

Ethanol conversion over Ga₂O₃–ZrO₂ solid solution: empirical evidences of the reaction pathway, the surface acid–base property, and role of gallium ion

Takashi Yamamoto^{1,2,}, Akihito Kurimoto², Riona Sato², Shoki Katada¹, Hirotaka Mine¹, Naoto Tanima², and Ryota Kamata²*

¹Department of Natural Science, Faculty of Science and Technology, Tokushima University, Tokushima 770-8506, Japan

²Department of Mathematical and Material Sciences, Faculty of Integrated Arts and Sciences, Tokushima University, Tokushima 770-8502, Japan

†To whom correspondence should be addressed.

E-mail: takashi-yamamoto.ias@tokushima-u.ac.jp

Table S1: Results of ethanol conversion at different contact time and reaction temperature.

<i>T</i> = 573 K																
GHSV /h ⁻¹	Conv. (%)	Yield (%)														
		CH ₄	DEE	C2	C2'	C3'	AcH	1-,2-C4'	iso-C4'	1,3-C4''	AcMe	AcOH	AcOEt	C3,4-ol	C4-al	CO ₂
96,109	0.2	0.0	0.0	0.0	0.0	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
26,492	0.7	0.0	0.0	0.0	0.0	0.0	0.3	0.0	0.1	0.0	0.0	0.0	0.2	0.0	0.0	0.0
9,515	1.2	0.0	0.0	0.0	0.1	0.0	0.5	0.0	0.1	0.0	0.1	0.0	0.3	0.0	0.0	0.0
4,746	2.1	0.0	0.0	0.1	0.1	0.0	0.7	0.0	0.3	0.0	0.5	0.0	0.5	0.0	0.0	0.0
1,315	8.8	0.0	0.0	0.1	0.5	0.2	1.1	0.0	0.4	0.0	2.1	0.0	0.8	0.8	0.0	2.9
238	24.6	0.0	0.0	0.0	1.1	1.7	1.3	0.0	0.5	0.1	6.6	0.2	0.6	3.9	0.1	8.5
<i>T</i> = 623 K																
GHSV /h ⁻¹	Conv. (%)	Yield (%)														
		CH ₄	DEE	C2	C2'	C3'	AcH	1-,2-C4'	iso-C4'	1,3-C4''	AcMe	AcOH	AcOEt	C3,4-ol	C4-al	CO ₂
96,109	1.5	0.0	0.0	0.0	0.1	0.0	0.7	0.0	0.3	0.0	0.2	0.0	0.1	0.0	0.0	0.0
26,492	5.7	0.0	0.0	0.1	0.5	0.0	1.9	0.0	0.9	0.0	1.9	0.0	0.4	0.0	0.0	0.0
9,515	12.8	0.0	0.0	0.1	0.9	0.1	3.0	0.0	1.3	0.0	3.9	0.0	0.7	0.0	0.0	2.9
4,746	23.4	0.0	0.0	0.0	1.7	0.2	4.2	0.0	2.6	0.2	8.4	0.1	0.7	0.0	0.1	5.2
1,315	73.4	0.0	0.0	0.0	4.1	5.6	1.9	0.2	0.1	0.0	30.0	1.3	0.0	1.0	2.5	26.5
238	98.9	0.4	0.0	0.0	5.0	16.1	0.0	0.1	2.0	0.6	30.7	2.0	0.0	0.0	4.2	37.8
<i>T</i> = 673 K																
GHSV /h ⁻¹	Conv. (%)	Yield (%)														
		CH ₄	DEE	C2	C2'	C3'	AcH	1-,2-C4'	iso-C4'	1,3-C4''	AcMe	AcOH	AcOEt	C3,4-ol	C4-al	CO ₂
96,109	11.9	0.0	0.0	0.0	1.3	0.1	3.4	0.0	1.5	0.0	5.3	0.0	0.3	0.0	0.0	0.0
26,492	51.5	0.0	0.0	0.0	3.9	1.1	5.2	0.1	1.6	0.2	22.6	0.1	0.3	1.1	0.5	14.9
9,515	75.4	0.0	0.0	0.0	5.1	2.5	4.2	0.0	3.6	0.6	32.4	0.9	0.0	1.6	1.4	23.2
4,760	100.0	0.0	0.0	0.1	6.0	5.0	1.8	0.0	1.5	0.0	42.2	1.3	0.0	2.3	2.4	37.4
1,315	99.5	1.3	0.0	0.0	7.3	8.0	0.0	0.0	6.7	0.3	37.9	2.0	0.0	1.3	2.5	32.3
238	98.9	5.5	0.0	0.0	6.9	12.6	0.0	0.1	14.0	0.0	13.5	2.1	0.0	0.0	4.2	40.1
<i>T</i> = 723 K																
GHSV /h ⁻¹	Conv. (%)	Yield (%)														
		CH ₄	DEE	C2	C2'	C3'	AcH	1-,2-C4'	iso-C4'	1,3-C4''	AcMe	AcOH	AcOEt	C3,4-ol	C4-al	CO ₂
96,109	50.9	0.1	0.0	0.0	4.3	1.5	5.3	0.1	2.8	0.0	20.7	0.1	0.2	0.0	0.4	15.6
26,492	92.7	0.7	0.0	0.0	6.3	5.0	1.8	0.7	2.4	0.0	44.6	0.1	0.0	0.6	0.5	29.7
9,515	98.4	1.7	0.0	0.0	6.3	5.5	0.6	0.6	5.0	0.0	44.2	0.2	0.0	0.6	0.7	33.0
4,746	99.6	5.0	0.1	0.0	6.6	7.2	0.0	0.1	10.7	0.0	32.9	0.0	0.0	0.5	0.0	36.5
1,315	99.8	9.6	0.0	0.0	7.1	11.3	0.0	0.0	22.1	0.0	4.7	0.4	0.0	0.1	1.5	42.9
238	99.5	12.0	0.0	0.0	5.7	11.6	0.0	0.0	22.2	0.0	0.4	0.0	0.0	0.0	0.8	46.9
<i>T</i> = 773 K																
GHSV /h ⁻¹	Conv. (%)	Yield (%)														
		CH ₄	DEE	C2	C2'	C3'	AcH	1-,2-C4'	iso-C4'	1,3-C4''	AcMe	AcOH	AcOEt	C3,4-ol	C4-al	CO ₂
96,109	71.5	0.9	0.0	0.0	7.2	2.8	6.1	0.0	5.2	0.0	28.5	0.1	0.0	0.0	0.5	20.3
26,492	97.8	6.4	0.0	0.0	5.6	5.3	0.8	0.4	9.1	0.0	34.8	0.1	0.0	0.0	0.3	35.1
9,515	100.0	10.7	0.0	0.0	5.8	5.6	0.1	0.1	14.5	0.0	22.3	0.1	0.0	0.0	0.3	40.6
4,746	100.0	17.9	0.0	0.0	6.6	7.5	0.0	0.0	15.4	0.0	6.7	0.0	0.0	0.0	0.2	45.8
1,315	100.0	19.3	0.0	0.0	7.2	5.8	0.0	0.0	19.0	0.0	0.3	0.2	0.0	0.0	0.2	48.0
238	99.7	19.0	0.0	0.0	3.9	5.8	0.0	0.1	21.3	0.0	0.2	0.0	0.0	0.0	0.1	49.3

Catalyst: Ga₂O₃-ZrO₂ 0.05–4 g; ethanol: 5%; H₂O: 40%; N₂: balance; total flow rate: 20 or 100 mL·min⁻¹. Conv.: ethanol conversion. AcH: acetaldehyde; AcMe: acetone; AcOEt: ethyl acetate; AcOH: acetic acid; C2–C3: sum of ethane and propane; C2': ethene; C3': propene; 1-, 2-C4': sum of 1- and 2-butenes; iso-C4': isobutene; 1,3-C4'': 1,3-butadiene; C4-al: butenals; C4-ol: butanols/butenols; DEE: diethyl ether.

Table S2: Results of ethanol conversion catalyzed by metal ion-doped ZrO₂.

T = 573 K

Doped- element	Conv. (%)	Yield (%)														
		CH ₄	DEE	C2	C2'	C3'	AcH	1-,2-C4'	iso-C4'	1,3-C4''	AcMe	AcOH	AcOEt	C3,4-ol	C4-al	CO ₂
-	0.5	0.0	0.0	0.0	0.4	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ca	0.5	0.0	0.0	0.0	0.4	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Sc	0.4	0.0	0.0	0.1	0.3	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ti	0.6	0.0	0.1	0.0	0.1	0.0	0.3	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
V	6.1	0.0	0.9	0.0	2.5	0.0	2.2	0.0	0.0	0.0	0.1	0.0	0.3	0.0	0.0	0.0
Cr	0.4	0.0	0.0	0.0	0.1	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Mn	0.7	0.0	0.0	0.0	0.1	0.0	0.3	0.0	0.0	0.0	0.1	0.0	0.1	0.0	0.0	0.0
Fe	0.5	0.0	0.0	0.0	0.3	0.0	0.2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Co	0.6	0.0	0.0	0.0	0.1	0.0	0.2	0.0	0.0	0.0	0.1	0.0	0.2	0.0	0.0	0.0
Ni	1.9	0.0	0.0	0.0	0.0	0.0	1.0	0.0	0.0	0.0	0.1	0.0	0.7	0.0	0.0	0.0
Cu	11.5	0.0	0.0	0.0	0.0	0.0	10.0	0.0	0.0	0.0	0.2	0.0	0.7	0.0	0.3	0.1
Zn	5.2	0.0	0.0	0.1	0.1	0.0	1.9	0.0	0.0	0.0	1.6	0.0	0.7	0.0	0.0	0.8
Ga	1.9	0.0	0.0	0.0	0.1	0.0	0.9	0.0	0.0	0.0	0.1	0.0	0.8	0.0	0.0	0.0

T = 723 K

Doped- element	Conv. (%)	Yield (%)														
		CH ₄	DEE	C2	C2'	C3'	AcH	1-,2-C4'	iso-C4'	1,3-C4''	AcMe	AcOH	AcOEt	C3,4-ol	C4-al	CO ₂
-	98.3	0.3	0.1	0.0	83.6	10.3	0.0	0.1	0.0	0.0	1.1	0.0	0.0	0.0	0.0	4.5
Ca	98.5	0.5	0.1	0.0	85.6	8.1	0.0	0.2	0.0	0.0	1.2	0.0	0.0	0.0	0.0	4.2
Sc	97.9	0.2	0.1	0.0	76.7	14.1	0.0	0.0	0.0	0.0	0.9	0.0	0.0	0.0	0.0	7.9
Ti	94.0	0.9	0.8	0.0	70.2	16.3	0.7	0.6	0.2	0.0	1.8	0.1	0.0	1.3	0.0	7.1
V	97.3	1.3	0.0	34.9	16.5	9.9	0.0	0.2	1.0	0.0	14.1	0.0	0.0	0.7	0.2	21.1
Cr	99.4	10.7	0.3	0.0	31.8	8.6	0.0	0.0	1.3	0.0	23.9	0.0	0.0	0.2	0.0	23.2
Mn	98.4	1.2	0.1	0.0	52.8	20.9	0.0	0.3	0.3	0.0	10.8	0.0	0.0	0.0	0.0	13.6
Fe	99.2	1.5	0.4	0.0	34.6	23.6	0.0	0.0	1.3	0.0	19.5	0.0	0.1	0.4	0.0	18.5
Co	99.3	1.0	0.0	0.0	22.2	7.9	0.1	0.1	5.7	0.0	39.5	0.0	0.0	0.1	0.0	23.3
Ni	98.2	1.5	0.0	0.0	9.4	3.2	0.3	0.2	7.4	0.0	51.0	0.0	0.0	0.0	0.0	27.0
Cu	98.5	0.3	0.5	0.0	55.9	26.4	0.2	0.0	0.0	0.0	4.1	0.0	0.0	0.6	0.0	11.9
Zn	97.8	4.3	0.0	0.0	3.5	3.6	0.0	0.0	35.0	0.0	19.9	0.0	0.0	0.4	0.2	33.1
Ga	99.5	3.6	0.0	0.0	4.6	4.1	0.0	0.0	17.5	0.0	39.4	0.0	0.0	0.4	0.0	30.5

Catalyst: 0.2 g; ethanol: 5%; H₂O: 40%; N₂: balance; total flow rate: 20 mL·min⁻¹.

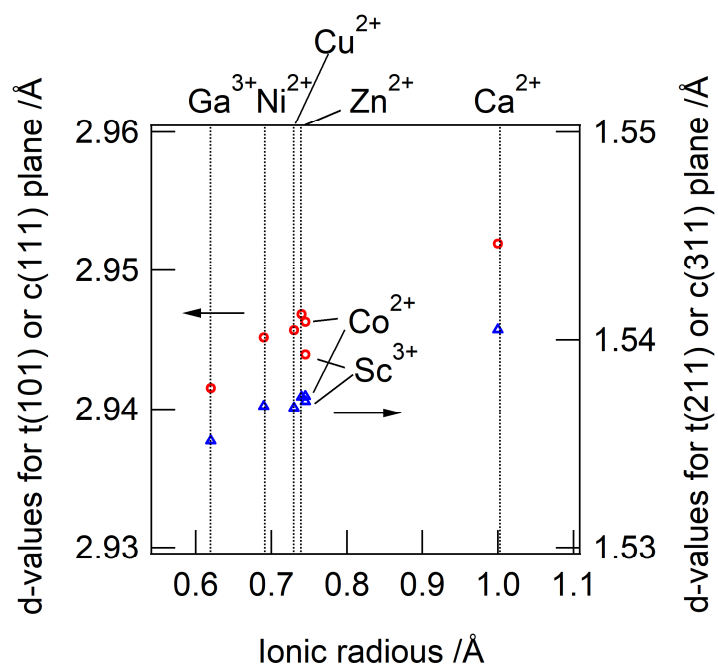


Fig. S1. Dependence of ionic radius of doped metal cation to ZrO₂ on *d*-values of the tetragonal/cubic phase. The ionic radius was taken from reference ¹ for six-fold coordination.

1. R. D. Shannon, Acta Crystallogr. A, 1976, 32, 751-767.

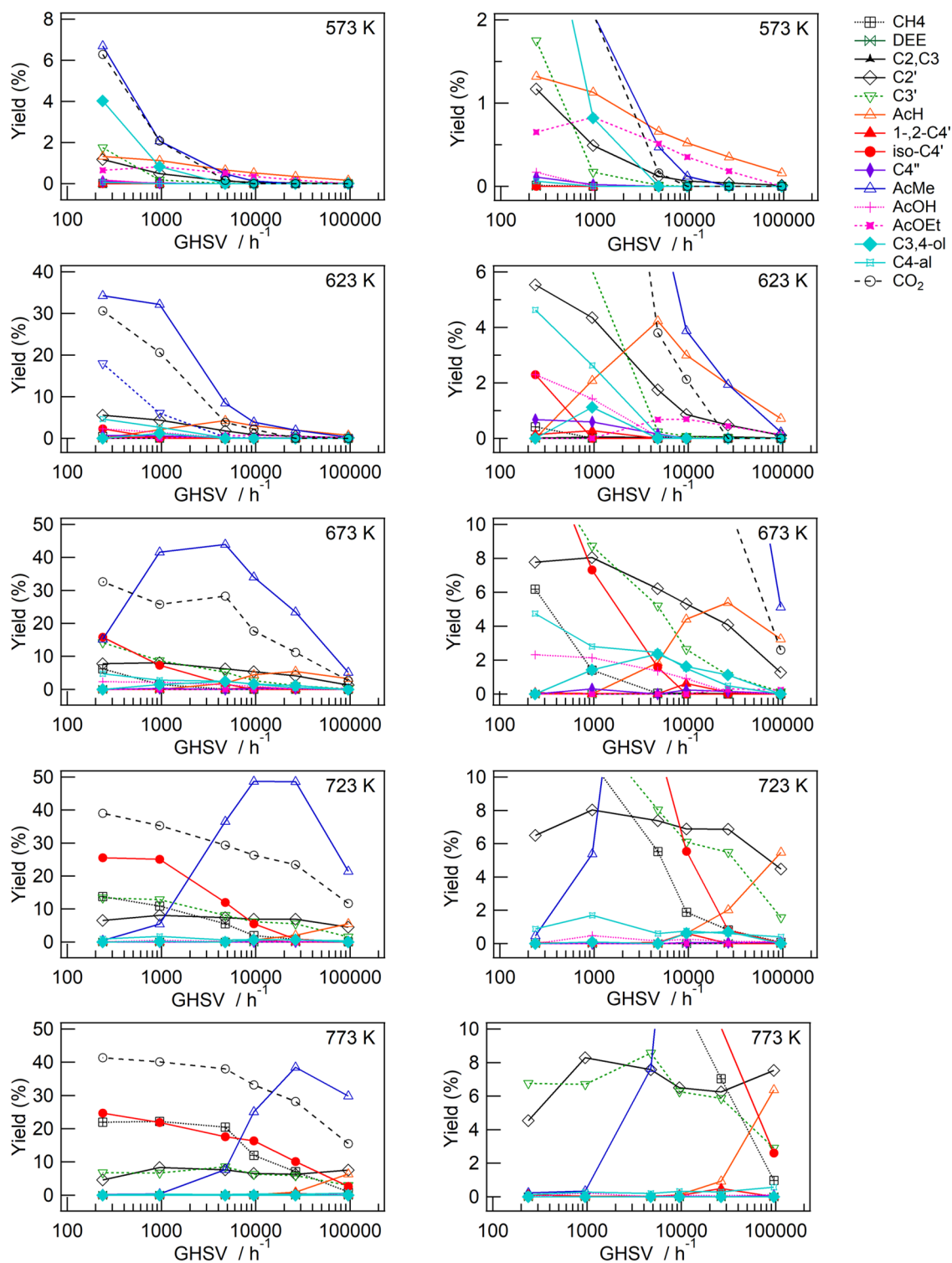


Fig. S2. Dependence of space velocity on ethanol conversion at 573 – 773 K. Catalyst: Ga₂O₃–ZrO₂ 0.05–4 g; ethanol: 5%; H₂O: 40%; N₂: balance; total flow rate: 20 or 100 mL·min⁻¹. Conv.: conversion of ethanol; AcH: acetaldehyde; AcMe: acetone; AcOEt: ethyl acetate; AcOH: acetic acid; C2-C3: sum of ethane and propane; C2' : ethene; C3' : propene; 1-, 2-C4' : sum of 1- and 2-butenes; iso-C4' : isobutene; 1,3-C4'' : 1,3-butadiene; C4-al: butenals; C4-ol: butanols/butenols; DEE: diethyl ether.