Supporting Information

Efficient conversion of ethanol to 1-butanol and C_5-C_9 alcohols over calcium carbide

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EXPERIMENTAL

(1) Quantitative calculation of gas products

After the indicated reaction time, the reactor was cooled to room temperature with ice water and the gage pressure was recorded as P_1. The total volume of gas product at the atmospheric pressure (termed V_g) was estimated based on *Eq.* (1), where V is the void volume of the reactor at the reaction condition and P_0 is the atmospheric pressure. The volume of each component in the injected gas (termed V_i) was determined by its corresponding standard curve and the content of each component (termed C_i) was calculated by *Eq.* (2), where the V_a is the volume of gas injected into the GC for analysis. The mole amount of each component in the gas product (termed M_i, mmol) was obtained by *Eq.* (3), where the V_g is the total volume of gas product.

$$V_g = \frac{P_1 \times V}{P_0} \tag{1}$$

$$C_i = \frac{V_i}{V_a} \times 100\% \qquad (i = C_2H_2, C_2H_4, H_2, CH_4 \text{ and } CO) \tag{2}$$

$$M_i = \frac{C_i \times V_g}{22.4} \tag{3}$$

The average density of gas product (ρ_g) can be obtained by *Eq.* (4), where ρ_i is the density of each gas product. The mass of gas product (m_g) was obtained by *Eq.* (5).

$$\rho_g = \sum \rho_i \times C_i \tag{4}$$

$$m_g = \rho_g \times V_g \tag{5}$$

(2) Calculation of ethanol conversion and products' yields

Ethanol conversion (X_{ethanol}), yields of various alcohols (Y_{alcohol}), carbon yields of gas product ($Y_{\text{gas-}C}$) and solid product ($Y_{\text{solid-}C}$), as well as the carbon balance (%C) were estimated by *Eqs.* (6)-(10), respectively.

$$X_{\text{ethanol}} = (1 - \frac{\textit{the total carbon in ethanol in the liquid product}}{\textit{the total carbon in ethanol fed into the reactor}}) \times 100\% \quad (6)$$

$$Y_{\text{alcohols}} = \frac{\textit{the total carbon in alcohol products}}{\textit{the total carbon in ethanol fed into the reactor}} \times 100\% \quad (7)$$

$$Y_{\text{gas}} = \frac{\textit{the total carbon in gas products}}{\textit{the total carbon fed into the reactor}} \times 100\% \quad (8)$$

$$Y_{\text{solid}} = \frac{\textit{the total carbon in solid products}}{\textit{the total carbon fed into the reactor}} \times 100\% \quad (9)$$

$$\%\text{C} = \frac{\textit{the total carbon identified in the products}}{\textit{the total carbon fed into the reactor}} \times 100\% \quad (10)$$

(3) Carbon balance of CaC_2

The alkynyl moiety in CaC_2 is converted to C_2H_2 and EVE according to *Re*. (1) and (2). If CaC_2 is completely converted and C_2H_2 and EVE don't consume, the total amount of C_2H_2 and EVE should be the same as that of CaC_2 (23 mmol). If the total amount of C_2H_2 and EVE is less than that of CaC_2, consumption of C_2H_2 or EVE such as EVE polycondensation should take place. The carbon balance of CaC_2 is shown in Table S3.

RESULTS

Table S1 Heterogeneous catalysts reported in literatures for coupling of ethanol to 1-butanol

Catalyst	Reactor	Temp. (°C)	Ethanol conv. (%)	1-butanol yield (%)	STY [a] (g_{pro} kg_{cat}^{-1} h^{-1})	Ref.
Sr-HAP (Sr/P=1.7)	Continuous	300	11.3	9.8	160	16
HAP (Ca/P=1.64)	Continuous	400	57.4	25.7	671	17
HAP	Continuous	440	30.0	15.0	257	18
HAP-CO_3	Continuous	400	40.0	22.4	290	19
MgO	Continuous	450	56.0	18.4	270	20
MgAl oxide (Mg/Al=3)	Continuous	350	32.0	13.0	400	22
MgAl oxide (Mg/Al=3)	Continuous	350	50.0	10.0	220	23
MgFe oxide	Continuous	350	50.0	9.0	220	24
Cu/CeO_2	Continuous	330	67.0	30.0	474	28
In-CuMgAl oxide	Batch	260	27.0	16.2	617	25
Cu-Mg-Al oxide	Batch	260	9.5	7.6	203	26
Ni/γ-Al_2O_3	Batch	230	40.0	20.0	187	29
$Cu_{10}Ni_{10}$-porous metal oxide	Batch	320	56.0	22.0	705	27

[a] Space-time yield of 1-butanol.

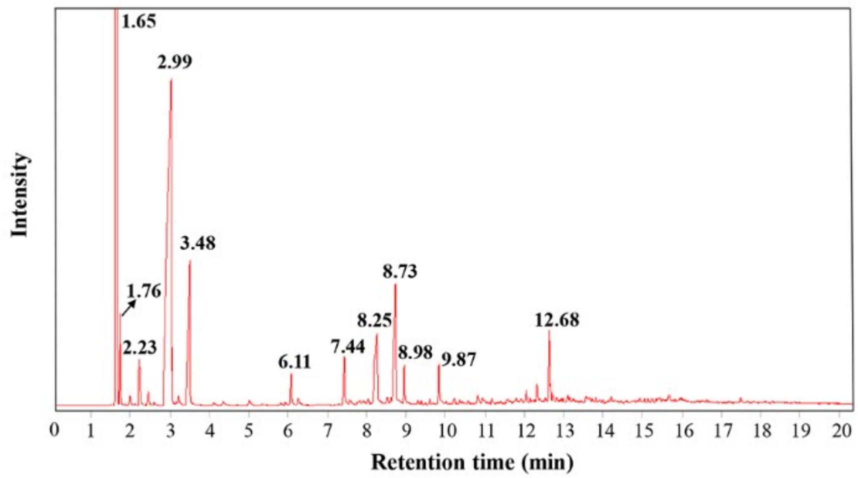
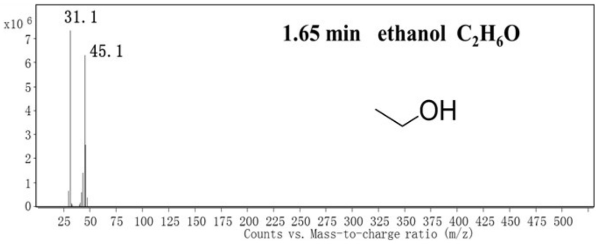
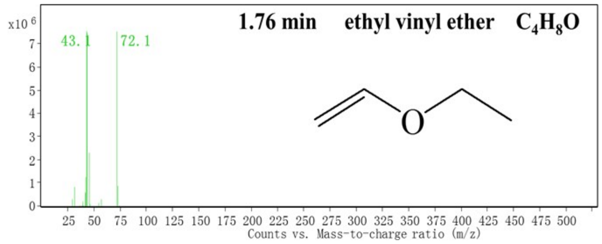
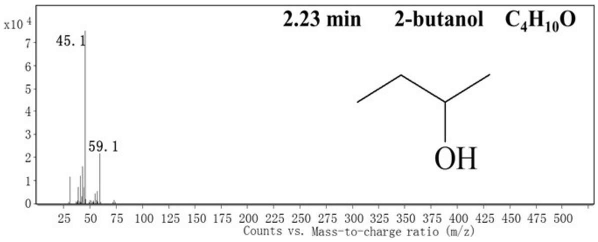


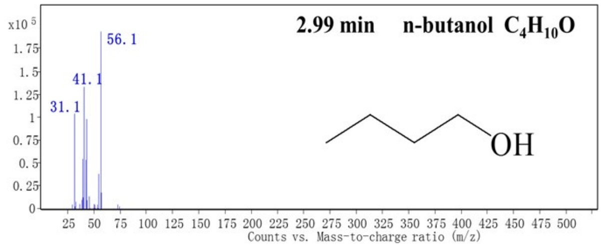
Fig. S1 Total ion chromatogram of the liquid product of ethanol reaction at 190 °C for 8 h over CaC_2.

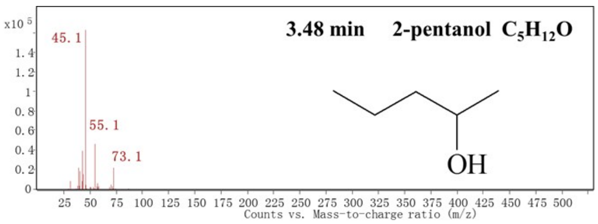
Table S2 The corresponding substance at each retention time in Fig. 1 identified by MS

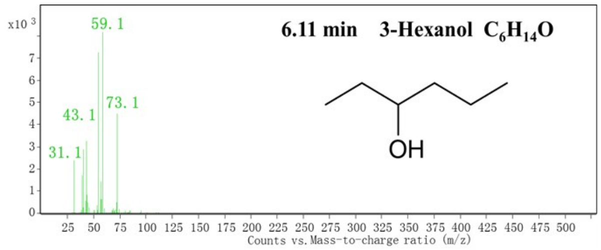


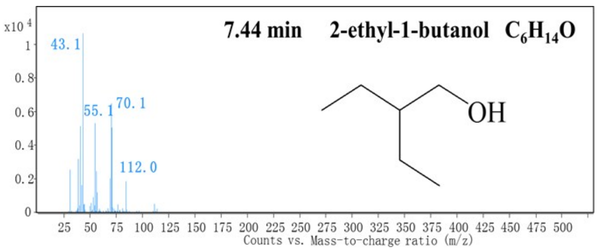


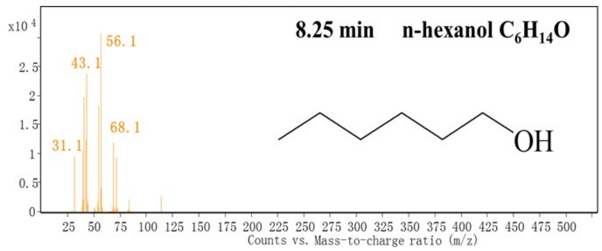


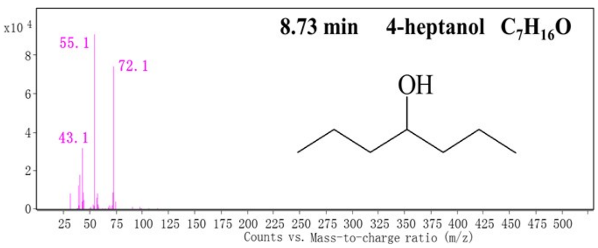


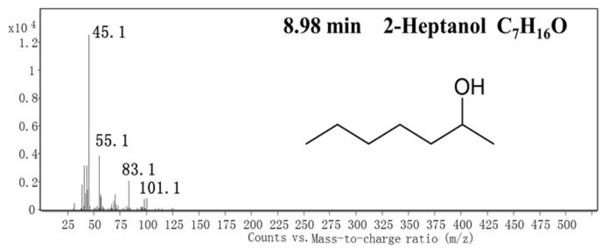


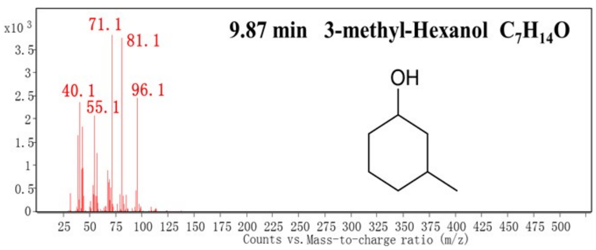












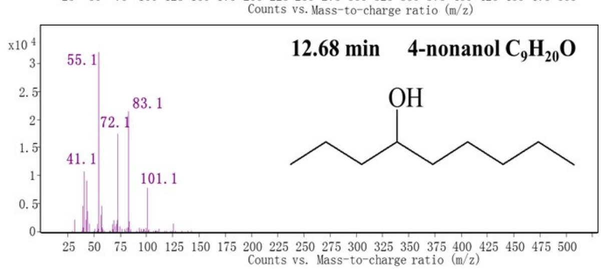


Table S3 The yield of various liquid products determined by GC

Entry	Calcium reactant	Temp. (°C)	Time (h)	Carbon balance (%)	Yield (%)			
					2-pentanol	hexanol[a]	heptanol[b]	4-nonanol
1	23 mmol CaC_2	190	6	95.7	2.2	2.2	0.6	0.9
2	23 mmol CaC_2	235	6	95.2	2.9	4.7	1.6	1.3
3	23 mmol CaC_2	255	6	96.1	3.5	5.4	2.4	2.0
4	23 mmol CaC_2	275	6	95.1	3.7	5.8	3.8	2.9
5	23 mmol CaC_2	300	6	95.0	4.5	7.4	5.4	2.0
6	23 mmol CaC_2	315	6	92.8	5.5	8.8	5.7	1.1
7	23 mmol CaC_2	275	1	96.6	2.7	3.1	1.1	1.3
8	23 mmol CaC_2	275	3	96.5	3.3	4.6	2.4	1.9
9	23 mmol CaC_2	275	8	94.9	5.1	7.1	4.6	3.3
10	23 mmol CaC_2	275	12	92.8	4.8	7.5	5.0	3.4
11	23 mmol CaC_2	275	15	92.3	4.7	8.3	5.4	3.2
12	12 mmol CaC_2	275	6	92.4	2.4	3.7	2.0	2.2
13	34 mmol CaC_2	275	6	96.2	4.7	8.3	6.7	3.8
14	23 mmol $Ca(OH)_2$	275	8	98.5	4.8	0.0	0.0	0.0
15	23 mmol $Ca(OCH_2CH_3)_2$	275	8	93.2	3.4	2.9	0.0	0.0

[a] Hexanol includes 1-hexanol, 3-hexanol and 3-ethylcyclohexanol;

[b] Heptanol includes 2-heptanol and 4-heptanol.

Table S4 The carbon balance of CaC_2 during ethanol conversion at 275 °C [a]

Entry	Time (h)	Amount (mmol)			EVE in solid residual due to its polymerization	
		EVE	C_2H_2	difference [b]	Theoretical	Experimental
1	6	1.2	7.4	14.4	28.8	25.9
2	8	1.3	6.9	14.8	29.6	24.5
3	12	1.4	6.9	14.7	29.4	23.5

[a] The amount of ethanol and CaC_2 are 217 and 23 mmol, respectively.

b The difference is obtained by subtracting the amounts of EVE and C_2H_2 from the total amount of CaC_2. These EVE were polymerized.

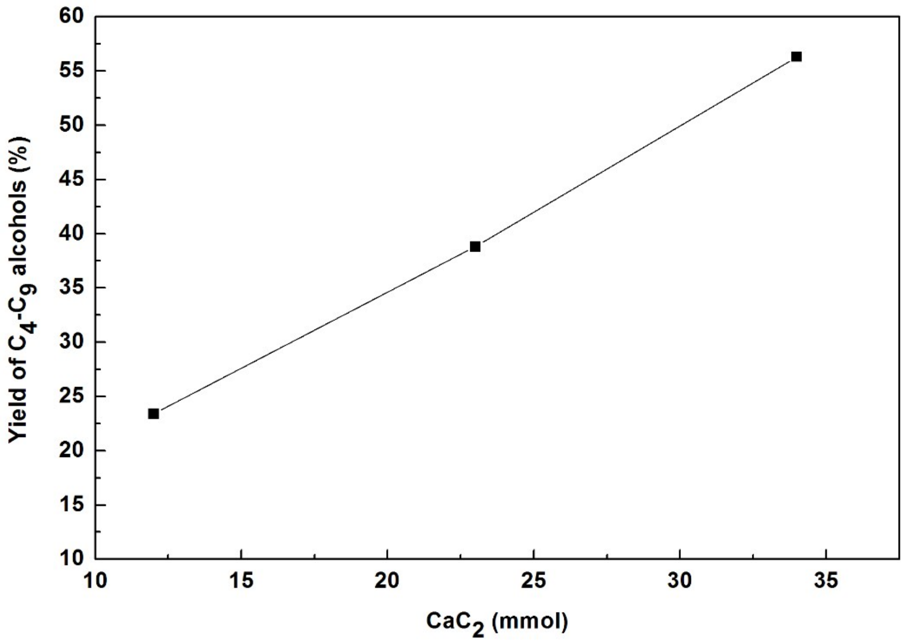


Fig. S2 The yield of C_4-C_9 alcohols at 275 ^oC for 6 h vs. the CaC_2 loading.