A two-step strategy for the selective conversion of ethanol to propene and hydrogen

Yuri Pyatnitsky1 · Lidiia Dolgikh1 · Liubov Senchylo1 · Larissa Stara1 · Peter Strizhak1

Received: 10 April 2021 / Accepted: 24 June 2021 / Published online: 2 July 2021
© Institute of Chemistry, Slovak Academy of Sciences 2021

Abstract
Simultaneous production of propene and hydrogen from ethanol is a promising way of a renewable feedstock conversion into value-added products. Conventional reaction schemes of the direct one-step catalytic conversion of ethanol into propene include the reaction of the isopropanol dehydration to propene. However, the dehydration ability of a catalyst inevitably gives rise to the ethanol dehydration to ethene that diminishes the propene yield. To avoid ethanol dehydration to ethene, the two-step process is composed of the ethanol conversion to acetone in the first step and the acetone conversion to propene in the second step. The thermodynamic analysis of the known reaction pathways for the ethanol conversion to propene shows that a 74.6% yield of propene can be achieved even at a low temperature of 200 °C. According to the literature data, possible catalysts can be Cu/La2Zr2O7 or Fe3O4 for the first step, and the mixed Ag–In/SiO2 and K3PW12O40 catalyst for the second step. We speculate that the propene yield may reach 72% using these catalysts in the two-step process.

Keywords Acetone · Catalyst · Ethanol · Hydrogen · Propene

Introduction
Propene is a substantial feedstock for the production of polypropene plastics, acrylonitrile, propene oxide, and many other valuable products (Li et al. 2016; Zacharopoulou and Lemonidou 2018; Huang et al. 2020). As a result, the propene market demand keeps growing (Hayashi et al. 2014). That forces scientists to search for alternative methods to produce propene. The ethanol to propene (ETP) process is one of these methods that uses bioethanol as a renewable feedstock. The ETP process is economically favorable and environmentally benign (Posada et al. 2013). It is worth noting that hydrogen may be produced in ETP as another significant product for modern economics.

Various oxide solids have been found as the ETP catalysts, particularly Sc2O3–In2O3, Y2O3–CeO2, Y2O3–ZrO2, In2O3–BEA, AgCeO2–ZrO2/SiO2 (Hayashi et al. 2013; Iwamoto 2015; Iwamoto et al. 2013; Xia et al. 2017; Wang et al. 2018; Pang et al. 2019; Xue et al. 2017; Matheus and Aguiar 2020; Matheus et al. 2018). The reaction pathway for these catalysts consists of dehydrogenation of ethanol to acetaldehyde, aldol condensation of acetaldehyde into acetone, conversion of acetone to isopropanol, and dehydration of isopropanol to propene (Iwamoto 2015):

\[
C_2H_5OH \rightleftharpoons CH_3CHO + H_2 \quad (R1)
\]

\[
2 CH_3CHO + H_2O \rightleftharpoons CH_3COCH_3 + CO_2 + 2 H_2 \quad (R2)
\]

\[
CH_3COCH_3 + H_2 \rightleftharpoons \text{iso} - C_3H_7OH \quad (R3)
\]

\[
\text{iso} - C_3H_7OH \rightleftharpoons C_3H_6 + H_2O \quad (R4)
\]

According to (R1)–(R4), the ETP stoichiometry is given by the following reaction:

\[
2 C_2H_5OH \rightleftharpoons C_3H_6 + CO_2 + 3 H_2 \quad (R5)
\]

According to reaction (R5), hydrogen, which is considered the most viable energy carrier for the future (Liu et al. 2019), is produced as a valuable by-product of the process. Various reaction schemes of ETP always include isopropanol dehydration (R4) (Hayashi et al. 2013; Iwamoto 2015; Iwamoto et al. 2013; Xia et al. 2017; Wang et al. 2018; Pang et al. 2019). For this reaction, the dehydration ability of a catalyst must be high enough to overcome the
thermodynamic limitations of reaction (R3) at elevated temperatures because the equilibrium of reaction (R3) is shifted toward acetone and hydrogen at temperatures above 200 °C (Pyatnytsky et al. 2019). However, a high dehydration ability of a catalyst inevitably results in the undesirable dehydration of ethanol to ethene. Numerous studies show a significant decrease in the propene selectivity as a result of ethanol dehydration (Hayashi et al. 2013; Iwamoto 2015; Iwamoto et al. 2013; Xia et al. 2017; Wang et al. 2018; Pang et al. 2019; Xue et al. 2017):

$$\text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2\text{O} \quad (R6)$$

That may result in a higher ethene yield comparing to the yield of propene (Hayashi et al. 2013; Iwamoto 2015; Iwamoto et al. 2013). For the ethanol steam reforming over the Y$_2$O$_3$–CeO$_2$ catalyst (20 atm.% Y), the ethene yield was 36.8%, and the propene yield was just 31.2% at a temperature of 430 °C (Hayashi et al. 2013).

Another reaction of the isopropanol formation has been revealed over the Y$_2$O$_3$–CeO$_2$ catalyst (Xia et al. 2017). It was found that not hydrogen but ethanol reduces acetone according to the Meerwein–Ponndorf–Verley (MPV) reaction:

$$\text{CH}_3\text{COCH}_3 + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}_3\text{CHO} + \text{iso-C}_3\text{H}_7\text{OH} \quad (R7)$$

Earlier, we introduced the two-step ETP process where the ethanol conversion to acetone is the first step and the acetone conversion to propene is the second step (Pyatnytsky et al. 2019). The basic idea of the two-step process is to avoid undesirable dehydration of ethanol to ethene. In the present study, we perform a thermodynamic analysis of various reaction pathways determining the most favorable reaction conditions that result in a high yield of propene and hydrogen. Moreover, based on the favorable reaction routes and the data presented in the literature, we analyze possible catalysts and the process parameters devoting much attention to the practical features.

**Thermodynamics**

Equilibrium constants, $K_p$, of separate reactions of the ETP process as a function of temperature ($T$, $K$) were evaluated according to the following equation:

$$\ln K_p = AT^{-1} + B \ln T + CT + DT^2 + E \quad (1)$$

Numerical values of coefficients $A$, $B$, $C$, $D$, and $E$ (Appendix, Table 1) for separate ETP reactions were determined from the thermodynamic parameters (Stull et al. 1969) for temperatures of 500, 700, and 900 K. Computation of the equilibrium reaction mixtures for given conditions was obtained employing the procedure described in detail in the textbook (Pyatnytsky and Strizhak 2018).

Figure 1 shows the equilibrium conversion of ethanol into propene and ethene according to the reactions (R5) and (R6).

Figure 1 illustrates that the conversion of ethanol to ethene reaches almost 100% at temperatures above 200 °C. As a result, this undesirable reaction always takes place at relatively low temperatures. Therefore, increasing selectivity for propene requires introducing an additional approach for finding ways to exclude the reaction of the ethanol conversion to ethene.

Reactions (R1) and (R2) present the first step of the overall ETP process. Figure 2 shows the temperature dependencies of the equilibrium concentrations of the reaction components for the ethanol conversion to acetone according to the reactions (R1) and (R2). The ratio of the initial concentration of ethanol, $m_{\text{Et}_2\text{O}}$, to the initial concentration of water, $m_{\text{H}_2\text{O}}$, is taken corresponding to the stoichiometry of the chemical equation for the first step:

$$2\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COCH}_3 + \text{CO}_2 + 4 \text{H}_2 \quad (R8)$$

The equilibrium concentration of acetaldehyde is negligible at any temperature that follows from the data presented in Fig. 3. At temperatures above 200 °C, the equilibrium concentrations of other species correspond to the following composition: $m_{\text{acetone}} = m_{\text{CO}_2} = 1/6$, $m_{\text{H}_2} = 2/3$. These values were used for the thermodynamic calculation of the second step presented by the reactions (R3) and (R4).

Ethanol conversion to acetone may follow various reaction pathways.

Fig. 1 Temperature dependence of equilibrium conversion of ethanol for reactions (R5) and (R6) at $m_{\text{Et}_2\text{O}} = 1$ and total pressure = 101.3 kPa

Springer
Reaction pathway 1

Elliott and Pennella (1989) proposed the following mechanism for the acetaldehyde conversion to acetone with aldol type adsorbed species:

\[
\begin{align*}
2 \text{CH}_3\text{CHO} + \text{H}_2O &\rightleftharpoons \text{CH}_3\text{COCH}_3 + \text{CO}_2 + 2 \text{H}_2 \\ 
\text{CH}_3\text{CHO} + \text{H}_2O &\rightleftharpoons \text{CH}_3\text{COOH} + \text{H}_2 \\ 
2 \text{CH}_3\text{COOH} &\rightleftharpoons \text{CH}_3\text{COCH}_3 + \text{CO}_2 + \text{H}_2O
\end{align*}
\]

The summation of these reactions gives the gas phase reaction (R2). Figure 2 presents the results of thermodynamic analysis according to reaction pathway 1 that shows the monotonic increase in the concentration of hydrogen and acetone with increasing temperature.

Reaction pathway 1a

C\(_2\)H\(_5\)OH ⇌ CH\(_3\)CHO + H\(_2\) (R1)

\[
\begin{align*}
2 \text{CH}_3\text{CHO} + \text{H}_2O &\rightleftharpoons \text{CH}_3\text{COCH}_3 + \text{CO}_2 + 2 \text{H}_2 \\
\text{CH}_3\text{CHO} + \text{H}_2O &\rightleftharpoons \text{CH}_3\text{COOH} + \text{H}_2
\end{align*}
\]

This reaction pathway describing the acetaldehyde ketonization has been proposed by Iwamoto (2015) for the Sc\(_2\)O\(_3\)–In\(_2\)O\(_3\) catalyst and Bussi et al. (1998) for the Cu/La\(_2\)Zr\(_2\)O\(_7\) catalyst.

Reaction pathway 1b

This reaction pathway describing the acetaldehyde conversion to ethyl acetate according to the Tishchenko reaction followed by the ethyl acetate decomposition to form acetic acid and ethane. Reaction pathway 1b has been proposed for the Y\(_2\)O\(_3\)–CeO\(_2\) catalyst (Iwamoto 2015).

Reaction pathway 1c

According to this reaction pathway, acetone is formed by reactions (R1) and (R2) producing CO\(_2\) as a by-product. The reaction pathway contains ethanol dehydration to ethene. Figure 3 gives the equilibrium yield of acetone and ethene for different reaction pathways where Y1, Y1a, Y1b, and Y1c denote the acetone yield for reaction pathways 1, 1a, 1b, and 1c, respectively, and Y1b(C2H4) and Y1c(C2H4) denote the ethene yield for reaction pathways 1b and 1c, respectively.

The acetone yield for reaction pathways 1 and 1a is practically the same. A difference does not exceed 0.3%. Equality
in the acetone yield for these two pathways is associated with small equilibrium concentrations of acetaldehyde and acetic acid.

Values of the yields for reaction pathways 1b and 1c at a temperature above 100 °C are practically identical as follows from the data presented in Fig. 3. Similar to reaction pathways 1 and 1a, it is associated with small amounts of intermediate substances, e.g., acetaldehyde, acetic acid, and ethyl acetate.

Noteworthy, the addition of reaction (R6), which describes the ethanol dehydration to ethane, to reaction pathway 1b does not change the results of thermodynamics calculations because the reaction (R6) is not linearly independent but a linear combination of reactions (R12) and (R13). Therefore, for both reaction pathways 1b and 1c, the same reaction describes the thermodynamic equilibrium. It is the main reason that equilibrium concentrations of species are almost the same for reaction pathways 1b and 1c.

Acetone conversion to propene follows reaction pathway 2 with diisopropyl ether (DIPE) as the undesirable product.

**Reaction pathway 2**

The reaction pathway 2 of acetone conversion to propene is described by the following reactions:

\[
\text{CH}_3\text{COCH}_3 + \text{H}_2 \rightleftharpoons \text{iso} - \text{C}_3\text{H}_7\text{OH} \quad (\text{R3})
\]
\[
\text{iso} - \text{C}_3\text{H}_7\text{OH} \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2\text{O} \quad (\text{R4})
\]
\[
2 \text{iso} - \text{C}_3\text{H}_7\text{OH} \rightleftharpoons (\text{C}_3\text{H}_7)_2\text{O} + \text{H}_2\text{O} \quad (\text{R14})
\]

where (C\text{H}_7)_2\text{O} is DIPE.

According to Larmier et al. (2015), the formation of DIPE is accompanied by iso–C\text{H}_7\text{OH} dehydration (R4) over Al\text{2O}_3.

Figure 4a presents the temperature dependence of the equilibrium yield of propene, and Fig. 4b presents the temperature dependencies of the equilibrium concentrations of reaction components for the acetone conversion to propene according to reaction pathway 2. At temperatures above 200 °C, the equilibrium concentrations of the reaction component are the following: 16.56% propene, 50.11% hydrogen, 16.56% H\text{2O}, 16.67% CO\text{2}.

Thermodynamics shows that reaction pathways 1b and 1c give a lower propene yield comparing to reaction pathways 1 and 1a. Therefore, the highest propene yield may be obtained if the first step proceeds according to pathways 1 or 1a. For both these cases, combining the first and the second steps, thermodynamics gives the carbon-based yield of 74.6% for propene at temperatures above 200 °C. This situation may be realized for the Cu/La\text{2Zr}_2\text{O}_7 and Fe\text{3O}_4 catalysts. Both these catalysts have a high performance for the ethanol conversion to acetone giving a high acetone yield and a very small ethene yield (Bussi et al. 1998; Dolgykh et al. 2018a, 2018b). It is worth noting that the calculated equilibrium yield of 74.6% for propene is very close to the stoichiometric yield of 75%. Therefore, the practically stoichiometric yield of propene may be achieved by the proposed two-step ETP process that consists of the reactions (R1) and (R2) as the first step and reactions (R3) and (R4) as the second step.

Defining two steps for the ETP by the reactions (R1)–(R4) or other reaction schemes considered above allows us to make an appropriate choice of a catalyst based on the numerous data presented in the literature for each step.

**Catalysts for the first step**

A variety of solids has been found to catalyze the ethanol conversion to acetone (the first step). Murthy et al. (1988) studied Fe\text{2O}_3–ZnO, Fe\text{2O}_3–CaO, and Fe\text{2O}_3–MnO catalysts. The Fe\text{2O}_3–ZnO catalyst has shown higher stability as well
as high activity and selectivity. Nakajima et al. (1987, 1989, 1994) obtained the carbon-based yield of acetone close to the stoichiometric value over Fe₂O₃–ZnO and ZnO–CaO. According to Nishiguchi et al. (2005), acetone was the main product for the steam reforming of ethanol over Cu/CeO₂ at 380 °C, and ethene was formed in relatively small amounts. Recently, we found that Fe₃O₄ with the spinel structure gives the carbon-based selectivity on acetone of 71.3% at 400 °C (Dolgykh et al. 2018a, b).

Bussi et al. (1998) have shown that the Cu/La₂Zr₂O₇ catalyst gives 72% for the carbon-based selectivity on acetone for 100% of the ethanol conversion at 400 °C. The catalyst shows a very small selectivity on ethene.

It is worth noting that the high conversion of ethanol of the order of 100% for the first step minimizes the undesirable reactions of ethanol dehydration (R6) and MPV reaction (R7) over catalysts for the second step.

Catalysts for the second step

The second step requires using a catalyst that can accelerate the acetone hydrogenation to isopropanol and the isopropanol dehydration to propene. The hydrogenating catalyst or its component may contain copper or silver. Both these metals are known as efficient catalysts for the mild hydrogenation of carbonyl compounds, e.g., hydrogenation of acetone to isopropanol (Yurieva 1999; Cunningham et al. 1986a, b). For example, the acetone conversion achieves 35% over partially reduced copper chromite CuCr₂O₄ at a low temperature of 75 °C (Yurieva 1999).

The best catalyst for the second step seems to be the mixed catalyst that consists of 5% Ag–0.5% In/SiO₂ (hydrogenation component) and K₃PW₁₂O₄₀ (dehydrating component) (Ohkubo et al. 2013). After 100 h, the acetone conversion at 300 °C with an 11:1 hydrogen:acetone molar ratio was 99.9%, and selectivity for propene was 98.2%. Selectivity for by-products was as follows: 0.5% propane, 1.2% propene dimer, 0.1% other. Thermodynamic simulations give 99.86% for acetone conversion and 99.99% for equilibrium selectivity of propene for 11:1 hydrogen:acetone molar ratio. Figure 5a and b show the influence of the hydrogen:acetone molar ratio on the acetone conversion to propene according to reaction pathway 2.

Figure 5 indicates that increasing hydrogen:acetone molar ratio results in increasing both acetone conversion and selectivity for propene. The conversion of acetone is the smallest in the case of a stoichiometric ratio. For hydrogen:acetone molar ratio of 11:1, it increases to 99.81% at 500 °C (Fig. 5a). The selectivity for propene significantly depends on the ratio of hydrogen:acetone only at relatively low temperatures. At temperatures above 200 °C, the selectivity for propene is at least 99.5% at any hydrogen:acetone molar ratio (Fig. 5b).

A choice of a catalyst for the second step has a limitation associated with the thermodynamic restriction for the reaction (R3). Figure 6 demonstrates the temperature dependence of equilibrium conversion of acetone according to the following reaction pathway:

**Reaction pathway 2a**

\[
\text{CH}_3\text{COCH}_3 + \text{H}_2 \rightleftharpoons \text{iso-C}_3\text{H}_7\text{OH} \quad (R3)
\]

2 \text{iso-C}_3\text{H}_7\text{OH} \rightleftharpoons \text{(C}_3\text{H}_7\text{)}_2\text{O} + \text{H}_2\text{O} \quad (R14)

Figure 6 shows that the equilibrium conversion of acetone decreases gradually down to a negligible value at about 350 °C. Therefore, a sufficiently high yield of propene is possible only at temperatures below 100 °C if a catalyst of hydrogenation reaction (R3) and a catalyst of dehydration reaction (R4) are arranged in a reactor consequently. To realize the overall process at high temperatures, it is necessary to use the mixed or bifunctional catalyst which can efficiently accelerate
both reactions, acetone hydrogenation to isopropanol and isopropanol dehydration to propene. Various oxide catalysts containing surface acid centers are acceptable for alcohol dehydration, e.g., Al$_2$O$_3$, an efficient catalyst for the isopropanol dehydration to propene (Larmier et al. 2015).

Therefore, a realization of the proposed two-step ETP process may be performed using catalysts reported in the literature. A catalyst for the first step may be chosen between Cu/La$_2$Zr$_2$O$_7$ and Fe$_3$O$_4$. Both catalysts give the acetone carbon-based yield above 70% for 100% of ethanol conversion at 400 °C. A catalyst for the second step may be the mixture of 5% Ag–0.5% In/SiO$_2$ and K$_3$PW$_{12}$O$_{40}$. As a result, combining catalysts for the first and second steps together allows one to reach the propene yield above 70%. Practical implementation of the proposed strategy can be performed by placing two appropriate catalysts into the same reactor as different layers or placing each catalyst separately in consequent reactors. The data presented in Figs. 3 and 4a show that both, the acetone yield and propene yield, have maximum values at temperatures above 200 °C which is governed by the maximum for the acetone yield. Therefore, at temperatures above 200 °C, a single reactor may be used to conduct the overall ETP process. However, contrary to the acetone yield, the propene yield reaches a maximum at temperatures just above 100 °C. Therefore, a two-reactor design may be used where ethanol transforms to acetone at temperatures in the range of 100–200 °C in the first reactor and acetone transforms to propene at temperatures above 200 °C in the second reactor. A two-reactor setup seems to be preferable because it allows exploring a different temperature for each reactor.

**Conclusions**

Analysis of the literature reveals that one of the essential shortcomings of ETP concerns a high selectivity on ethene that diminishes the yield of propene and hydrogen as another valuable product. Here, we performed the thermodynamic analysis of various ETP pathways suggested in the literature. We show that the recently suggested two-step process (Pyatnytsky et al. 2019) has advantages compared to the one-step process allowing to eliminate the ethene formation. The two-step process is composed of the ethanol conversion to acetone in the first step and the acetone conversion to propene in the second step. Based on the analysis of various catalysts reported in the literature for each step, we suggest that the Cu/La$_2$Zr$_2$O$_7$ or Fe$_3$O$_4$ catalysts seem to be good candidates for the first step, and the mixed Ag–In/SiO$_2$ and K$_3$PW$_{12}$O$_{40}$ catalyst is a good one for the second step. Using these catalysts for the two-step ETP process give the propene yield close to the thermodynamic yield. That illustrates the industrial attractiveness of the proposed two-step EPT process.

**Table 1** Numerical values of coefficients $A$, $B$, $C$, $D$, and $E$ in Eq. (1)

| Reaction | $A$     | $B$     | $C$     | $D$     | $E$     |
|---------|---------|---------|---------|---------|---------|
| R1      | -8836.5 | 11.8912 | -9.4631 | 1.3063  | -37.4022|
| R2      | 5654.3  | 4.8383  | -2.3375 | 2.0338  | -24.8010|
| R3      | 6183.4  | -2.3383 | 2.4079  | -3.7951 | 0.2324  |
| R4      | -5868.0 | 2.0915  | -3.8496 | 5.7661  | 5.5744  |
| R5      | -8836.5 | 11.8912 | -9.4631 | 1.3063  | -37.4022|
| R6      | -4765.6 | 3.3294  | -3.8496 | 6.1854  | -5.0456 |
| R7      | -1219.7 | 1.3115  | -6.6677 | 7.3386  | -8.9716 |
| R8      | -9152.0 | 12.1381 | -8.4868 | 1.1092  | -43.2090|
| R9      | 3484.7  | 0.4123  | 1.7688  | -4.8016 | -8.5562 |
| R10     | -1315.1 | 4.0138  | -5.8751 | 1.1637  | -7.6886 |
| R11     | 13,129.2| -1.4071 | 3.7993  | -8.7015 | -12.5518|
| R12     | -2241.3 | -1.8305 | 1.0442  | -6.2903 | 13.1996 |
| R13     | -7006.9 | 1.4990  | -2.8055 | 5.5564  | 8.1540  |
| R14     | 1960.8  | 1.2832  | -1.8997 | 3.7742  | -12.1012|

**Appendix 1**
Acknowledgements This work was supported by the Target Program of the National Academy of Sciences of the Ukraine “Development of scientific grounds for hydrogen production, storage, and use in autonomous energy supply systems”.

Declarations

Conflict of interest The authors have no competing interests to declare.

References

Bussi J, Parodi S, Irigaray B, Kieffer R (1998) Catalytic transformation of ethanol into acetone using copper–pyrochlore catalysts. Appl Catal A 172:117–129

Cunningham J, Al-Sayyed GH, Cronin J, Fierro JLG, Healy C, Cunningham J, Al-Sayyed GH, Cronin JA, Hirschwald C, Hirschl W, Ilyas M, Tobin JP (1986a) Surface synergisms between copper and its oxides. I. Isopropanol dehydrogenation over unsupported CuO, Cu2O, and Cu metal. J Catal 102:160–171

Cunningham J, Al-Sayyed GH, Cronin JA, Healy C, Hirschwald W (1986b) Surface synergisms between copper and its oxides in catalytic isopropanol/acetone interconversions at 430–523 K. Appl Catal 25:129–138

Dolgykh LY, Stolyarchuk IL, Staraya LA, Pyatnytsky YI (2018a) Steam reforming of ethanol on ferrites. Theor Exp Chem 54:349–357

Dolgykh LY, Pyatnytsky YI, Strizhak PE (2018). In: Brienzo M (ed) Future Directions. Nova Sci Publ, New York

Elliott DJ, Pennella F (1989) The formation of ketones in the presence of carbon monoxide over CuO/ZnO/Al2O3. J Catal 119:359–367

Hayashi F, Iwamoto M (2013) Yttrium-modified ceria as a highly durable catalyst for the selective conversion of ethanol to propylene and ethylene. ACS Catal 3:14–17

Hayashi F, Tanaka M, Lin D, Iwamoto M (2014) Surface structure of yttrium-modified ceria catalysts and reaction pathways from ethanol to propylene. J Catal 316:112–120

Huang R, Fung V, Wu Z, Jiang D (2020) Understanding the conversion of ethanol to propene on In2O3 from first principles. Catal Today 350:19–24

Iwamoto M (2015) Selective catalytic conversion of bio-ethanol to propylene: a review of catalysts and reaction pathways. Catal Today 242:243–248

Iwamoto M, Mizuno S, Tanaka M (2013) Direct and selective production of propylene from bio-ethanol on Sc-Loaded In2O3 Catalysts. Chem Eur J 19:7212–7220

Larmier K, Chizallet C, Cadran N, Maury S, Abboud J, Lamic-Humblot A-F, Marceau E, Lauron-Pernot H (2015) Mechanistic investigation of isopropanol conversion on alumina catalysts: location of active sites for alkene/ether production. ACS Catal 5:4423–4437

Li X, Kant A, He Y, Thakkar HV, Atanga MA, Rezaei F, Ludlow DK, Ali A, Rownaghil AA (2016) Light olefins from renewable resources: Selective catalytic dehydration of bioethanol to propylene over zeolite and transition metal oxide catalysts. Catal Today 276:62–77

Liu Z, Senanayake SD, Rodriguez JA (2019) Catalysts for the steam reforming of ethanol and other alcohols. In: Iulianelli A, Dalena F, Zevisorglu TN (eds) Basile A. Ethanol Science and Engineering, Elsevier, pp 133–158

Matheus CRV, Aguiar EFS (2020) The role of MPV reaction in the synthesis of propene from ethanol through the acetone route. Catal Commun 145:106096

Matheus CRV, Chagas LH, Gonzalez G, Sousa-Aguiar EF, Appel LG (2018) The synthesis of propylene from ethanol: a mechanistic study. ACS Catal 8:7667–7678

Murthy RS, Patnaik P, Sidheswaran P, Jayamani M (1988) Conversion of ethanol to acetone over promoted iron oxide catalysts. J Catal 109:298–302

Nakajima T, Yamaguchi T, Tanabe K (1987) Efficient synthesis of acetone from ethanol over ZnO-CaO catalyst. J Chem Soc Chem Commun. https://doi.org/10.1039/C39870000394

Nakajima T, Tanabe K, Yamaguchi T, Matsuizaki I, Mishima S (1989) Conversion of ethanol to acetone over zinc oxide-calcium oxide catalyst: optimization of catalyst preparation and reaction conditions and deduction of reaction mechanism. Appl Catal 52:237–248

Nakajima T, Nameta H, Mishima S, Matsuizaki I, Tanabe K (1994) A highly active and highly selective oxide catalyst for the conversion of ethanol to acetone in the presence of water vapour. J Mater Chem 4:853–858

Nishiguchi T, Matsumoto T, Kanai H, Utani K, Matsumura Y, Shen WJ, Imamura S (2005) Catalytic steam reforming of ethanol to produce hydrogen and acetone. Appl Catal A 279:273–277

Ohkubo T, Fujisawa K, Fujita T, Ishibashi M, (Mitsui Chemicals, Inc Tokyo), (2013) Olefin production process. United States Patent US 8(552):239

Pang J, Zheng M, Zhang T (2019) Synthesis of ethanol and its catalytic conversion. Adv Catal 64:89–191

Posada JA, Patel AD, Rogers A (2013) Potential of bioethanol as a chemical building block for biorefineries: preliminary sustainability assessment of 12 bioethanol-based products. Bioresource Technol 135:490–499

Pyatnytsky YI, Strizhak PE (2018) Calculating Equilibrium and Simulating Kinetics of Heterogeneous Catalytic Reactions. https://www.free-ebooks.net/ebook/Calculating-Equilibrium-and-Simulating-Kinetics-of-Heterogeneous-Catalytic-Reactions.

Pyatnytsky YI, Dolgykh LY, Sencilho LM, Staraya LA, Strizhak PE (2019) Catalytic two-step process for the production of propylene from bioethanol. Theor Exp Chem 55:50–55

Stull RD, Westrum EF, Sinke GC (1969) The Chemical Thermodynamics of Organic Compounds. John Wiley, New York

Wang F, Xia W, Mu X, Chen K, Si H, Li Z (2018) A combined experimental and theoretical study on ethanol conversion to propylene over Y2Zr2O7 catalyst. Appl Surf Sci 439:405–412

Xia W, Wang F, Mu X, Chen K, Takahashi A, Nakamura I, Fujitani T (2017) Highly selective catalytic conversion of ethanol to propylene over yttrium-modified zirconia catalyst. Catal Commun 90:10–13

Xue F, Miao C, Yue Y, Hua W, Gao Z (2017) Direct conversion of bioethanol to propylene in high yield over the composite of In2O3 and zelite beta. Green Chem 19:5582–5590

Yurieva TM (1999) Mechanisms for activation of hydrogen and hydrogenation of acetone to isopropanol and of carbon oxides to methanol over copper-containing oxide catalysts. Catal Today 51:457–467

Zacharopoulou V, Leonidou AA (2018) Olefins from Biomass Intermediates: a Review. Catalysts 8:2–19

Publisher’s Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.