

Supporting Information for:

Kinetics and mechanisms of alcohol dehydration pathways on alumina materials

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S.1. Structural characterization of alumina materials

Scanning electron microscopy (SEM) experiments were performed using a Hitachi SU8230 field emission gun scanning electron microscope at an electron acceleration voltage of 1.0 kV. The SEM images of α -, γ -, and η -Al₂O₃ are shown in Figure S1. Because α -Al₂O₃ is synthesized by heating γ -Al₂O₃ powder, particles of α -Al₂O₃ look like agglomerates of particles of γ -Al₂O₃. The crystal size of γ -Al₂O₃ is too small to distinguish in Figure S1(b). The particle shape of η -Al₂O₃ is plate-like.

S.2. Site densities of ethanol dehydration on different alumina materials at 573 K from in-situ pyridine titration

In-situ pyridine titration was employed to study the site densities of ethanol dehydration on different alumina polymorphs at 573 K. Figure S2 is an example of in-situ pyridine titration. After the synthesis rates of ethene and diethyl ether (DEE) reach the steady state, pyridine was introduced to reactant flow. We extrapolated the initial linear decrease of ethene and DEE formation rates to determine the required amount of pyridine to completely deactivate ethene and DEE synthesis. All data sets from independent titrations at different pyridine pressures on different alumina materials are shown in Table S1.

S.3. Site heterogeneity on alumina materials

S.3.1. Inhibition of ethene and DEE synthesis rates in ethanol-pyridine co-feed studies

The reported ethene and DEE formation rates in this work are net synthesis rates of ethene and DEE. The net synthesis rates ($r_{ethene, net}$ and $r_{DEE, net}$) which we measure experimentally include the formation rates of ethene and DEE from ethanol dehydration ($r_{ethene, deh}$ and $r_{DEE, deh}$) and the DEE decomposition rate ($r_{DEE, dec}$) as shown in Equation S1 and S2.

$$r_{ethene, net} = r_{ethene, deh} + r_{DEE, dec} \quad (S1)$$

$$r_{DEE, net} = r_{DEE, deh} - r_{DEE, dec} \quad (S2)$$

We wish to compare $r_{ethene, deh}$ and $r_{DEE, deh}$ to examine the possibility that distinct active sites catalyze parallel ethanol dehydration reactions on alumina materials. The reaction conditions that we used in the report (573 K and 10% of ethanol conversion on $\gamma\text{-Al}_2\text{O}_3$ and 16% of ethanol conversion on $\eta\text{-Al}_2\text{O}_3$) result in low DEE pressure (0.09 and 0.17 kPa on $\gamma\text{-Al}_2\text{O}_3$ and $\eta\text{-Al}_2\text{O}_3$, respectively) at the reactor outlet, implying that the DEE decomposition rate would be negligible compared to $r_{ethene, deh}$ and $r_{DEE, deh}$, resulting $r_{ethene, net} \cong r_{ethene, deh}$ and $r_{DEE, net} \cong r_{DEE, deh}$ (see also Figure S3 and the discussion in the following paragraph). Therefore, the normalized rates reported in Figure 5 represent the change in $r_{ethene, deh}$ and $r_{DEE, deh}$ with and without pyridine. $r_{ethene, deh}$ and $r_{DEE, deh}$ are differently inhibited by pyridine, implying at least two pools of active sites exist on alumina materials as discussed in section 3.3.

Figure S3 shows observed normalized net synthesis rates ($\frac{r_{ethene, net, w/ pyridine}}{r_{DEE, net, w/ pyridine}}$ and $\frac{r_{ethene, net, w/ pyridine}}{r_{ethene, deh, w/ pyridine}}$) and calculated normalized formation rates from ethanol dehydration ($\frac{r_{ethene, net, w/ pyridine}}{r_{ethene, deh, w/ pyridine}}$ and $\frac{r_{DEE, net, w/ pyridine}}{r_{DEE, deh, w/ pyridine}}$) of ethene and DEE at 623 K using the rate expression and kinetic and thermodynamic parameters that we have reported previously for DEE decomposition at 623 K¹. We calculate $r_{DEE, dec, w/ pyridine}$ using ethanol and DEE pressure (the highest value of DEE pressure at the outlet was used to test the limiting case scenario) and obtain $r_{ethene, deh, w/ pyridine}$ and $r_{DEE, deh, w/ pyridine}$ using Equation S1 and S2. $r_{ethene, net, w/ pyridine}$ and $r_{DEE, net, w/ pyridine}$ are used in the numerator for normalized formation rates from ethanol dehydration to consider the bookend scenario. The normalized formation rate of ethene from ethanol dehydration is slightly higher than the normalized synthesis rate of ethene. Conversely, the normalized formation rate of DEE from ethanol dehydration obtained after adding the rate of DEE decomposition is apparently lower than the normalized synthesis rate of DEE. The distinction between the inhibition of ethene and DEE synthesis rates by pyridine persists even after considering the bookend scenario for DEE decomposition pathways as shown in Figure S3 suggesting the existence of multiple active sites on alumina materials.

S.3.2. 2-propanol partial pressure dependence of olefin and ether synthesis rates at 488 K

The ratio of olefin formation to ether formation rate for parallel 2-propanol dehydration reactions on $\gamma\text{-Al}_2\text{O}_3$ at 488 K as a function of 2-propanol partial pressure is shown in Figure S4. The olefin and ether formation rates for 2-propanol dehydration are from our previous reports². The ratio is noted to be independent of 2-propanol partial pressure at 2-propanol partial pressures exceeding 4 kPa, which will not be the case if the sites for mono- and di-alcohol dehydration are same as discussed in section 3.3.

Reference

- 1 J. F. DeWilde and A. Bhan, *Appl. Catal. A Gen.*, 2015, **502**, 361–369.
- 2 M. Kang, J. F. DeWilde and A. Bhan, *ACS Catal.*, 2015, **5**, 602–612.

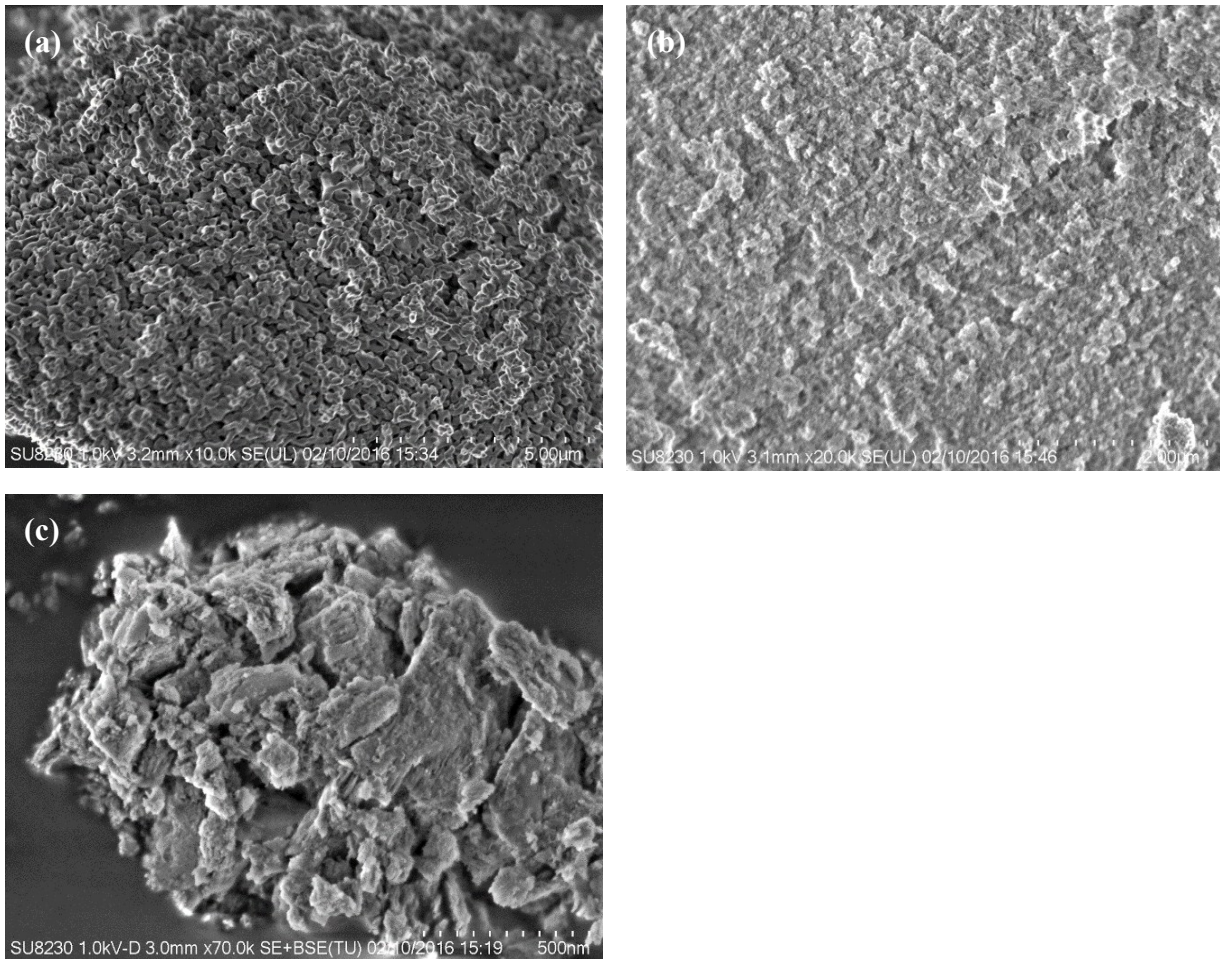


Figure S1. SEM images of (a) α -, (b) γ -, and (c) η - Al_2O_3

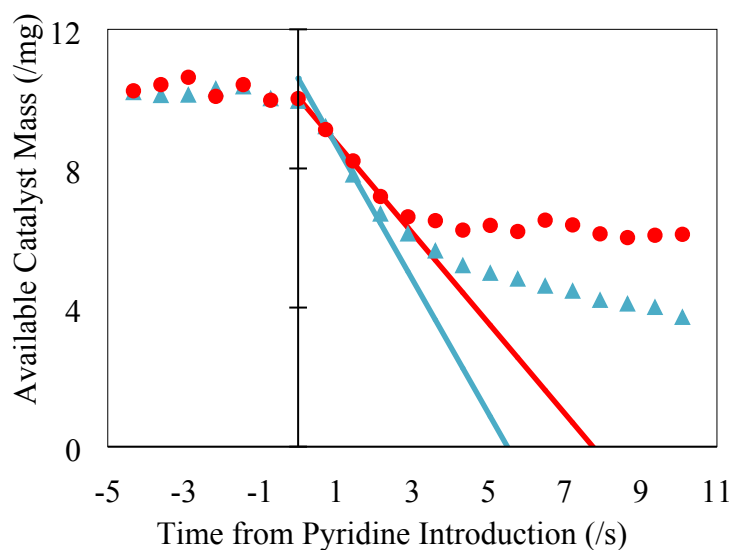


Figure S2. Available catalyst mass for (▲) ethene and (●) DEE formation on 10.2 mg of $\gamma\text{-Al}_2\text{O}_3$ at 573 K with 2.2 kPa of ethanol and 1.0 kPa of water partial pressure (total gas flowrate = $3.4 \text{ cm}^3 \text{ s}^{-1}$) as a function of time from the introduction of 0.02 kPa of pyridine to reactant flow. The blue and red solid lines representing ethene and DEE, respectively, show the linear extrapolation to calculate the pyridine uptake to completely inhibit ethanol dehydration.

Table S1. Numbers of catalytic sites for ethene and DEE formation from parallel ethanol dehydration on ~10 mg of γ - and η -Al₂O₃ at 573 K with 2.2 kPa of ethanol and 1.0 kPa of water partial pressure assessed using in-situ pyridine titration.

Alumina materials	Pyridine partial pressure (/kPa)	Ethene		DEE	
		Pyridine uptake (/10 ⁻⁵ mol g ⁻¹)	Sites per surface area (/nm ⁻²)	Pyridine uptake (/10 ⁻⁵ mol g ⁻¹)	Sites per surface area (/nm ⁻²)
γ -Al ₂ O ₃	0.02	2.3	0.099	1.9	0.082
		2.1	0.091	3.6	0.15
		1.8	0.077	2.6	0.11
		2.3	0.097	1.9	0.079
	0.05	N/A	N/A	3.1	0.13
		3.0	0.13	2.7	0.12
		3.2	0.14	3.1	0.13
		3.3	0.14	3.2	0.14
		2.8	0.12	5.9	0.25
		3.0	0.13	3.8	0.16
		3.2	0.14	3.4	0.14
		3.1	0.13	3.5	0.15
	η -Al ₂ O ₃	0.02	2.4	0.040	6.8
3.4			0.056	5.8	0.097
3.1			0.051	5.1	0.085
2.3			0.038	4.3	0.072
0.05		4.2	0.071	6.3	0.10
		6.1	0.10	4.1	0.068
		4.2	0.071	4.5	0.075
		4.6	0.077	2.8	0.047
		3.7	0.063	8.5	0.14
		4.4	0.074	7.2	0.12
		4.6	0.078	5.2	0.087
		4.5	0.076	4.1	0.068

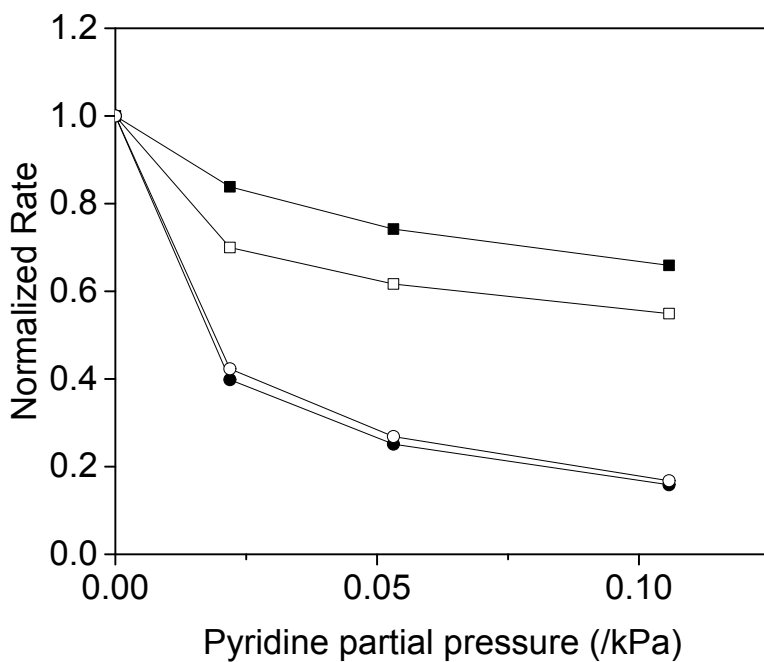


Figure S3. Normalized net synthesis rates (net synthesis rate with pyridine/net synthesis rate without pyridine) of (●) ethene and (■) DEE and normalized ethanol dehydration rates (net synthesis rate with pyridine/formation rate from ethanol dehydration without pyridine) of (○) ethene and (□) DEE for ethanol dehydration at 623 K on 1.1 mg of γ -Al₂O₃ (28% of ethanol conversion) as a function of pyridine partial pressure with 2.2 kPa of ethanol and 1.0 kPa of water partial pressure. Solid lines are meant to guide the eye.

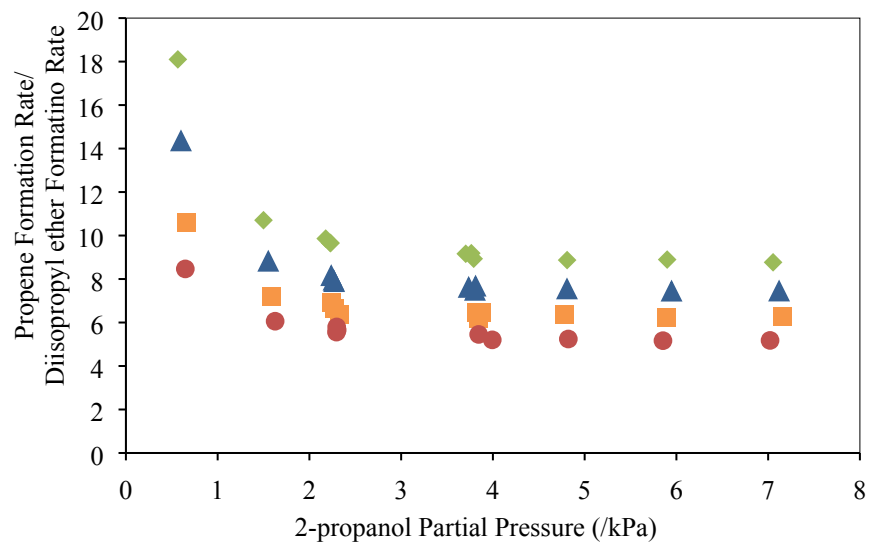


Figure S4. The ratio of propene formation rate to diisopropyl ether formation rate as a function of 2-propanol partial pressure with different water partial pressures (\blacklozenge 0.33, \blacktriangle 0.65, \blacksquare 1.1, and \bullet 2.1 kPa) using 10 mg of γ - Al_2O_3 at 488 K (total gas flow rate = $3.4 \text{ cm}^3 \text{ s}^{-1}$, 2-propanol conversion <10%).