Electronic Supplementary Information

High-throughput development of highly active catalyst system to convert bioethanol to 1,3-butadiene

Yu Shinke[a,b], Tomohisa Miyazawa[c], Misao Hiza[b], Isao Nakamura[c], Tadahiro Fujitani*[c]

a Research Association of High-Throughput Design and Development for Advanced Functional Materials (ADMAT), Tsukuba, Ibaraki 305-8565, Japan.
b Advanced Materials Innovation Team, Research & Development Center, The Yokohama Rubber Co., Ltd., Hiratsuka, Kanagawa 254-8601, Japan.
c Interdisciplinary Research Center for Catalytic Chemistry, National Institute of Advanced Industrial Science and Technology (AIST), Tsukuba, Ibaraki 305-8565, Japan. E-mail: t-fujitani@aist.go.jp

Contents

………………………………………………………………………………………………………

Lebedev and Ostromyslensky processes

The ETB reactions were first reported in the early 20th century by Lebedev [S1] and Ostromyslensky [S2]. Lebedev used aluminum and zinc oxides catalysts at 673 K for one-step reaction. Ostromyslensky proposed a conversion from a mixture of ethanol and acetaldehyde over alumina or clay catalysts at 713–733 K, yielding 18% of BD. It was theoretically a two-step process from ethanol to butadiene, involving dehydrogenation of ethanol to acetaldehyde in a separate step.
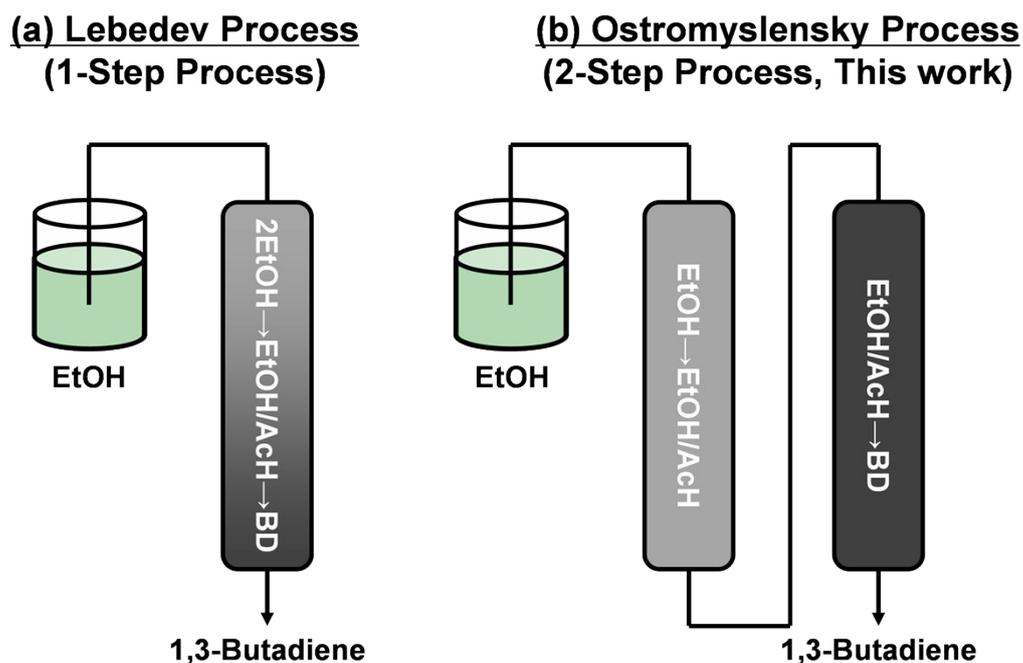
Figure S1 Diagrams of Lebedev (a) and Ostromyslensky (b) processes.

[S1] S.V. Lebedev, A.O. Yakubchik, J. Chem. Soc., (1929) 220–225.

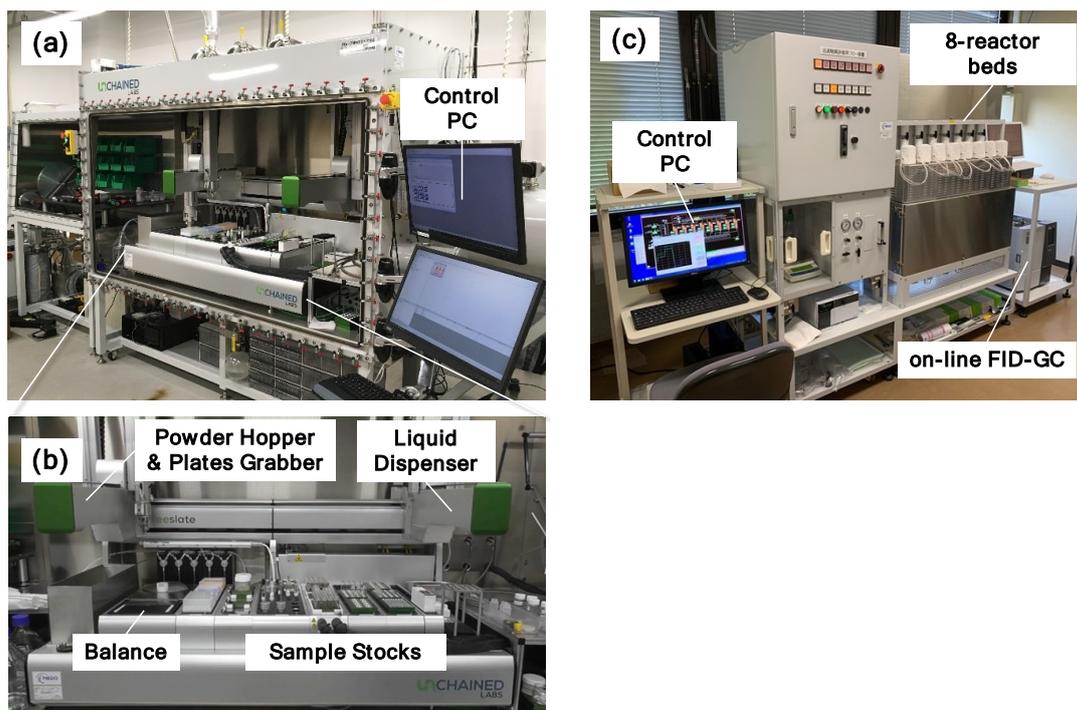[S2] J. Ostromyslensky, J. Russ. Phys. Chem. Soc., 47 (1915) 1472-1506.

Figure S2 Photographs of the high-throughput apparatus for the catalyst preparation (a,b) and the evaluation of catalytic activity (c).
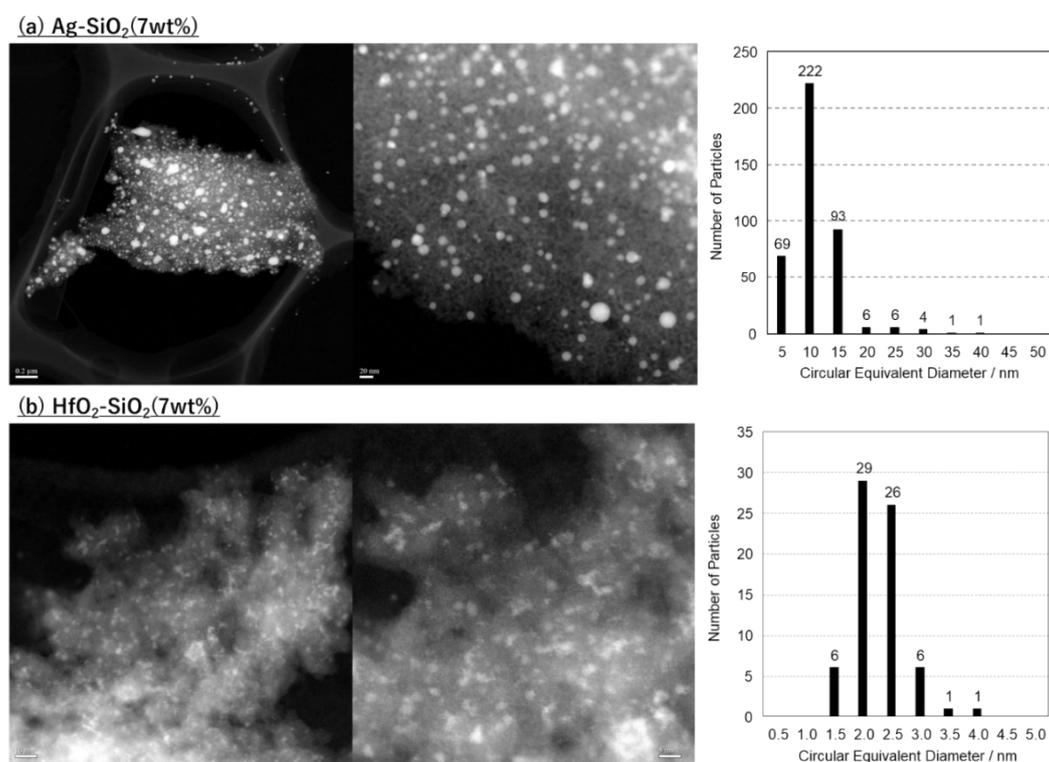

Figure S3 DF–STEM images and particle size distributions of (a) Ag/SiO$_2$ and (b) HfO$_2$/SiO$_2$ catalysts.

Experimental Procedures

1. Catalyst Preparation

CARiACT SiO_2 (Fuji Silysia Chemical, G-6 grade; particle size = 75–150 μm; average pore diameter = 6 nm; pore volume = 0.7 mL/g; surface area = 500 m^2/g) was used as the catalyst support. Various SiO_2-supported metal oxides were prepared by a pore-filling impregnation method using a high-throughput catalyst preparation system (freeslate, Unchained Labs, Fig. S2(a) and (b)). Metal nitrates, metal chlorides, a hydrogen tetrachloroaurate(III) tetrahydrate, and a zirconium oxynitrate were used as the precursors of metal oxides. These precursors were dissolved in an amount of water equal to the pore volume of SiO_2, whose solutions in glass vials were placed in an aluminum plate dedicated to the high-throughput system. On the other hand, the dried SiO_2 at 383 K for 1 h was placed in a hopper equipped with the high-throughput system. Then, the aqueous solutions of precursors were automatically impregnated to a predetermined amount of SiO_2 by the protocols programmed on the software. The impregnated sample was dried at 383 K for 5 h and then calcined at 773 K for 3 h. Calcination time was 5 h when using metal chlorides for the precursors. The metal oxide loading in supported catalyst was 5 wt%.

On the other hand, the mixed-metal-oxide catalysts ($Ag-HfO_2/SiO_2$ and $ZnO-ZrO_2/SiO_2$) were prepared by a two-step pore-filling impregnation procedure. Specifically, an aqueous solution of Ag nitrate or Zn nitrate was firstly added dropwise to SiO_2, and the impregnated sample was dried at 383 K for 5 h and then calcined at 773 K for 3 h. Subsequently, an aqueous solution of Hf chloride or Zr nitrate was added to calcined sample, which was dried at 383 K for 5 h and then calcined at 773 K for 5 h.

2. Catalytic Activity Evaluation

The catalytic reactions were performed at 548–698 K and atmospheric pressure using a high-throughput reactor system with 8-parallel catalyst reactor (S-14-8Rx, Taiyo System Co., Ltd., Fig. S2(c)). EtOH used in the reaction was purchased from Imazu Chemical Co., Ltd. The reactor is made of quartz glass and has an inner diameter of 10 mm. Typically, 0.30 g of catalyst was placed in the reactor and heated to the desired temperature at 10 K min^{-1} under flowing N_2. Once the desired temperature was reached, EtOH was introduced into the reactor via a plunger pump (Shimadzu LC-20AT dual reciprocating plunger HPLC pump). Weight hourly space velocity (WHSV) was used as the contact time for the catalytic reaction. In a typical catalytic activity test experiment, 0.3 g of catalyst was used and EtOH was supplied at 0.3 mL min^{-1} (1.41 g h^{-1}), resulting in a WHSV of 4.7 h^{-1}. The products were analyzed with an on-line gas chromatograph equipped with a flame ionization detector. The reaction products were quantified by means of an absolute calibration method. EtOH conversion and product selectivity were calculated as follows:

$$EtOH\ conversion = \left(1 - \frac{unreated\ EtOH\ C\ number}{total\ C\ number}\right) \times 100\%$$

$$Selectivity = \frac{product\ C\ number}{total\ products\ C\ number} \times 100\%$$

$$Yield = EtOH\ Conversion \times Selectivity \times 100\%$$

In the case of EtOH/AcH reactions, conversion and selectivity were calculated by the following equations [S3].

$$Conversion = \left(1 - \frac{unreacted\ EtOH\ C\ number + unreacted\ AcH\ C\ number}{total\ C\ number}\right) \times 100\%$$

$$Selectivity = \frac{product\ C\ number}{total\ products\ C\ number} \times 100\%$$

$$Yield = Total\ conversion \times Selectivity \times 100\%$$

We conducted multiple catalytic activity tests on each sample and confirmed the reproducibility of the experiments. The experimental error of the product selectivity was typically <0.05%.

[S3] H.J. Chae, T.W. Kim, Y.K. Moon, H.K. Kim, K.E. Jeong, C.U. Kim, S.Y. Jeong, Appl. Catal. B, 150 (2014) 596-604.

3. Catalyst Characterization

Dark field scanning transmission electron microscopy (DF–STEM) images were taken on an JEM-2100F Field Emission Electron Microscope (JEOL) operating at 120 kV. Temperature programmed desorption (TPD) of NH_3 was performed using BELCAT (Microtrac BEL) equipped with thermal conductivity detector. At first, the samples were heated at 823 K in an Ar flow with a ramp of 5 K/min. Then the samples were cooled to ambient temperature, and gas flow switched to 10% NH_3/Ar mixture for 30 min. After being purged with pure He for 2 h at 373 K, the sample was heated at 10 K/min to 973 K under He flow. The desorbed amounts of NH_3 were determined by calibration of the TCD signal.

Table S1 EtOH conversion reactions with various SiO_2 supported catalysts prepared using a high-throughput system.

Catalyst	EtOH conv. / %	AcH yield / %	Selectivity / %						
			BD	AcH	Ethylene	Crotonaldehyde	1-Butanol	Crotyl Alcohol	Others
CuO	74	70	0	95	0	0	0	0	4
Ag	55	52	0	94	1	1	0	0	3
SnO$_2$	46	40	0	88	7	0	0	0	4
IrO$_2$	37	25	0	68	29	0	0	0	2
ZnO	32	22	9	68	7	6	1	0	9
MoO$_3$	53	19	5	37	48	0	0	0	10
Ga$_2$O$_3$	52	19	6	36	23	0	0	0	35
V$_2$O$_5$	32	14	3	45	45	2	0	0	5
Nb$_2$O$_5$	19	13	1	68	31	0	0	0	0
NiO	12	8	1	70	0	1	2	2	25*
Co$_3$O$_4$	8	6	1	82	4	3	0	3	6
ZrO$_2$	10	6	1	62	38	0	0	0	0
In$_2$O$_3$	7	6	0	92	6	0	0	0	1
Cr$_2$O$_3$	16	6	15	37	31	1	3	0	13
Sc$_2$O$_3$	13	6	1	45	52	0	0	0	3
ReO$_3$	6	5	0	95	4	0	0	0	1
Fe$_2$O$_3$	7	5	2	64	21	2	0	0	10
Al$_2$O$_3$	89	3	0	3	97	0	0	0	0
TiO$_2$	7	2	1	36	33	1	0	0	29
Rh$_2$O$_3$	3	2	0	60	38	0	0	0	1
MgO	5	2	0	33	65	0	0	0	1
Au	2	1	0	82	14	1	0	0	2
MnO$_2$	2	1	1	78	10	1	1	2	7
Pb$_3$O$_4$	1	1	11	88	0	0	0	0	1
RuO$_2$	1	1	0	77	20	0	0	0	3
HfO$_2$	10	1	1	11	49	0	0	0	40
Tb$_4$O$_7$	2	1	3	30	40	0	2	0	26
Sm$_2$O$_3$	2	1	3	36	32	0	3	1	25
PdO	14	1	0	4	0	0	0	0	96*
Pr$_6$O$_{11}$	1	1	3	38	34	0	3	1	20
Dy$_2$O$_3$	2	1	1	21	51	0	1	0	26
Lu$_2$O$_3$	3	0	1	14	54	0	0	0	31
Y$_2$O$_3$	3	0	1	13	54	0	0	0	30
Tm$_2$O$_3$	3	0	1	15	54	0	0	0	30
BaO	1	0	0	82	15	0	0	0	3
Er$_2$O$_3$	3	0	1	16	54	0	0	0	29
Eu$_2$O$_3$	1	0	1	31	41	0	0	0	27
Ta$_2$O$_5$	1	0	0	26	43	0	0	0	30
Gd$_2$O$_3$	2	0	1	19	52	0	0	0	28
La$_2$O$_3$	1	0	1	31	39	1	2	1	26
Nd$_2$O$_3$	1	0	1	21	49	0	1	0	28
LiO$_2$	1	0	0	37	4	1	0	1	57
CeO$_2$	0	0	0	56	33	0	0	0	9
SrO	1	0	1	32	54	0	1	1	12
CaO	1	0	1	22	68	0	0	0	8
Cs$_2$O	0	0	0	56	35	1	0	0	7
Na$_2$O	0	0	1	52	29	0	0	0	18
K$_2$O	0	0	0	50	42	0	0	0	7
Rb$_2$O	1	0	0	17	34	3	1	0	45

Reaction conditions: EtOH feed rate: 0.03 mL min^{-1}, carrier gas (N$_2$) feed rate: 10 mL min^{-1}, temperature: 623 K, WHSV: 4.7 h^{-1}, loading amount: 5 wt%.

*The others were CH$_4$ and CO produced by the decomposition reaction of EtOH.

Table S2 EtOH conversion reactions with various SiO_2 supported catalysts prepared using a high-throughput system.

Catalyst	EtOH conv. / %	AcH yield / %	Selectivity / %						
			BD	AcH	Ethylene	Crotonaldehyde	1-Butanol	Crotyl Alcohol	Others
Ag	69	63	0	92	2	1	0	0	4
SnO_2	55	50	0	92	6	0	0	0	1
ZnO	70	40	12	58	9	7	1	0	13
Nb_2O_5	66	30	2	45	52	0	0	0	1
Ga_2O_3	86	29	11	33	42	1	0	0	13
V_2O_5	73	27	4	37	50	2	0	0	6
MoO_3	65	23	6	35	54	0	0	0	5
In_2O_3	15	14	0	92	6	0	0	0	1
ZrO_2	32	14	2	42	56	0	0	0	0
Cr_2O_3	38	13	13	35	37	1	2	0	12
ReO_3	18	13	1	73	23	0	0	0	3
CuO	13	13	0	94	4	0	0	0	1
Sc_2O_3	41	12	2	29	68	0	0	0	1
Co_3O_4	15	12	1	82	7	3	1	2	4
Fe_2O_3	21	11	3	53	31	2	1	0	11
IrO_2	30	11	0	36	63	0	0	0	0
TiO_2	26	6	3	24	45	0	0	0	28
MnO_2	8	5	4	70	10	2	2	4	8
Au	6	5	1	78	16	1	0	1	3
MgO	17	4	1	26	74	0	0	0	0
HfO_2	32	3	2	9	68	0	0	0	21
Rh_2O_3	3	2	0	91	8	0	0	0	1
Tb_4O_7	11	2	7	19	54	0	2	0	18
RuO_2	2	2	0	83	13	0	0	0	2
Y_2O_3	16	2	5	11	64	0	1	0	19
Pr_6O_{11}	7	2	8	26	47	0	4	0	15
Dy_2O_3	13	2	4	14	62	0	1	0	18
Lu_2O_3	16	2	2	11	66	0	1	0	20
Pb_3O_4	3	2	1	59	37	0	0	0	3
Sm_2O_3	8	2	6	21	50	0	3	0	19
BaO	2	2	0	73	24	1	0	0	2
LiO_2	2	2	0	85	8	0	0	0	6
Tm_2O_3	13	1	1	12	65	0	1	0	21
Eu_2O_3	5	1	4	28	51	0	2	0	16
Er_2O_3	12	1	2	12	65	0	1	0	20
Ta_2O_5	5	1	1	27	48	0	0	0	23
CeO_2	3	1	2	52	34	0	2	1	9
Gd_2O_3	9	1	3	15	63	0	1	0	17
La_2O_3	5	1	7	25	46	0	5	0	17
Nd_2O_3	6	1	3	16	62	0	1	0	18
Al_2O_3	94	1	0	1	99	0	0	0	0
SrO	3	1	1	26	66	0	1	1	5
CaO	4	1	1	17	76	0	1	0	5
Cs_2O	2	1	1	36	61	0	0	0	2
K_2O	1	0	0	55	41	0	0	0	3
Rb_2O	2	0	1	19	75	0	0	0	5
Na_2O	1	0	1	56	36	0	0	0	7
PdO	1	0	0	64	0	0	0	0	35*
NiO	100	0	0	0	0	0	0	0	100*

Reaction conditions: EtOH feed rate: 0.03 mL min^{-1}, carrier gas (N_2) feed rate: 10 mL min^{-1}, temperature: 673 K, WHSV: 4.7 h^{-1}, loading amount: 5 wt%.

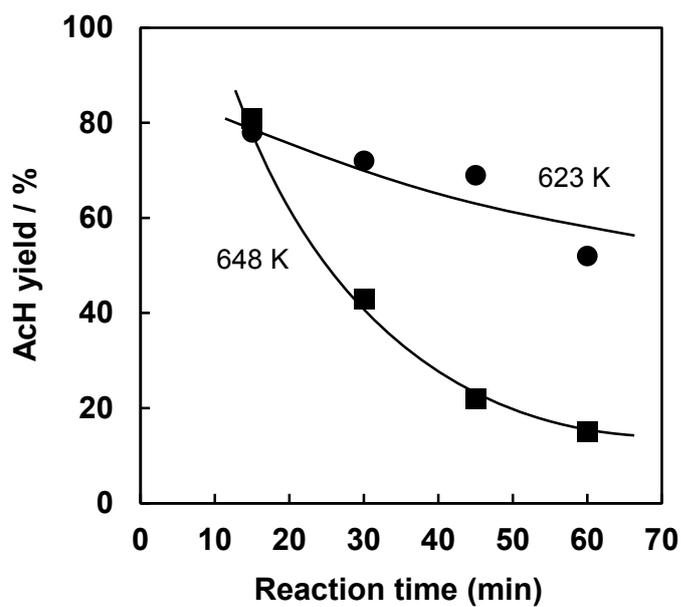*The others were CH_4 and CO produced by the decomposition reaction of EtOH.

Figure S4 AcH yield of the Cu/SiO$_2$ catalyst as a function of reaction time at 623 and 648 K.
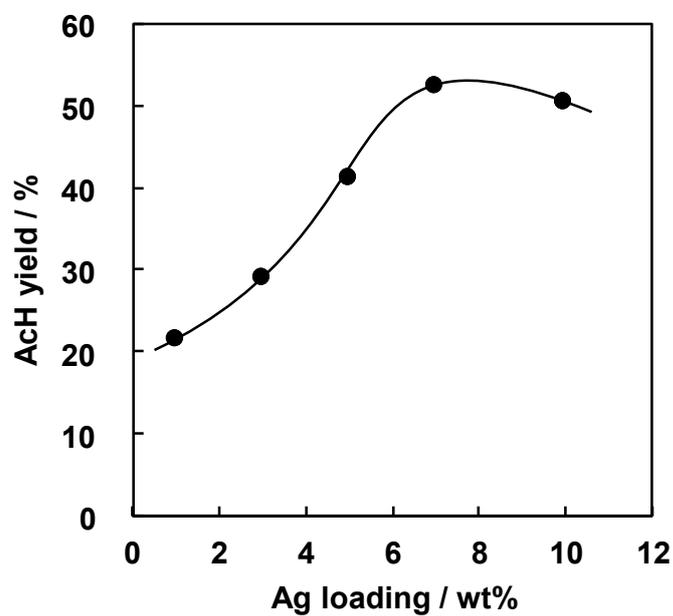

Figure S5 Effect of Ag loading on the AcH yield of the Ag/SiO$_2$ catalyst. EtOH feed rate: 0.03 mL min^{-1}, carrier gas (N$_2$) feed rate: 10 mL min^{-1}, WHSV: 4.7 h^{-1}, Reaction temperature: 598 K.

Table S3 EtOH/AcH conversion reactions with various SiO_2 supported catalysts prepared using a high-throughput system.

Catalyst	Conversion / %	BD yield / %	Selectivity / %					
			BD	Ethylene	Crotonaldehyde	1-Butanol	Crotyl alcohol	Others
HfO_2	56	32	57	1	4	2	2	34
ZrO_2	56	31	55	1	4	2	2	36
Al_2O_3	49	15	32	40	3	0	2	24
Sc_2O_3	39	14	36	3	14	4	4	39
Nb_2O_5	33	12	35	11	15	1	2	36
Ga_2O_3	31	11	34	25	7	2	0	32
Lu_2O_3	25	5	20	2	26	2	1	50
Tm_2O_3	27	4	14	1	28	2	1	54
Y_2O_3	27	4	14	1	32	2	1	50
Er_2O_3	26	4	14	1	33	2	2	49
Cr_2O_3	20	4	18	4	33	2	3	41
MgO	23	3	14	3	39	1	1	42
ZnO	19	3	16	4	38	1	1	40
Dy_2O_3	24	3	11	1	32	1	2	52
Tb_4O_7	23	3	11	1	33	1	2	52
Ta_2O_5	13	2	18	2	29	0	2	49
TiO_2	30	2	7	2	26	1	3	60
Gd_2O_3	23	2	9	1	36	1	2	51
MoO_3	21	2	9	54	9	0	0	28
Sm_2O_3	19	2	9	1	48	1	2	39
V_2O_5	23	2	7	30	32	1	1	29
Pr_6O_{11}	19	1	7	1	48	1	2	41
Fe_2O_3	12	1	10	3	57	0	1	29
Nd_2O_3	19	1	6	1	44	1	2	47
Eu_2O_3	19	1	5	1	42	1	3	48
La_2O_3	5	0	8	1	39	1	1	50
MnO_2	11	0	2	1	55	0	4	38
Ag	7	0	3	8	26	1	0	62
Pb_3O_4	7	0	2	1	54	0	6	38
ReO_3	3	0	3	4	34	0	3	56
SnO_2	3	0	3	28	11	3	1	54
CeO_2	7	0	1	1	60	0	3	35
CaO	17	0	0	0	53	0	2	44
In_2O_3	3	0	2	6	61	0	2	29
Co_3O_4	3	0	1	1	65	0	3	30
Au	4	0	1	1	64	0	4	31
NiO	2	0	1	1	71	0	6	21
CuO	2	0	1	3	40	0	1	55
IrO_2	4	0	0	66	12	0	1	20
SrO	16	0	0	0	53	0	1	46
Rb_2O	13	0	0	2	55	0	0	43
BaO	6	0	0	1	53	0	1	45
PdO	2	0	0	2	66	0	3	28
RuO_2	2	0	0	5	51	0	2	42
Rh_2O_3	2	0	0	5	69	0	3	23
Cs_2O	8	0	0	2	61	0	0	37
LiO_2	6	0	0	0	73	0	1	26
Na_2O	6	0	0	1	68	0	0	30
K_2O	3	0	0	1	25	2	0	72

Reaction conditions: EtOH/AcH: 50/50 molar ratio, feed rate: 0.03 mL min^{-1}, carrier gas (N_2) feed rate: 10 mL min^{-1}, temperature: 623 K, WHSV: 4.7 h^{-1}, loading amount: 5 wt%.

Table S4 EtOH/AcH conversion reactions with various SiO_2 supported catalysts prepared using a high-throughput system.

Catalyst	Conversion / %	BD yield / %	Selectivity / %					
			BD	Ethylene	Crotonaldehyde	1-Butanol	Crotyl alcohol	Others
HfO_2	67	41	61	4	2	1	1	31
ZrO_2	68	40	58	3	1	2	2	34
Sc_2O_3	55	22	40	7	4	3	3	43
Al_2O_3	59	13	21	57	2	0	1	18
Ga_2O_3	42	12	30	46	5	0	0	20
Lu_2O_3	38	11	28	5	11	4	1	52
Y_2O_3	40	11	26	4	10	4	1	55
Tm_2O_3	37	10	27	4	12	4	1	53
Er_2O_3	35	10	27	4	15	4	1	49
Nb_2O_5	48	9	18	46	11	0	1	23
Dy_2O_3	32	9	26	4	19	4	1	46
MgO	32	8	26	11	19	2	1	41
Tb_4O_7	32	8	25	3	14	5	1	52
Gd_2O_3	34	8	24	4	16	4	1	52
Cr_2O_3	30	8	26	13	16	2	1	42
ZnO	32	6	20	9	24	1	0	47
Sm_2O_3	31	6	20	3	20	3	1	52
Ta_2O_5	18	6	32	6	22	1	1	38
Eu_2O_3	27	5	19	3	24	3	2	49
Pr_6O_{11}	26	4	16	2	27	3	2	50
Nd_2O_3	26	4	15	2	27	2	1	51
TiO_2	31	3	11	10	19	3	3	55
MoO_3	30	3	9	71	5	0	0	16
V_2O_5	35	2	6	55	17	0	1	21
ReO_3	11	2	20	6	39	1	2	32
MnO_2	17	2	12	3	37	1	3	43
Fe_2O_3	19	2	11	19	30	1	0	39
La_2O_3	8	2	24	5	17	4	1	49
CaO	20	0	2	2	46	0	2	47
CeO_2	10	0	4	2	53	0	3	37
Co_3O_4	8	0	5	3	49	0	4	39
Au	6	0	4	5	54	0	4	33
Ag	8	0	2	21	19	0	0	58
NiO	4	0	3	3	63	1	7	23
SrO	17	0	1	2	49	0	2	47
In_2O_3	3	0	3	18	38	1	2	38
SnO_2	3	0	3	50	9	1	1	37
Pb_3O_4	2	0	3	10	47	0	5	35
Rb_2O	20	0	0	11	31	0	0	58
K_2O	17	0	0	5	49	0	0	45
PdO	3	0	1	5	58	0	4	32
BaO	6	0	0	2	57	0	2	38
Cs_2O	13	0	0	10	44	0	0	45
CuO	1	0	1	12	32	0	2	54
IrO_2	2	0	0	9	62	0	3	26
RuO_2	2	0	0	13	49	0	3	35
Na_2O	9	0	0	2	67	0	0	31
Rh_2O_3	2	0	0	10	59	0	3	28
LiO_2	4	0	0	1	46	0	1	52

Reaction conditions: EtOH/AcH: 50/50 molar ratio, feed rate: 0.03 mL min^{-1}, carrier gas (N_2) feed rate: 10 mL min^{-1}, temperature: 673 K, WHSV: 4.7 h^{-1}, loading amount: 5 wt%.
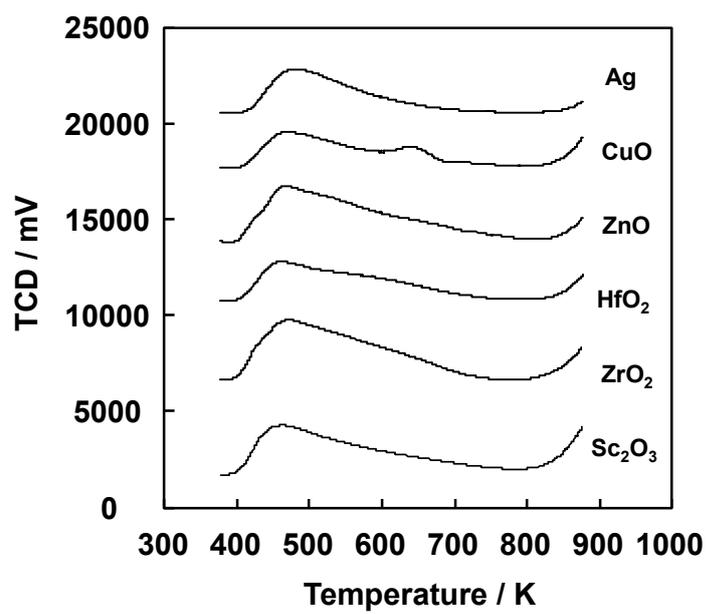
Figure S6 NH$_3$–TPD of silica-supported Ag, CuO, ZnO, HfO$_2$, ZrO$_2$ and Sc$_2$O$_3$ catalysts.
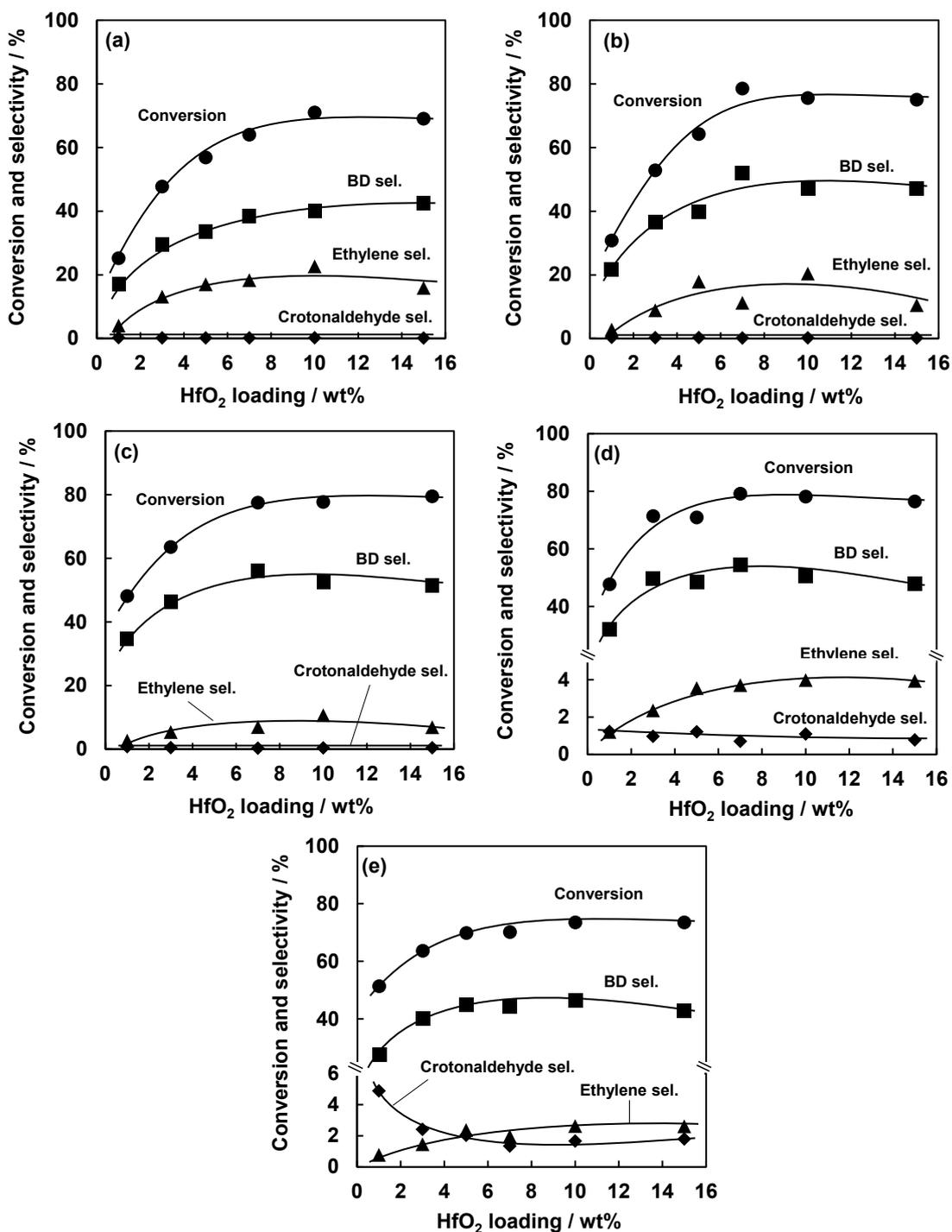
Figures S7 Effects of EtOH/AcH molar ratio and HfO$_2$ loading on the catalytic activity of HfO$_2$/SiO$_2$ catalysts. EtOH/AcH: (a) 75/25 (3.0), (b) 70/30 (2.3), (c) 60/40 (1.5), (d) 50/50 (1.0), and (e) 40/60 (0.67), EtOH/AcH mixture feed rate: 0.03 mL min^{-1}, carrier gas (N$_2$) feed rate: 10 mL min^{-1}, WHSV: 4.7 h^{-1}, Reaction temperature: 623 K.
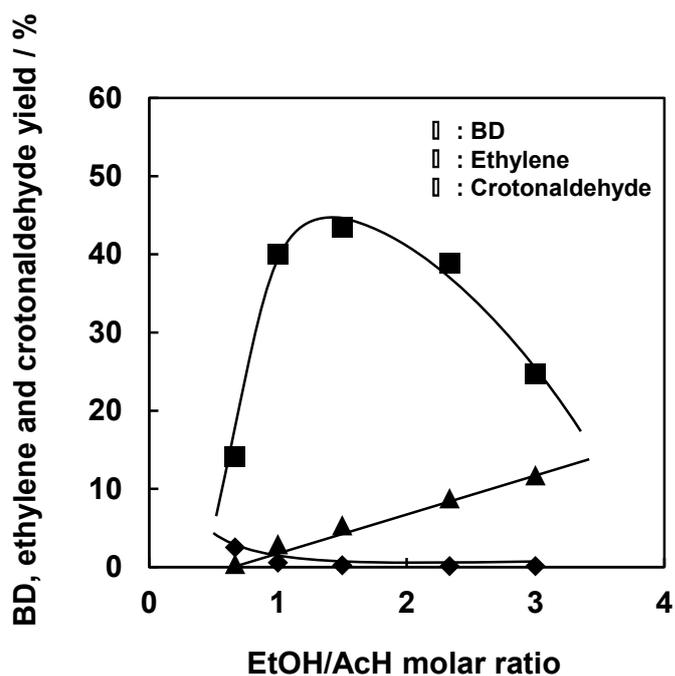
Figure S8 Effect of EtOH/AcH molar ratio on the catalytic activity of 7 wt% HfO_2/SiO_2 catalyst. EtOH/AcH mixture feed rate: 0.03 mL min^{-1}, carrier gas (N_2) feed rate: 10 mL min^{-1}, WHSV: 4.7 h^{-1}, Reaction temperature: 623 K.
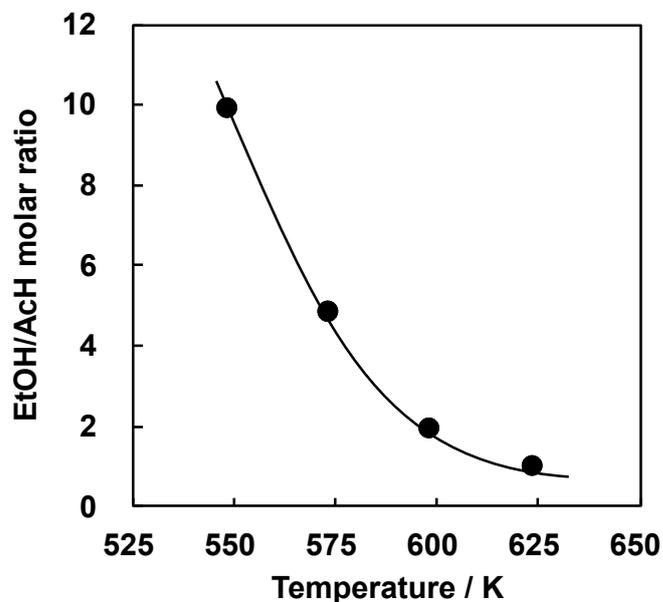
Figure S9 Effect of reaction temperature on the EtOH conversion (EtOH/AcH ratio) of the Ag/SiO_2 catalyst. EtOH feed rate: 0.03 mL min^{-1}, carrier gas (N_2) feed rate: 10 mL min^{-1}, WHSV: 4.7 h^{-1}, Ag loading: 7 wt%.
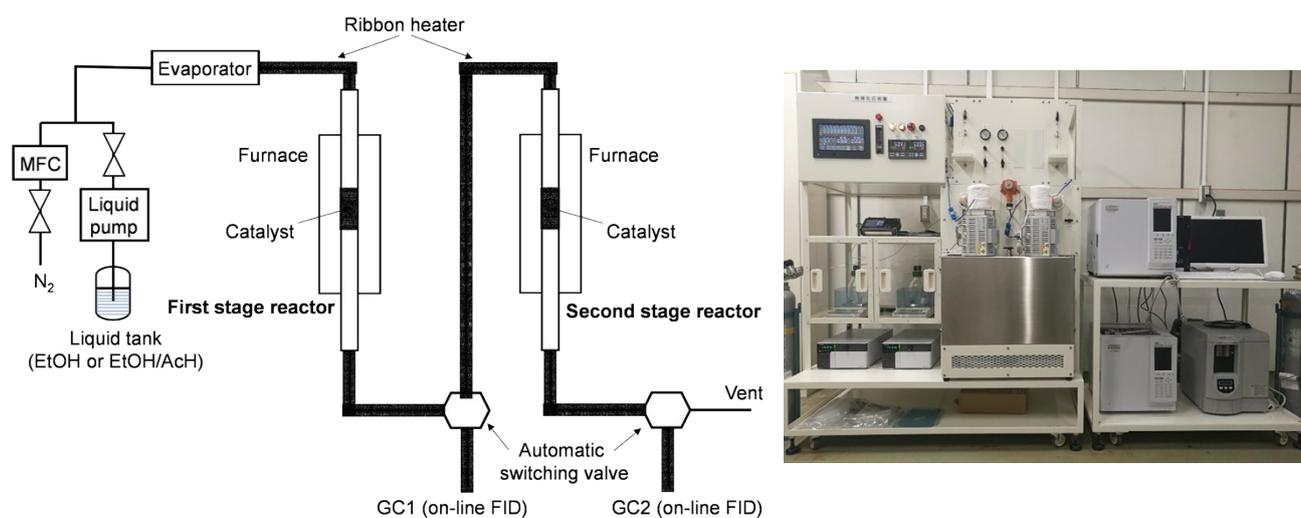
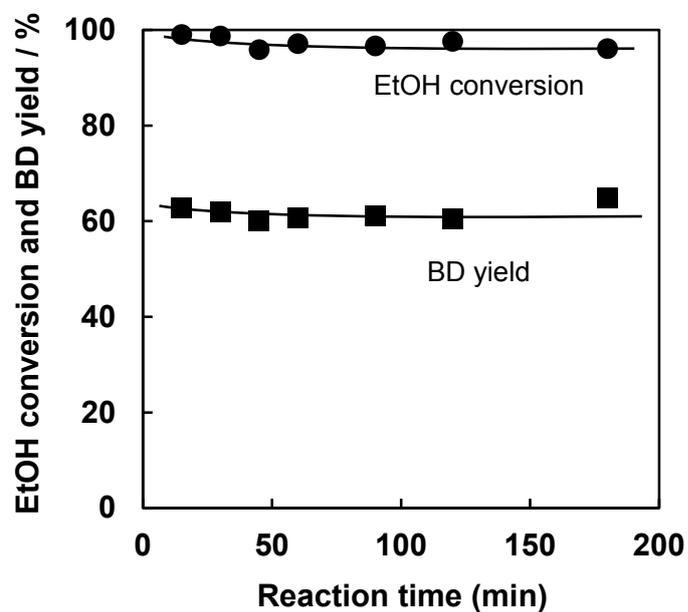**Figure S10** Flowchart and photograph of the two-stage tandem reactor system.

Figure S11 Activity of the Ag/SiO$_2$ + HFO$_2$/SiO$_2$ catalyst using the two-stage tandem reactor system as a function of reaction time.