

Supplementary Materials

Selective Conversion of Bio-Derived Ethanol to Renewable BTX over Ga-ZSM-5

Zhenglong Li,^a Andrew W. Lepore,^{b,c} Mariam F. Salazar,^{b,1} Guo Shiou Foo,^d
Brian H. Davison,^e Zili Wu,^{d,f} Chaitanya K. Narula*^{b,c}

^a Energy & Transportation Science Division, Oak Ridge National Laboratory,
Oak Ridge, TN 37831, USA

^b Materials Science & Technology Division, Oak Ridge National Laboratory

^c Bredeesen Center for Interdisciplinary Research, 821 Volunteer Blvd., The University of
Tennessee, Knoxville, TN 37996, USA

^d Chemical Sciences Division, Oak Ridge National Laboratory

^e BioSciences Division, Oak Ridge National Laboratory

^f The Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Manuscript for submission to:
Green Chemistry

*Corresponding author: Chaitanya K. Narula

E-mail address: narulack@ornl.gov

¹ Current address: Technip Stone & Webster Process Technology, Inc., 56 Woodrock Rd., Weymouth, MA 02189

This manuscript has been authored by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725 with the U.S. Department of Energy. The United States Government retains and the publisher, by accepting the article for publication, acknowledges that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

Table S1. Unit cell parameters obtained from the Rietveld refinements and calculated cell volumes for the ZSM-5 phase.

Sample	a (Å)	b (Å)	c (Å)	Volume (Å ³)
H-ZSM-5	20.14	19.95	13.42	5392
6.2% Ga-ZSM-5	20.14	19.94	13.42	5389
1.7% Ga-ZSM-5	20.13	19.93	13.41	5378
Physical mixture 5.9% Ga ₂ O ₃ /H-ZSM-5	20.14	19.94	13.42	5388

Table S2. Surface species atomic ratio based on the XPS analysis

	Si/Al	Ga/Si
4.4% Ga-ZSM-5 with uniform distribution	11.5	0.05
4.4% Ga-ZSM-5	13.8	0.11

Table S3. Liquid (C₅₊) hydrocarbon distributions for various catalysts at 450 °C and 1.6 h⁻¹

	C ₅₊ product distribution, wt%					C ₅₊ yield
	Paraffins	Olefins	Aromatics	BTX	Benzene	
H-ZSM-5	6.6	10.6	82.8	80.3	14.1	25.5
Physical mixture Ga ₂ O ₃ /H-ZSM-5 (5.9%) before reduction	6.9	14.0	79.1	74.1	12.0	26.4
Physical mixture Ga ₂ O ₃ /H-ZSM-5 (15%) before reduction	7.2	9.6	83.2	79.0	13.1	24.7
Physical mixture Ga ₂ O ₃ /H-ZSM-5 (50%) before reduction	9.6	9.3	81.1	77.0	12.8	24.2
Physical mixture Ga ₂ O ₃ /H-ZSM-5 (5.9%) after reduction	0.6	0.7	99	94	22.9	52
4.4% Ga-ZSM-5 ion exchange	0.9	2.0	97	88	23.6	52
Physical mixture Ga ₂ O ₃ /H-ZSM-5 (15%) after reduction	1.6	2.2	96	90	20.9	47
Physical mixture Ga ₂ O ₃ /H-ZSM-5 (50%) before reduction	1.7	2.5	96	88	20	44

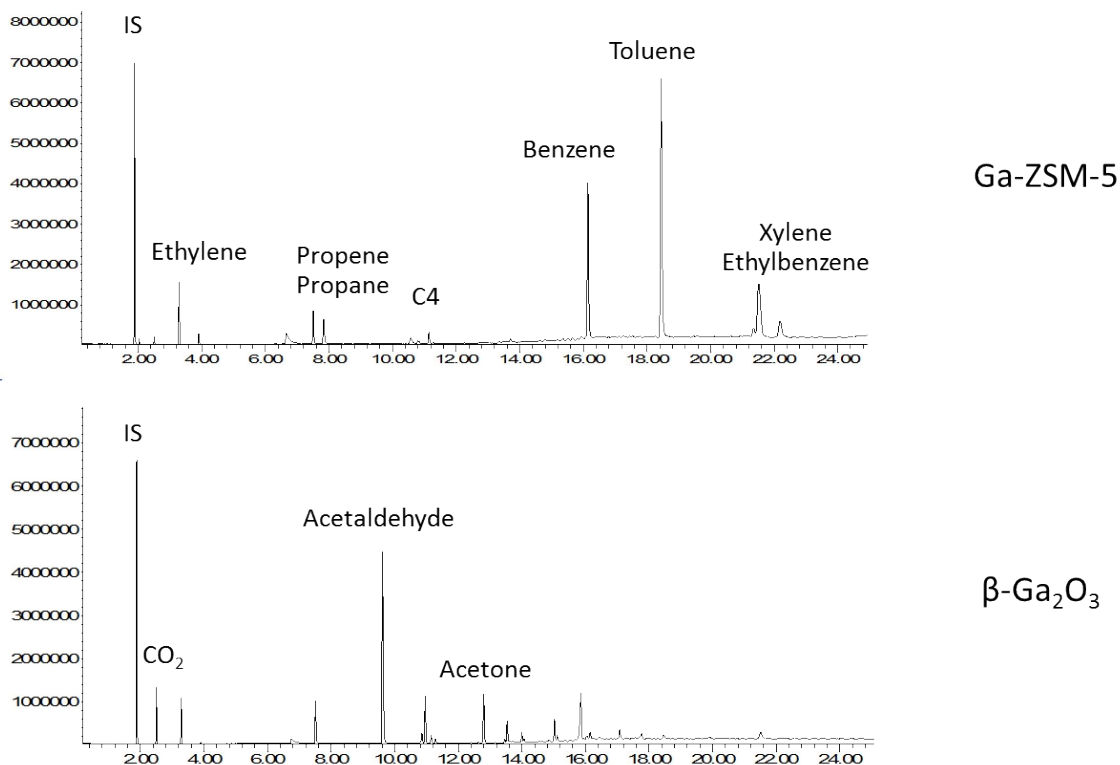


Fig. S1. GC chromatography comparison between Ga-ZSM-5 and β -Ga₂O₃. IS: internal standard nitrogen

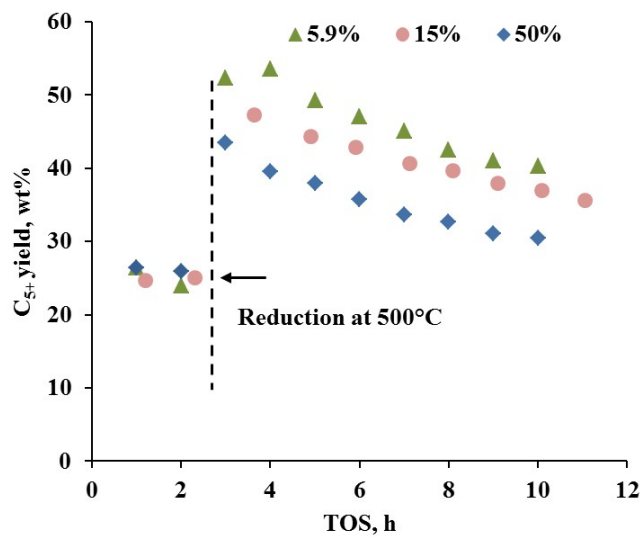


Fig. S2. C₅₊ yield for physical mixtures of Ga₂O₃/H-ZSM-5 with different Ga loadings before and after hydrogen reduction pretreatment at 500 °C. Reaction condition: 450 °C and 1.6 h⁻¹.

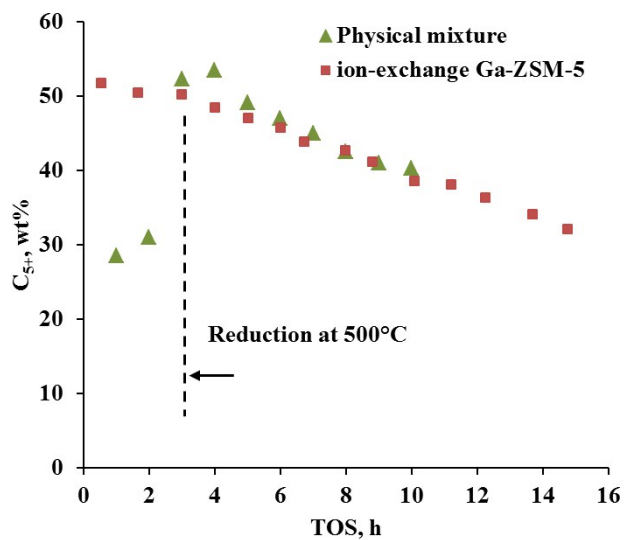
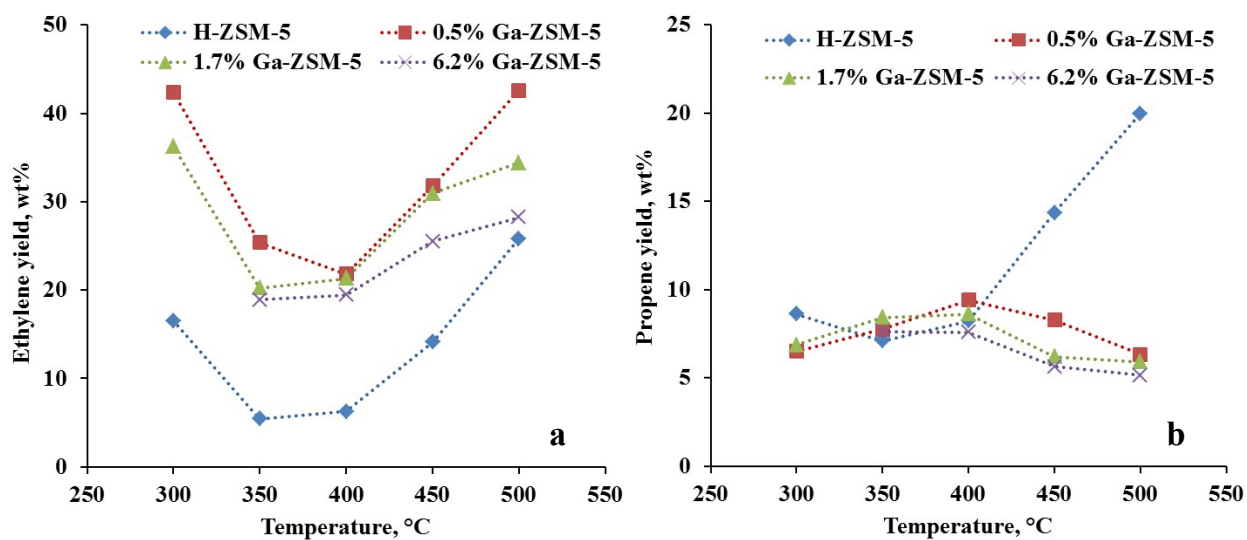


Fig. S3. Liquid (C_{5+}) hydrocarbon yield for ion-exchange 4.4% Ga-ZSM-5 and physical mixture 5.9% $Ga_2O_3/H-ZSM-5$ (Ga loading: 4.4%) before and after hydrogen reduction at 500 °C, the ethanol reaction is performed at 450 °C and 1.6 h⁻¹.



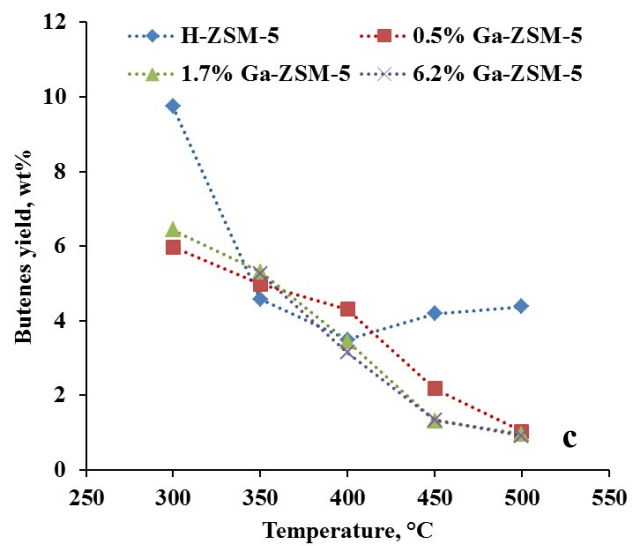


Fig. S4. (a) Ethylene, (b) propene and (c) butenes yield vs temperature for H-ZSM-5 and Ga-ZSM-5 with different Ga loadings