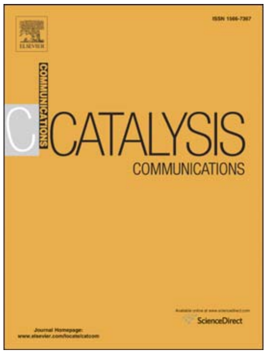

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Short Communications

One-step catalytic conversion of ethanol into 1,3-butadiene using zinc-containing talc

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Abstract

Compared with previously reported catalysts, zinc-containing talc exhibited the highest formation rate of 1,3-butadiene in one-step conversion of ethanol at 673 K. Our results showed that talc containing just 1.4 wt% of ZnO produced 1,3-butadiene at a rate of 1.9×10^{-2} mol g^{-1} h^{-1}.

Keywords:
Ethanol
1,3-Butadiene
Zinc-containing talc
High production rate

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1. Introduction

Ethanol is mainly produced by fermentation of sugars and is considered one of the most abundant and sustainable raw materials, especially in view of the CO_2 emissions and man-made global warming resulting from the production and processing of most industrial feedstock. The conversion of ethanol into industrial materials is an important application of the chemical. Among the converted products, 1,3-butadiene is widely used in the production of polymers and polymer intermediates such as styrene–butadiene rubbers. At present, 1,3-butadiene (referred to herein as butadiene) is mainly produced as the isolation product from naphtha-steam-cracker fractions of paraffinic hydrocarbons for manufacturing ethylene and its homologues.

The industrial process for the catalytic conversion of ethanol into butadiene was initially attempted in the 1950s when the US and the former USSR tried to produce rubber using non-petrochemical-based methods.[1] Since then, the effects of reaction conditions on the conversion of ethanol, butadiene yield, and the selectivity of the process have been examined using various catalysts to produce butadiene with higher space–time yield, while various reaction mechanisms have also been proposed for butadiene formation.[1]

Corson *et al.* examined the catalytic activities of various kinds of single, binary, and ternary metal oxides such as $MgO–SiO_2$, while the effects of operating parameters on the yield of butadiene were also investigated.[2,3] Bhattcharya *et al.* investigated various features of ethanol conversion to butadiene by testing binary metal oxides catalysts such as Al_2O_3–ZnO.[4]

In other studies, ternary metal oxides were also used to increase the catalytic activity and selectivity for butadiene.[1,2,5] For example, ZnO, Cr_2O_3, and Ta_2O_3 were used as dopants in the binary $MgO–SiO_2$ system. Compared with the catalytic activity of binary $MgO–SiO_2$, the addition of a small amount of ZnO led to a very high yield of butadiene and suppressed ethylene formation.[5] Impregnating the $MgO–SiO_2$ catalyst with NaOH or KOH instead of ZnO also increased the butadiene yield.[6]

A recent investigation by Jones *et al.* focused on bi- and tri-metallic systems such as zirconia–zinc supported on silica ($Zr–Zn/SiO_2$).[7] Among these catalysts, $Zr–Zn/SiO_2$ showed the highest butadiene yield from ethanol at 648 K. Ag or Cu supported on the $MgO–SiO_2$ catalyst was also reported to produce butadiene at 673 K.[8]

The catalysts mentioned above either do not have specific crystal structures or consist of mixtures of various metal oxides. On the other hand, catalysts that have specific crystal structures have also generated butadiene from ethanol.[9–11] For example, sepiolite,[9,10] which is a fibrous silica–magnesia clay material, and hydroxyapatite ($Ca_{10}(PO_4)(OH)_2$) catalyzed the conversion of ethanol into butadiene.[11]

Among the constituents of previously reported catalysts, MgO and SiO_2 appear to play important roles in the production of butadiene with high yield in one-step conversion of ethanol. Compared with earlier catalysts, we found zinc-containing talc the most active for butadiene production. Talc is one of the minerals consisting of magnesium silicate; a model of its structure is shown in Fig. 1. Talc has a 1:2 layered structure, where one octahedral sheet is sandwiched between two tetrahedral sheets. The unit cell of talc includes six octahedral sites and eight tetrahedral sites. As shown in Fig. 1, the tetrahedral cations are Si^{4+}, while the octahedral cations are Mg^{2+}. The Si^{4+} cations are coordinated to four oxygen atoms and linked to the adjacent tetrahedron by sharing three corners (the basal oxygen atoms, O_b). The corners (the tetrahedral apical oxygen atoms, O_a) of all tetrahedra point toward the same side of the sheet, and they connect the tetrahedral and octahedral sheets to form a common plane at the octahedral positions (the octahedral oxygen atoms, O_{oct}).

In this work, we examined the catalytic performance of talc in one-step conversion of ethanol to butadiene, while the effects of the talc structure and the amount of Zn contained in the talc on catalytic activities were examined.

2. Experimental

Three kinds of talc were obtained from Mizusawa Industrial Chemicals, Ltd., Japan,[12] which were sold under the trade name MIZUKALIFE P-1. They contained Zn and are referred to as P1-(I), P1-(II), and P1-(III) in this study. Talc was also synthesized according to the preparation method reported in Ref. 12; this catalyst is referred to as P1-(IV). MgO was prepared by calcination of magnesium hydroxide (Wako Pure Chemicals Co. Ltd., Japan) at 873 K for 6 h, and P1-(IV) was prepared using the prepared MgO and colloidal silica (Nissan Chemicals Co. Ltd., Japan). The powder X-ray diffraction (XRD) patterns of P1-(IV) are in good agreement with that of talc reported in Ref. 12. Furthermore, the XRD patterns of P1-(I), P1-(II), and P1-(III) are not different from those of P1-(IV), as shown in Fig. 2.

The amounts of Mg, Si, and other elements contained in these materials were determined by inductively coupled plasma atomic emission spectroscopy. The compositions of these materials are summarized in Table 1; P1-(I), P1-(II), and P1-(III) contained Zn, while P1-(IV) did not contain any Zn.

A binary oxide, referred to as $MgO–SiO_2$ in this manuscript, was prepared by kneading magnesium hydroxide (Wako Pure Chemicals Co. Ltd.) and colloidal silica (Nissan Chemicals Co. Ltd.) for 3 h at room temperature.[13] The resulting gel was dried at 393 K in an oven for 24 h. The amounts of Mg and Si in $MgO–SiO_2$ are also shown in Table 1.

The conversion reaction was carried out in a continuous-flow reactor at atmospheric pressure. Prior to the reaction, all of the catalysts were pressed, crushed, and sorted into grains using 16-32 mesh. The grains were packed into a reactor of silica-tubing (internal diameter: 8 mm). The reactor was placed in a vertical furnace, where they were heated under a nitrogen stream (flow rate of 500 cm^3 min^{-1}) at a heating rate 1 K min^{-1} from room temperature to 673 K. The catalyst was then heated at the same temperature for 8 h. In the case of $MgO–SiO_2$, the material was heated at 673 K under air (flow rate of 500 cm^3 min^{-1}) at a heating rate 1 K min^{-1} from room temperature to 673 K; the catalyst was then heated at the same temperature for 3 h.

After heating the catalysts, the conversion of ethanol was carried out in a continuous-flow reactor under atmospheric pressure at 673 K. Ethanol was continuously delivered by a syringe infusion micro pump to a preheating zone of the reactor containing quartz sand, where it would be vaporized. The contact time (W/F) was 5.49 g h mol^{-1}, where W is the weight of the catalyst (g) and F is the total flow rate (mol h^{-1}). The pressure of ethanol was 101.3 kPa.

To determine the amounts of the reaction products and that of ethanol, effluent gas was periodically withdrawn in sampling tubes and directly injected into a gas chromatograph. Thus, ethanol, acetaldehyde, and lower hydrocarbons (with three carbon atoms) were quantitatively analyzed using a Porapak Q column, while the hydrocarbons and oxygenates with more than four carbon atoms were also quantitatively analyzed by a DB-1 column. Furthermore, the amounts of CO and CO_2 were measured by a Unicarbon column. The product distributions are expressed on a carbon-number basis.

3. Results and Discussion

The conversion of ethanol was carried out to examine the catalytic performance of P1-(I) at 673 K. The distributions of all products together with the conversion of ethanol and the rate of butadiene formation, expressed as moles of butadiene per g-catalyst per hour (mol g^{-1} h^{-1}), are summarized in Table 2. The conversion of ethanol and the rate of butadiene formation were almost constant at about 43% and 1.9×10^{-2} mol g^{-1} h^{-1} after 7 h on stream. The predominant products were butadiene and acetaldehyde. The selectivities for butadiene and acetaldehyde were also almost constant at about 49 and 22%, respectively, after 7 h on stream.

As shown in Table 2, the other products were ethylene and diethyl ether, while butenes and butanols were also produced. The main oxygenates produced were acetaldehyde and diethyl ether, and the distributions of other oxygenates such as butanols and butyraldehyde were very low. The formation of croton aldehyde was observed; however, only a very small amount of this compound was detected and crotyl alcohol (2-butene-1-ol) was not observed. These results show that croton aldehyde was quickly converted to butadiene *via* crotyl alcohol. The distributions of CO_2 and CO were very small.

The catalytic activity of P1-(I) gradually decreased after it was on stream for more than 9 h. Thus, the conversion of ethanol decreased to 35.6% after 9 h and became 24.2% after 14 h, along with a decrease in the distribution of butadiene. On the contrary, the distribution of acetaldehyde increased to 30.8% after 9 h, and further increased to 34.7% after 14 h. The distributions of other reaction products such as ethylene and butanols remained almost unchanged with increasing reaction time.

To examine the effect of Zn and the crystal structure on the rate of conversion, the reaction was carried out using Zn-containing talc P1-(I), P1-(II), and P1-(III), and Zn-free talc P1-(IV) as catalysts. The results are summarized in Table 3. The effect of the amount of Zn in talc on the formation rate of butadiene was crucial.

Thus, the rate of butadiene formation was considerably increased by the presence of a small amount of Zn in talc. For example, the rate was 1.9 × 10^{-2} mol g^{-1} h^{-1} at 673 K when P1-(I), which contained 1.4 wt% ZnO, was used as a catalyst, while it was drastically decreased to 7.8 × 10^{-4} mol g^{-1} h^{-1} after 1 h on stream and the selectivity for butadiene was very low when Zn-free P1-(IV) was used as the catalyst. The catalytic activity of P1-(IV) also quickly decreased from 28.0% ethanol conversion after 1 h on stream to 17.2 % after 2 h on stream. These results show that the very small amount of Zn was essential to generating the catalytic activity of talc for butadiene formation. In the case of catalytic conversion with P1-(IV), mostly ethylene was produced, even though the concentrations of Mg and Si in P1-(IV) were almost equal to those in P1-(I). The very small amount of Zn also prolonged the catalyst life.

Furthermore, among the Zn-containing talc, the catalytic activity for butadiene formation strongly depended on the amount of Zn. The rate of butadiene formation was decreased from 1.9 × 10^{-2} to 1.3 × 10^{-2} mol g^{-1} h^{-1} when the ZnO content decreased from 1.4 to 0.3 wt% with the switch from P1-(I) to P1-(II) as the catalyst, while the composition of other constituents remained almost constant.

The rate of butadiene formation was decreased from 1.3 × 10^{-2} to 9.1 × 10^{-3} mol g^{-1} h^{-1} by decreasing the composition of MgO from 34.1 to 32.8 wt% with the change from P1-(II) to P1-(III), while the composition of ZnO remained constant at 0.3 wt%. These results show that the amounts of Mg and Zn in the talc affected the catalytic activity for butadiene formation.

Although the catalytic activity strongly depends on the presence of Zn in the talc, the XRD spectrum of Zn-free P1-(IV) was not different from those of Zn-containing P1-(I), P1-(II), and P1-(III) as shown on Fig. 2. However, P1-(IV) showed butadiene selectivity of 25.8% and a butadiene formation rate of 3.2 × 10^{-4} mol g^{-1} h^{-1}, which are much lower than the values for P1-(I), P1-(II), and P1-(III).

Therefore, the presence of Zn in talc is presumably an important criterion for generating high catalytic activity in butadiene formation.

To examine the effect of the crystal structure on the catalytic activity for ethanol conversion to butadiene, $MgO–SiO_2$ was prepared by kneading magnesium hydroxide and colloidal silica, according to the procedure reported in Ref. 13. When the effect of the MgO/SiO_2 ratio on the catalytic activity was independently examined at 673 K and 101.3 kPa of ethanol in this work, the $MgO–SiO_2$ with MgO/SiO_2 ratio of 9.5:0.5 showed the highest catalytic activity for butadiene formation. The rate of butadiene formation was 2.8×10^{-3} mol g^{-1} h^{-1} for up to 3 h on stream, and it decreased with time and reached 1.7×10^{-3} mol g^{-1} h^{-1} after 4 h on stream.

In Ref. 13, Niiyama et al. reported that $MgO–SiO_2$ (Mg/Si = 3) yielded butadiene at a rate of 1.7×10^{-3}) mol g^{-1} h^{-1} at 653 K. This catalytic activity was a little lower than that of the catalyst of $MgO–SiO_2$ with MgO/SiO_2 ratio of 9.5:0.5.

However, the Zn-containing talc showed much higher catalytic activity for butadiene formation than $MgO–SiO_2$, suggesting that the Zn-containing talc crystal structure was an important factor for generating the catalytic activity for butadiene formation.

To further compare the catalytic activity of P1-(I) with those of previously reported catalysts, their rates of butadiene formation are also summarized in Table 3, together with the reaction conditions as well as the ethanol conversion, and butadiene yield or selectivity. The $MgO–SiO_2$ catalysts co-existing with Ag,[8] Cu,[8] and Na_2O [6] showed lower rates of butadiene formation than P1-(I), P1-(II), and P1-(III). The rate of butadiene formation using P1-(I) as the catalyst was also higher than those using $Zr–Zn/SiO_2$ and $Al_2O_3–ZnO$. These results again confirm that the Zn-containing talc structure is essential to the catalytic activity required for butadiene production. However, the XRD patterns do not show features that can be used to distinguish the structures of P1-(I) and P1-(IV).

These results presumably show that chemical properties of talc, such as the electron density of O^{2-} or Mg^{2+}, are influenced by the introduction of Zn^{2+} in talc. At the current stage, the elucidation of the role of Zn^{2+} has progressed through measuring the X-ray photoelectron (XP) spectra of oxygen, Mg, and Si, and magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra of Mg.

4. Conclusions

Both talc structure and the presence of Zn in talc are crucial to producing butadiene at a high formation rate in one-step conversion of ethanol. Moreover, Zn in talc drastically prolongs the catalyst life.

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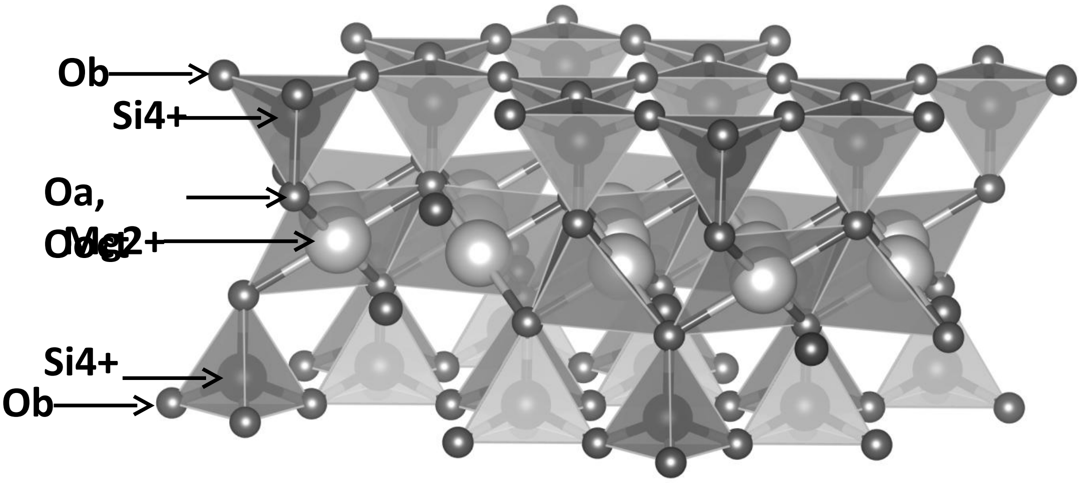

Fig. 1 Model of the structure of talc

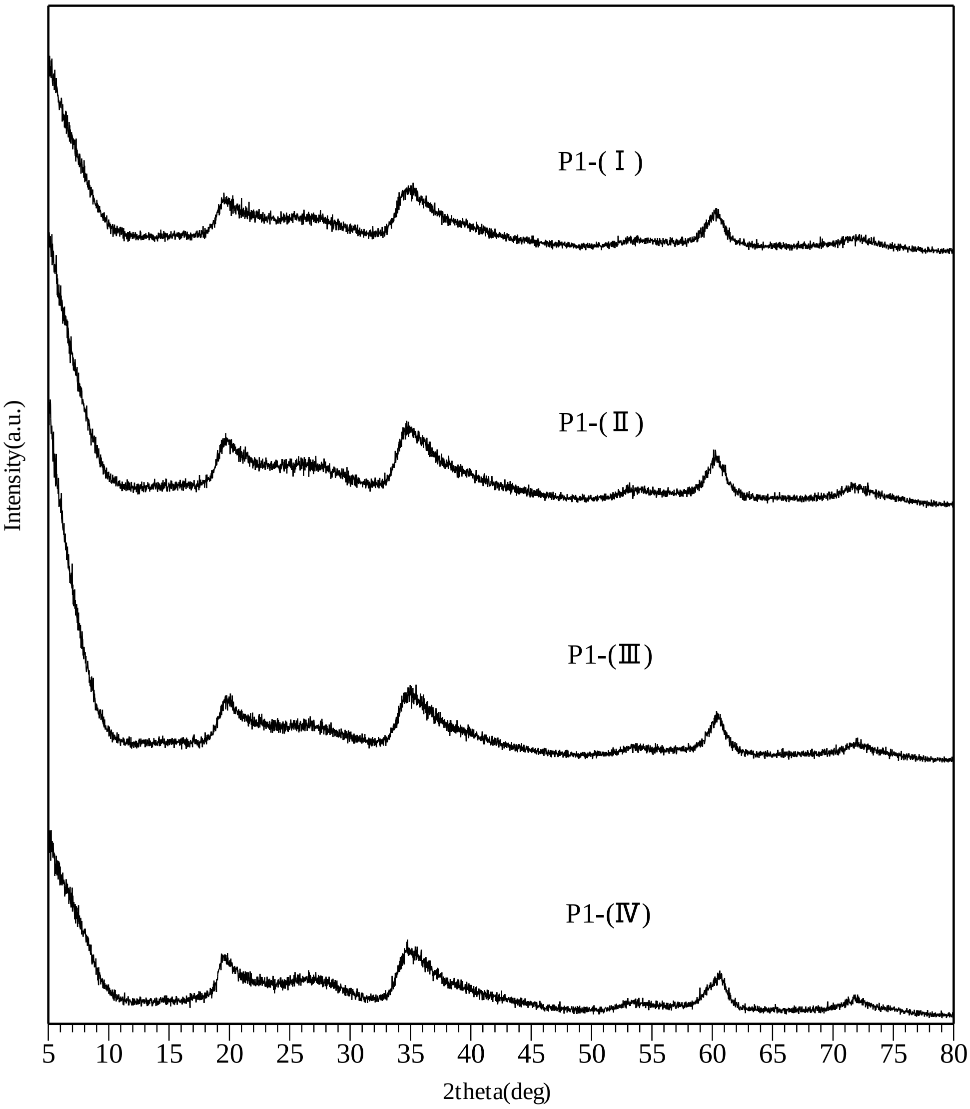

Fig.2 XRD spectra of talc-based catalysts

Table 1 Composition and surface area of catalysts used in this work

	Composition / wt%							Mg/Si molar ratio	Surface area / m^2 g^{-1}
	MgO	SiO_2	ZnO	Na_2O	CaO	Al_2O_3	B_2O_3		
P1-(I)	34.1	63.6	1.4	0.4	0.1	0.3	0.1	3.2/4.0	390
P1-(II)	34.1	65.0	0.3	0.3	0.1	0.1	0.1	3.1/4.0	407
P1-(III)	32.8	66.3	0.3	0.2	0.2	0.1	0.1	3.0/4.0	482
P1-(IV)	35.5	64.5	NO[a)]	NO[a)]	NO[a)]	NO[a)]	NO[a)]	3.3/4.0	364
$MgO–SiO_2$[b)]	92.0	7.3	NO[a)]	0.3	NO[a)]	NO[a)]	NO[a)]	9.5/0.5	285

[a)] NO means that the composition was not observed by ICP analysis.

[b)] $MgO–SiO_2$ was prepared by kneading magnesium hydroxide and colloidal silica.

Table 2 Ethanol conversion, product distribution, and rate of 1,3-butadiene formation using P1-(I) at 673 K

Time on stream / h	1	2	3	7	9	11	15
C_2H_5OH conversion / %	41.8	44.5	43.2	45.7	35.6	25.6	24.2
Product distribution / C-atm%							
1,3-Butadiene	50.1	49.1	49.4	48.3	41.8	38.2	37.3
Acetaldehyde	21.4	22.9	23.7	21.6	30.8	31.9	34.7
Crotonaldehyde	0.2	0.2	0.2	0.2	0.3	0.4	0.4
Ethylene	8.3	8.1	8.3	7.8	9.2	8.2	8.9
Diethyl ether	8.0	8.0	7.3	7.7	7.7	8.0	7.1
Butyraldehyde	0.2	0.2	0.2	0.3	0.3	0.4	0.3
Butanols	1.2	1.1	1.1	0.9	0.6	1.5	1.9
Butenes	3.4	3.3	3.3	3.5	2.9	2.9	3.0
CO	0.3	0.1	0.2	2.2	1.8	1.2	1.0
CO_2	0.2	0.1	0.1	0	0	0	0
Other hydrocarbons	5.7	5.8	4.8	5.7	3.1	4.0	2.5
Other oxygenates	1.0	0.8	1.4	1.8	1.5	3.3	2.9

Rate of 1,3-butadiene formation / mol g^{-1} h^{-1}	1.9×10^{-2}	2.0×10^{-2}	1.9×10^{-2}	2.0×10^{-2}	1.4×10^{-2}	8.9×10^{-3}	8.2×10^{-3}

Reaction conditions: Ethanol pressure = 101.3 kPa; W/F = 5.49 g h mol^{-1}

Table 3 Catalytic activities of MIZUKALIFE P1 and previously reported catalysts

Catalyst	React. temp. a)	Catal. weight b)	Ethanol feed rate	Ethanol conversion c) / %	1,3-Butadiene yield or selectivity d) / %	Rate of 1,3-butadiene formation	Reference
P1-(I)	673 K	0.30 g	5.5×10^{-2} mol h^{-1}	43.2 % (3 h)	49.1% (selectivity)	1.9×10^{-2} mol g^{-1} h^{-1}	This work
P1-(I)	673 K	0.30 g	5.5×10^{-2} mol h^{-1}	45.7% (7 h)	48.3% (selectivity)	2.0×10^{-2} mol g^{-1} h^{-1}	This work
P1-(II)	673 K	0.30 g	5.5×10^{-2} mol h^{-1}	33.1% (3 h)	44.5% (selectivity)	1.3×10^{-2} mol g^{-1} h^{-1}	This work
P1-(III)	673 K	0.30 g	5.5×10^{-2} mol h^{-1}	25.9% (3 h)	38.4% (selectivity)	9.1×10^{-3} mol g^{-1} h^{-1}	This work
P1-(IV)	673 K	0.30 g	2.8×10^{-2} mol h^{-1}	23.1% (3 h)	5.1% (selectivity)	5.5×10^{-4} mol g^{-1} h^{-1}	This work
P1-(IV)	673 K	0.30 g	2.8×10^{-2} mol h^{-1}	14.1% (7 h)	4.8% (selectivity)	3.2×10^{-4} mol g^{-1} h^{-1}	This work
MgO–SiO$_2$ h) (Mg/Si = 9.5:0.5)	673 K	0.30 g	5.5×10^{-2} mol h^{-1}	11.8% (3 h)	25.8% (selectivity)	2.8×10^{-3} mol g^{-1} h^{-1}	This work
Zr (1.5 wt%):Zn(0.5 wt%)/SiO$_2$	648 K	1.0 g	0.1 mL min^{-1} (1.0×10^{-1} mol h^{-1}) e)	48.0 (1 h)	47.9% (selectivity)	1.2×10^{-2} mol g^{-1} h^{-1} f)	7
Al$_2$O$_3$ (60 wt%):ZnO (40 wt%)	698 K	not shown	1.875 mL g-cat^{-1} h^{-1} (3.2×10^{-2} mol g-cat^{-1} h^{-1}) e)	100 (1 h)	55.8% (yield)	8.9×10^{-3} mol g^{-1} h^{-1} f)	4

Ag/MgO - SiO_2 (Ag/Si = 0.05, Mg/Si = 3)	673 K	0.20 g	5.7×10^4 ppm in Ar 20 mL min^{-1} (2.8×10^{-3} mol h^{-1})[e]	91.8 (7–8 h)	49.2% (yield)	0.20 g g^{-1} h^{-1} 3.7×10^{-3} mol g^{-1} h^{-1} [f]	8
Cu/MgO–SiO_2 (Cu/Si = 0.05, Mg/Si = 3)	673 K	0.20 g	5.7×10^4 ppm in Ar 20 mL min^{-1} (2.8×10^{-3} mol h^{-1})[e]	98.7 (7–8 h)	45.4% (yield)	0.20 g g-cat^{-1} h^{-1} 3.7×10^{-3} mol g^{-1} h^{-1} [f]	8
MgO–SiO_2–Na_2O (1 wt%) (MgO/SiO_2 = 1)	623 K	0.20 g	6.5×10^{-4} mol h^{-1}	100 (10 min)	87% (yield)	1.4×10^{-3} mol g^{-1} h^{-1} [f]	6
Ag–Sepiolite	553 K	Not shown	Contact time 75 min 1.7×10^{-2} mol g-cat^{-1} h^{-1} [e]	63	6% (yield) (20 min)	5.2×10^{-4} mol g^{-1} h^{-1} [f]	9
Mn–Sepiolite	573 K	0.30 g	20 mmHg (240 cm^3)[g]	Not shown	27.9% (yield) (30 min)	1.4×10^{-4} mol g^{-1} h^{-1} [f]	10

[a] Reaction temperature in K; [b] Catalyst weight in g; [c] Ethanol conversion at time on stream shown in parenthesis; [d] Selectivity based on carbon number basis; [e] Ethanol feed rate was re-calculated by the authors; [f] Rate of 1,3-butadiene formation was re-calculated by the authors; [g] Batch reactor in the gas circulation system

[h] MgO–SiO_2 was prepared by kneading magnesium hydroxide and colloidal silica.