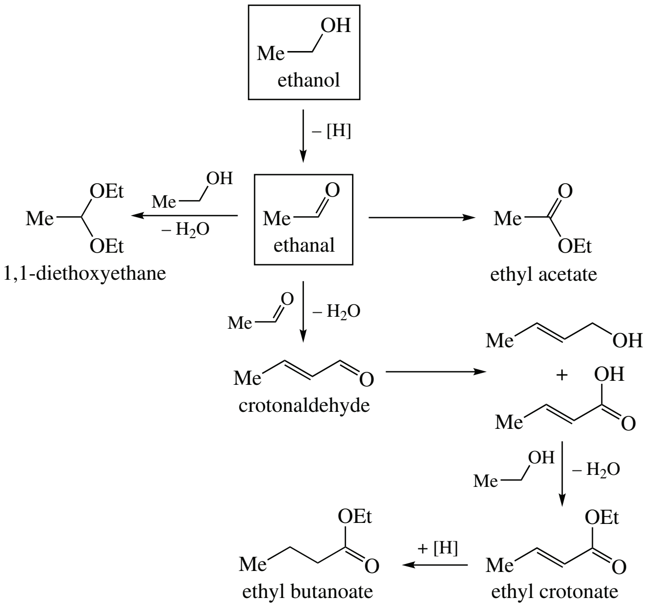
Figure 1 Catalytic data: (*a*) conversion of ethanol over $CaSnO_3$ (400 °C, 120 atm); (*b*) selectivities to the main products.

depended on the ethanol consumption rate: at low rates, ethanal formation is the limiting step, while at high rates ethyl acetate is formed. A one-pot synthesis of ethyl acetate from ethanol using transition metals or their oxides deposited on an oxide substrate as the catalysts was also reported.[30,31] Examples of the use of alkaline-earth metal oxides (MgO, CaO, SrO) as Tishchenko reaction catalysts are available in literature.[32]

Crotonaldehyde formed upon condensation of two ethanal molecules disproportionates into 2-buten-1-ol and crotonic acid by the Tishchenko reaction (Scheme 1). Ethanol is more reactive than 2-buten-1-ol, therefore ethanol first undergoes the Tishchenko cross-reaction with crotonic acid to give ethyl crotonate. Hydrogenation of this unsaturated ester results in ethyl butanoate.

In the synthesis of ethyl butanoate from ethanol, ethanol dehydrogenation first occurs, and at the last stage after a series of successive reactions, hydrogenation of the C=C bond in ethyl crotonate occurs. This allows us to believe that the conversion of ethanol into ethyl butanoate proceeds *via* the borrowing hydrogen mechanism,[33,34] *i.e.* it involves hydrogen adsorption on the catalyst.

Note that under the same conditions, the formation of butanol through hydrogenation of 2-buten-1-ol at the C=C bond does not occur (in detectable amounts). There is the contradictory information in the literature about the role of the basic catalyst centers in butanol formation. On the one hand, it is noted that the presence of acid centers in a catalyst results in an increase in the selectivity with respect to *n*-butanol, while the presence of basic centers favors the formation of ethyl acetate.[35] On the other hand, a study of ethanol-to-butanol conversion on M–Mg–Al–O mixed oxides (M = Cu, Pd, Ag, Mn, Fe, Sm, Yb) showed that Pd- and Sm-based catalysts with more pronounced basic properties manifested higher selectivity (73 and 66%, respectively), whereas increasing the Cu content decreased the density of basic centers and the selectivity to *n*-butanol also decreased.[36] This indicates that the ratio between the acid and basic catalyst centers affects the selectivity. At the same time, it was noted[36] that increasing the strength of acid centers favored the formation of 1,1-diethoxyethane, which was found in small amounts in our experiment.



Scheme 1 Conversion of ethanol on $CaSnO_3$ catalyst (400 °C, 120 atm).

A study on the effect of temperature on the formation of *n*-butanol[37] showed that raising the temperature from 300 to 450 °C increased ethanol conversion and decreased the selectivity with respect to butanol from 76 to 6%. This indicates that low temperatures are preferable for the formation of *n*-butanol.

The conversion of 2-propanol on calcium stannate under supercritical conditions results in predominant dehydrogenation to acetone followed by aldol-crotonic condensation of acetone to yield dimerization and trimerization products,[21] while the hydrogenation of unsaturated products occurs predominantly at the C=C bond rather than the C=O bond. Ethanol conversion over calcium stannate catalyst predominantly involves dehydrogenation reactions, the Tishchenko reaction, and hydrogenation of unsaturated esters.

Ethanol conversion varied from 16 to 13% during the experiment (270 min). It is known that the catalyst structure can change in the course of a chemical reaction.[18–20,38–40] In particular, the crystallinity of an amorphous sample increases. It has been shown[21] that the conversion of 2-propanol on calcium and magnesium stannates was accompanied by degradation of the catalyst structure under the action of hydrogen that was released. In view of this, it was of interest to study the changes in the catalyst structure in the course of ethanol conversion.

Previously, we have shown[20] that aldol-crotonic condensation of acetone at 400 °C and 120 atm was accompanied by crystallization of amorphous $CaSnO_3$ catalyst with formation of a $CaSnO_3$ modification having a perovskite structural type, with small admixtures of tin oxide SnO_2. At the same time, a more perfect crystalline phase of calcium stannate is formed under the reaction conditions compared to a crystalline sample obtained by calcination of $CaSn(OH)_6$ at 750 °C (hereinafter designated as $CaSnO_3$-750). Figure 2 shows the powder diffractograms of the $CaSnO_3$ catalyst: the initial amorphous compound and crystalline $CaSnO_3$-750 in comparison with $CaSnO_3$ samples after treatment in ethanol and acetone at 400 °C and 120 atm.

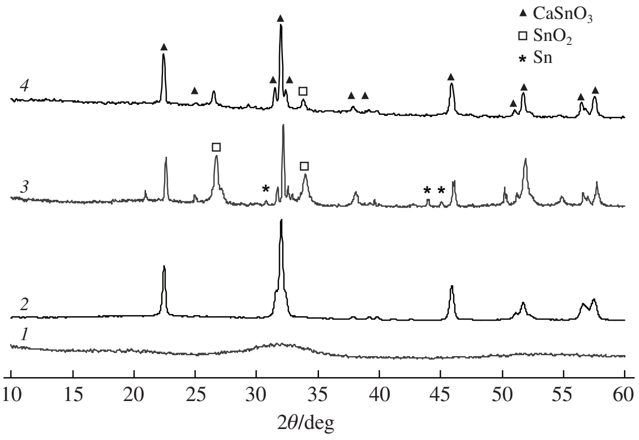


Figure 2 Diffractograms of (*1*) $CaSnO_3$ and (*2*) $CaSnO_3$-750 catalysts before the reaction and of the $CaSnO_3$ catalyst after treatment at 400 °C and 120 atm in (*3*) ethanol and (*4*) acetone.

Comparison of the diffractograms of $CaSnO_3$ samples after the reactions with acetone and ethanol with those of $CaSnO_3$-750 shows that the former have a smaller width of reflexes and higher resolution of lines. We believe that the formation of the crystalline phase of calcium stannate occurs under the action of water that is released in the conversion of acetone or ethanol and exists in supercritical state under the reaction conditions. The mechanism of water impact on the solid-phase mobility and oxides crystallization has been reported previously.[41–43] The phase composition of $CaSnO_3$ catalyst samples after the reaction with acetone and ethanol coincides in general. However, there are differences. The intensity of tin oxide (SnO_2) reflexes after the reaction with ethanol is much higher than that after the reaction with acetone. Moreover, the reflexes corresponding to metallic tin appear on the diffractogram of the sample after the reaction with ethanol (like in the case of 2-propanol conversion[21]). The first stage of alcohol conversion, *i.e.* dehydrogenation of 2-propanol[21] and ethanol, promotes the adsorption of borrowed hydrogen on the catalyst; this hydrogen is then involved in the reduction of tin(+4) to the metal. The dehydrogenation stage is missing in the conversion of acetone,[20] so the catalyst retains a stable crystalline structure.

In summary, the conversion of ethanol under supercritical conditions at 400 °C and 120 atm over calcium stannate catalyst starts with the dehydrogenation to give ethanal. Further, direct and cross Tishchenko reactions lead to ethyl acetate and ethyl butanoate. The main conversion product is ethyl acetate, which is of interest as a solvent and co-solvent.[44,45] The formation of ethyl butanoate occurs *via* hydrogenation of ethyl crotonate, which is possible due to the ‘borrowing hydrogen’ mechanism.[33,34] The reaction involves modifications of the catalyst structure: (1) formation of a crystalline phase from an amorphous sample; (2) partial destruction of the catalyst due to reduction of tin(+4) to metallic state due to adsorption of hydrogen on the catalyst at the first stage of ethanol conversion.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.02.019.

References

1 R. Muktham, S. K. Bhargava, S. Bankupalli and A. S. Ball, *J. Sustainable Bioenergy Syst.*, 2016, **6**, 72.
2 N. Tabassum and S. S. Ali, *Catal. Surv. Asia*, 2022, **26**, 261.
3 J. Rass-Hansen, H. Falsig, B. Jørgensen and C. H. Christensen, *J. Chem. Technol. Biotechnol.*, 2007, **82**, 329.
4 R. Vinayagamoorthi, B. Viswanathan and K. R. Krishnamurthy, in *Catalysis for Clean Energy and Environmental Sustainability*, eds. K. K. Pant, S. K. Gupta and E. Ahmad, Springer, Cham, 2021, pp. 505–590.
5 N. M. Eagan, M. D. Kumbhalkar, J. S. Buchanan, J. A. Dumesic and G. W. Huber, *Nat. Rev. Chem.*, 2019, **3**, 223.
6 J. D. Kozlowski and R. J. Davis, *ACS Catal.*, 2013, **3**, 1588.
7 H. Aitchison, R. L. Wingad and D. F. Wass, *ACS Catal.*, 2016, **6**, 7125.
8 T. Seki, T. Nakajo and M. Onaka, *Chem. Lett.*, 2006, **35**, 824.
9 X. Wu, G. Fang, Y. Tong, D. Jiang, Z. Liang, W. Leng, L. Liu, P. Tu, H. Wang, J. Ni and X. Li, *ChemSusChem*, 2018, **11**, 71.
10 D. Wang, Z. Liu and Q. Liu, *RSC Adv.*, 2019, **9**, 18941.
11 V. Rathinasamy, A. Arjunan, K. K. Ramaswamy, V. Balasubramanian and S. Kannan, *React. Kinet., Mech. Catal.*, 2023, **136**, 713.
12 T. Moteki and D. W. Flaherty, *ACS Catal.*, 2016, **6**, 4170.
13 E. M. Martsinkevich, L. G. Bruk, L. V. Dashko, A. A. Afaunov, V. R. Flid and I. V. Sedov, *Pet. Chem.*, 2018, **58**, 1032 (*Neftekhimiya*, 2018, **58**, 686).
14 E. M. Martsinkevich, A. A. Afaunov, V. R. Flid and L. G. Bruk, *Russ. Chem. Bull.*, 2021, **70**, 2031.
15 F. C. Meunier, J. Scalbert and F. Thibault-Starzyk, *Appl. Catal., A*, 2015, **504**, 220.
16 A. E. Koklin, G. M. Hasyanova, L. M. Glukhov and V. I. Bogdan, *Russ. Chem. Bull.*, 2017, **66**, 488.
17 G. A. Veshchitsky, A. V. Smirnov, N. V. Mashchenko, A. E. Koklin and V. I. Bogdan, *Russ. J. Phys. Chem. B*, 2021, **15**, 1299 [*Sverkhkrit. Flyuidy: Theor. Prakt.*, 2021, **16** (2), 57].
18 T. V. Bogdan, A. E. Koklin, N. V. Mashchenko and V. I. Bogdan, *Russ. J. Phys. Chem. A*, 2022, **96**, 2344 (*Zh. Fiz. Khim.*, 2022, **96**, 1569).
19 T. V. Bogdan, P. A. Krasnikov, A. V. Smirnov, A. E. Koklin, N. V. Mashchenko and V. I. Bogdan, *Dokl. Phys. Chem.*, 2022, **507**, 147 (*Dokl. Ross. Akad. Nauk, Khim. Nauki Mater.*, 2022, **507**, 68).
20 T. V. Bogdan, A. E. Koklin, I. V. Mishin, N. V. Mashchenko, A. V. Smirnov, A. R. Savarets and V. I. Bogdan, *Russ. Chem. Bull.*, 2022, **71**, 1930.
21 T. V. Bogdan, A. R. Savarets, N. V. Mashchenko, A. E. Koklin and V. I. Bogdan, *Russ. Chem. Bull.*, 2024, in press.
22 A. R. Savarets, T. V. Bogdan, A. E. Koklin, N. V. Mashchenko and V. I. Bogdan, *Russ. J. Phys. Chem. B*, 2023, **17**, 77 [*Sverkhkrit. Flyuidy: Theor. Prakt.*, 2022, **17** (4), 71].
23 C. Yang and Z. Y. Meng, *J. Catal.*, 1993, **142**, 37.
24 A. S. Ndou, N. Plint and N. J. Coville, *Appl. Catal., A*, 2003, **251**, 337.
25 J. I. Di Cosimo, C. R. Apesteguia, M. J. L. Ginés and E. Iglesia, *J. Catal.*, 2000, **190**, 261.
26 T. Tsuchida, J. Kubo, T. Yoshioka, S. Sakuma, T. Takeguchi and W. Ueda, *J. Catal.*, 2008, **259**, 183.
27 E. S. Alekseev, A. Yu. Alentiev, A. S. Belova, V. I. Bogdan, T. V. Bogdan, A. V. Bystrova, E. R. Gafarova, E. N. Golubeva, E. A. Grebenik, O. I. Gromov, V. A. Davankov, S. G. Zlotin, M. G. Kiselev, A. E. Koklin, Yu. N. Kononevich, A. E. Lazhko, V. V. Lunin, S. E. Lyubimov, O. N. Martyanov, I. I. Mishanin, A. M. Muzafarov, N. S. Nesterov, A. Yu. Nikolaev, R. D. Oparin, O. O. Parenago, O. P. Parenago, Ya. A. Pokusaeva, I. A. Ronova, A. B. Solovieva, M. N. Temnikov, P. S. Timashev, O. V. Turova, E. V. Filatova, A. A. Philippov, A. M. Chibiryaev and A. S. Shalygin, *Russ. Chem. Rev.*, 2020, **89**, 1337.
28 R. C. Reid, J. M. Prausnitz and T. K. Sherwood, *The Properties of Gases and Liquids*, 3rd edn., McGraw–Hill, New York, 1977.
29 A. B. Gaspar, A. M. L. Esteves, F. M. T. Mendes, F. G. Barbosa and L. G. Appel, *Appl. Catal., A*, 2009, **363**, 109.
30 K. Inui, T. Kurabayashi, S. Sato and N. Ichikawa, *J. Mol. Catal. A: Chem.*, 2004, **216**, 147.
31 A. B. Sánchez, N. Homs, S. Miachon, J.-A. Dalmon, J. L. G. Fierro and P. R. de la Piscina, *Green Chem.*, 2011, **13**, 2569.
32 T. Seki, H. Tachikawa, T. Yamada and H. Hattori, *J. Catal.*, 2003, **217**, 117.
33 B. G. Reed-Berendt, D. E. Latham, M. B. Dambatta and L. C. Morrill, *ACS Cent. Sci.*, 2021, **7**, 570.
34 A. Corma, J. Navas and M. J. Sabater, *Chem. Rev.*, 2018, **118**, 1410.
35 T. Riittonen, K. Eränen, P. Mäki-Arvela, A. Shchukarev, A.-R. Rautio, K. Kordas, N. Kumar, T. Salmi and J.-P. Mikkola, *Renewable Energy*, 2015, **74**, 369.
36 I.-C. Marcu, N. Tanchoux, F. Fajula and D. Tichit, *Catal. Lett.*, 2013, **143**, 23.
37 T. Tsuchida, S. Sakuma, T. Takeguchi and W. Ueda, *Ind. Eng. Chem. Res.*, 2006, **45**, 8634.
38 I. I. Mishanin, T. V. Bogdan, A. V. Smirnov, P. A. Chernavskii, N. N. Kuznetsova and V. I. Bogdan, *Mendeleev Commun.*, 2023, **33**, 422.
39 T. V. Bogdan, A. N. Kalenchuk, L. M. Kustov and V. I. Bogdan, *Phys. Chem. Chem. Phys.*, 2023, **25**, 690.
40 I. I. Mishanin, T. V. Bogdan, A. E. Koklin and V. I. Bogdan, *Chem. Eng. J.*, 2022, **446**, 137184.
41 M. N. Danchevskaya, Yu. D. Ivakin, S. N. Torbin and G. P. Muravieva, *J. Supercrit. Fluids*, 2007, **42**, 419.
42 Yu. D. Ivakin, M. N. Danchevskaya, A. A. Kholodkova, G. P. Muravieva and V. V. Rybalchenko, *J. Supercrit. Fluids*, 2020, **159**, 104771.
43 Yu. D. Ivakin, A. V. Smirnov, M. N. Kormilitsin, A. A. Kholodkova, A. A. Vasin, M. V. Kornyushin, V. P. Tarasovskii and V. V. Rybal’chenko, *Russ. J. Phys. Chem. B*, 2021, **15**, 1228 [*Sverkhkrit. Flyuidy: Theor. Prakt.*, 2021, **16** (1), 17].
44 C. Cheng, Y. Cong, C. Du, J. Wang, G. Yao and H. Zhao, *J. Chem. Thermodyn.*, 2016, **101**, 372.
45 A. Petek, M. Krajnc and A. Petek, *J. Mol. Liq.*, 2018, **272**, 313.

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