Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Table S1 TG-DTA measurement of $AgCuCeO_2ZrO_2$ catalysts at each temperature

Catalysts	200-400 (℃)	400-600 (℃)	600-800 (℃)	Total (mg)
1Ag9Cu45Ce45Zr	0.20	1.17	2.07	3.44
2Ag8Cu22.5Ce67.5Zr	0.28	1.28	1.71	3.27
2Ag8Cu45Ce45Zr	0.62	0.3	0.59	1.51
2Ag8Cu67.5Ce22.5Zr	0.04	2.32	1.87	4.23
3Ag7Cu45Ce45Zr	-0.03	0.43	3.39	3.79
10Cu45Ce45Zr	0.11	0.96	2.13	3.21

Table S2 Nitrogen adsorption-desorption measurement of $AgCuCeO_2ZrO_2$ catalysts.

Sample name	BET SA[*1] (m^2/g)	Total PV[*2] (cm^3/g)	Avg. PD[*3] (nm)	BJH SA[*1] (m^2/g)	BJH PV[*2] (cm^3/g)	BJH PD[*3] (nm)
10Cu45Ce45Zr b	37	0.11	12	51	0.11	9.2
10Cu45Ce45Zr a	39	0.14	9.9	46	0.13	3.7
1Ag9Cu45Ce45Zr b	27	0.10	13	39	0.10	9.2
1Ag9Cu45Ce45Zr a	40	0.12	12	36	0.14	3.7
2Ag8Cu22.5Ce67.5Zr b	24	0.12	20	30	0.12	9.2
2Ag8Cu22.5Ce67.5Zr a	37	0.14	15	27	0.14	3.7
2Ag8Cu45Ce45Zr b	28	0.10	14	39	0.10	9.2
2Ag8Cu45Ce45Zr a	28	0.09	13	32	0.13	3.7
2Ag8Cu67.5Ce22.5Zr b	49	0.18	15	67	0.18	9.2
2Ag8Cu67.5Ce22.5Zr a	93	0.27	12	69	0.28	3.7
3Ag7Cu45Ce45Zr b	26	0.10	16	30	0.10	5.3

*1 Surface area, *2 Pore volume, *3 Pore diameter, b: before, a: after the reaction

Table S3 Elemental analysis of 2Ag8Cu67.5Ce22.5Zr catalyst before and after reaction by XRF

	CeO_2	ZrO_2	CuO	Ag
Before (%)	**55.84**	**30.90**	**10.34**	**2.92**

	CeO_2	**ZrO_2**	**Cu**	**Ag**
After (%)	**54.32**	**33.01**	**9.54**	**3.13**

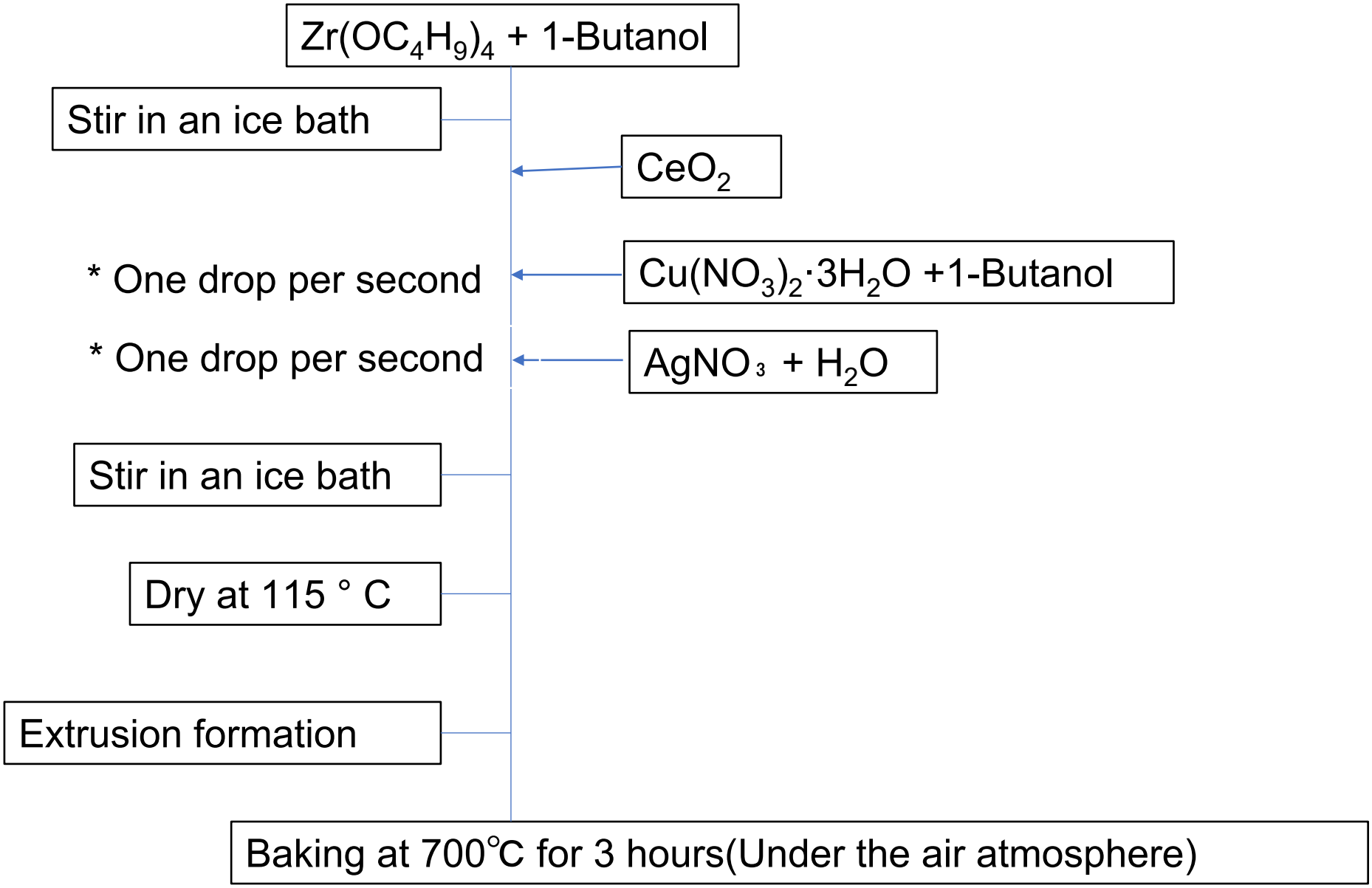

Fig. S1 A flowchart of preparation of $CuCeO_2ZrO_2$ and $AgCuCeO_2ZrO_2$ catalysts

Footnote of Fig. S1

2Ag8Cu45Ce45Zr catalyst as an example was prepared as follows: First, zirconium (IV) butoxide (8.76 g) and 1-butanol (9.95 g) were placed into a beaker (200 ml) and stirred on a magnetic stirrer with a hot plate, and ceria (2.25 g) was added to obtain a mixture including support components. Next, a solution of copper nitrate trihydrate (1.52 g) and 1-butanol (5.57 g) prepared was dropwise added to the mixture with a Pasteur pipette at 0^{o}C by one drop per second. Further, silvernitrate(I) (0.16 g) dissolved in water (0.32 g) was also dropwise added to the mixture with a Pasteur pipette at 0^{o}C by one drop per second. The resulted mixture was stirred for 1 hour at 0 °C and then heated to 115 °C using an oil bath with stirring. Thereafter, the obtained gel was heated with heating rate of 5°C/min and was calcined at 700^{o}C for 3 hours in an air atmosphere. In naming 2Ag8Cu45Ce45Zr, 2 means wt% of silver metal, 8 means wt% of copper metal, 45 before Ce means wt% of CeO_2 and 45 before Zr means wt% of ZrO_2. Other $CuCeO_2ZrO_2$ and $AgCuCeO_2ZrO_2$ catalysts were prepared similarly.

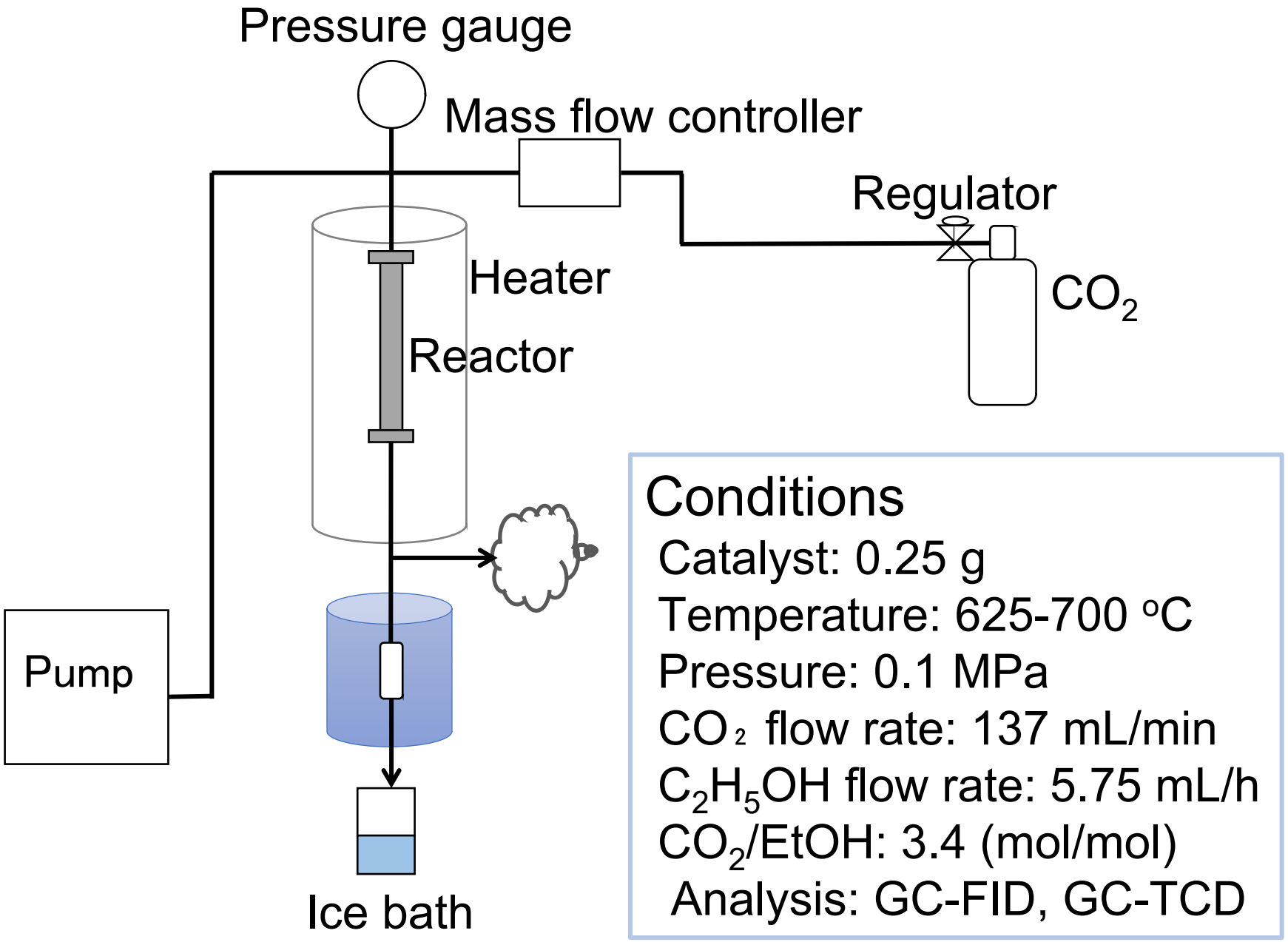

Fig. S2 Reaction apparatus for dry reforming of ethanol

Footnote of Fig. S2

Dry reforming of ethanol is shown in eq. (1).

$C_2H_5OH + CO_2 \rightarrow 3H_2 + 3CO$ ……..(1)

Ethanol and CO_2 conversions were calculated on the basis of eqs. (2) and (3), respectively.

Ethanol conversion (%)

$= 100 \times (W(EtOH)_{int}\,(g) - W(EtOH)_{prod}\,(g))/\, W(EtOH)_{int}\,(g)$ ……(2)

where $W(EtOH)_{int}$ is the weight of ethanol introduced and $W(EtOH)_{prod}$ is the weight of ethanol in liquid product.

CO_2 conversion (%) =

$100 \times (W(CO_2)_{int}\,(g) - W(CO_2)_{prod}\,(g))/\, W(CO_2)_{int}\,(g)$ ……(3)

where $W(CO_2)_{int}$ is the weight of CO_2 introduced and $W(CO_2)_{prod}$ is the weight of CO_2 in gas product.

H_2 and CO yields were calculated on the basis of eqs. (4), (5) and (6).

Yield of H_2 (%) = 100 x H_2 in product (mol) / 3 x $EtOH_{conv}$(mol) ……(4)

Yield of CO (%) = 100 x CO in product (mol) / (CO_2conv(mol) + 2 x $EtOH_{conv}$(mol)) ……(5)

$EtOH_{conv}(mol) = (EtOH_{int}(mol) - EtOH_{prod}(mol))$ ……(6)

where CO_2conv: CO_2 converted; $EtOH_{conv}$: Ethanol converted; $EtOH_{int}$: Ethanol introduced; $EtOH_{prod}$: Ethanol in liquid product

Reverse water gas shift reaction

$$CO_2 + H_2 \rightarrow CO + H_2O$$

Decomposition of ethanol

$$C_2H_5OH \rightarrow CO + CH_4 + H_2$$

Decomposition of methane

$$CH_4 \rightarrow C + 2H_2$$

Dry reforming of methane

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$

Fig. S3 Side reactions