Supplementary Information:

Direct speciation methods to quantify catalytically active species of AlCl₃ in glucose isomerization

Angela M. Norton, Hannah Nguyen, Nicholas L. Xiao, and Dionisios G. Vlachos*

Catalysis Center for Energy Innovation and Department of Chemical and Biomolecular Engineering,

University of Delaware, 221 Academy St., Newark, DE 19716

*Corresponding author: <u>vlachos@udel.edu</u>

Assessment of 3300 HT pH probe and qNMR



= 1.678 and (b) pH = 3 buffer solutions. The solid lines represent the expected pH. Solution temperature control was applied.



Figure S2. Concentration of Al³⁺ measured by ²⁷Al qNMR (closed circles) as a function of HCl concentration, along with OLI model predictions (line). Conditions: 303 K, 5 mM AlCl₃ with HCl concentration between 0 and 200 mM.



Figure S3. Effect of temperature on the distribution of (a) Al^{3+} , (b) AlO(OH), (c) $Al(OH)^{2+}$, and (d) $Al(OH)_2^{1+}$ in 5 mM AlCl₃ as function of HCl concentration, calculated using the OLI software.



Figure S4. pH measured ex situ (closed circles) or in situ (open circles) compared to pH calculated using the OLI speciation software (lines) at (a) 303 K and (b) 413 K. *Ex situ and in situ pH Measurements*



Figure S5. Average particle diameter (nm), obtained from DLS, as function of time. Experimental conditions: 5 mM AlCl₃ and HCl (specified), preheated at (a) 413 K and (b) 363 K for 24 h and cooled to room temperature.



Figure S6. (a) pH and (b) amount of solid vs. time at different HCl initial concentrations. Samples contained 5 mM AlCl₃ and were cooled from 363 K to 303 K prior to measurements.

²⁷Al qNMR Quantification



Figure S7. ²⁷Al qNMR spectra for Al³⁺. Experimental conditions: preheat 363 K for 24 h, 5 mM AlCl₃. qNMR measurements obtained at 363 K.

HCl	Chemical Shift (ppm)	Chemical Shift (Hz)	Intensity (a.u.)	Width (Hz)	Normalized Area
0	1.81 ± 0.08	188.0 ± 2.52	360.03 ± 4.93	7.59 ± 0.01	0.73 ± 0.05
3	1.78 ± 0.14	185.6 ± 2.69	378.6 ± 0.96	7.58 ± 0.01	0.82 ± 0.16
10	1.80 ± 0.09	187.7 ± 2.37	835.4 ± 0.89	7.55 ± 0.01	0.99 ± 0.13
20	1.82 ± 0.02	190.2 ± 2.42	847.2 ± 0.47	7.51 ± 0.01	1.00 ± 0.14
44	1.81 ± 0.02	188.2 ± 0.30	846.2 ± 1.19	7.48 ± 0.01	1.00 ± 0.08
100	1.79 ± 0.01	186.7 ± 0.56	848.6 ± 1.74	7.50 ± 0.04	1.00 ± 0.00

Table S1. Data of ²⁷Al qNMR spectra, obtained at 363 K for 24 h, 5 mM AlCl₃.

HCl	Chemical Shift (ppm)	Chemical Shift (Hz)	Intensity (a.u.)	Width (Hz)	Normalized Area
0	0.78 ± 0.02	82.6 ± 0.25	403.5 ± 0.50	7.25 ± 0.05	0.16 ± 0.04
3	0.81 ± 0.02	84.4 ± 0.25	510.1 ± 0.51	7.14 ± 0.03	0.20 ± 0.05
10	0.81 ± 0.05	84.3 ± 0.50	799.9 ± 0.75	7.10 ± 0.09	0.45 ± 0.05
20	0.81 ± 0.02	$84.0\ \pm 0.25$	1072.5 ± 0.25	6.76 ± 0.09	0.93 ± 0.06
44	0.81 ± 0.07	$84.2\ \pm 0.74$	1232.4 ± 0.25	6.84 ± 0.08	1.00 ± 0.05
100	0.79 ± 0.07	$82.7\ \pm 0.74$	1249.8 ± 0.86	6.84 ± 0.06	1.00 ± 0.11

Table S2. Data of ²⁷Al qNMR spectra, obtained at 413 K for 24 h, 5 mM AlCl₃.

The ²⁷Al qNMR spectra were processed using the Mestrelab Research software (mNOVA). Apodization was 5.09 Hz, zero filling was 64 K, spectra underwent manual phasing, and automatic baseline correction was applied. Error margins correspond to 95% confidence level.



Figure S8. DLS spectra of pre-filtered and post-filtered catalyst solution. Experimental conditions: 5 mM AlCl₃, 0 mM HCl, preheat at 413 K (24 h) and cooled to room temperature.

Measured Aluminum Speciation

HCl (mM)	Al ³⁺ (mM)	Solid Al (mM)	Al(OH) ²⁺ (mM)	$Al(OH)_2^{1+}(mM)$
0	0.80 ± 0.19	3.69 ± 0.08	0.024 ± 0.006	0.009 ± 0.002
3	1.00 ± 0.24	3.50 ± 0.03	0.029 ± 0.007	0.010 ± 0.002
10	2.25 ± 0.24	2.54 ± 0.03	0.057 ± 0.006	0.017 ± 0.001
20	4.65 ± 0.32	0.00 ± 0.00	0.061 ± 0.004	0.009 ± 0.001
44	4.99 ± 0.24	0.00 ± 0.00	0.040 ± 0.002	0.004 ± 0.001

Table S3. Total Aluminum Speciation, 5 mM AlCl₃, 413 K, measurements obtained from experiments.

Table S4. Total Aluminum Speciation, 5 mM AlCl₃, 363 K, measurements obtained from experiments.

HCl (mM)	Al ³⁺ (mM)	Solid Al (mM)	Al(OH) ²⁺ (mM)	Al(OH) ₂ ¹⁺ (mM)
0	3.67 ± 0.19	1.04 ± 0.19	0.027 ± 0.002	0.004 ± 0.001
3	4.02 ± 0.19	0.36 ± 0.19	0.029 ± 0.006	0.005 ± 0.001
10	4.79 ± 0.19	0.03 ± 0.19	0.014 ± 0.002	0.001 ± 0.000
20	4.70 ± 0.19	0 ± 0.19	0.007 ± 0.001	0.001 ± 0.000
44	4.87 ± 0.19	0 ± 0.19	0.003 ± 0.000	0.000 ± 0.000

The equilibrium constants obtained from the OLI software were:

<u>(413 K)</u>	<u>(363 K)</u>
$K_{A,1} = 0.28$	$K_{A,1} = 0.024$
$K_{A,2} = 0.91$	$K_{A,2} = 0.013$

$$[Al(H_2O)_6]^{3+} + H_2O \leftrightarrow [Al(H_2O)_5(OH)]^{2+} + H_3O^+$$
 $K_{A,1}$

$$[Al(H_2O)_6]^{3+} + 2 H_2O \leftrightarrow [Al(H_2O)_4(OH)_2]^{2+} + 2 H_3O^+ \qquad K_{A,2}$$

Initial Rate Constant at 413 K



Figure S9. (a) $-\ln(c_{glucose}/c_{glucose,0})$ vs. time, (b) - (f) conversion of glucose and carbon balance vs. time. Catalyst solutions were preheated at 413 K for 24 h prior to kinetic study. Reaction conditions: glucose 1 wt %, Al to glucose molar ratio 9:100, 413 K, and either (b) 0 mM, (c) 3 mM, (d) 10 mM, (e) 20 mM, or (f) 44 mM HCl.

Initial Rate Constant at 363 K



Figure S10. (a) $-\ln(c_{glucose,0}/c_{glucose,0})$ vs. time, (b) - (f) conversion of glucose and carbon balance vs. time. Catalyst solutions w study. Reaction conditions: glucose 1 wt %, Al to glucose molar ratio 9:100, 363 K, and either (b) 0 mM, (c) 3 mM, (d) 10 m



Figure S11. Glucose conversion as a function of measured Al species' concentrations, normalized to the maximum observed species' concentration (see Table S3 for observed species' concentrations). Catalyst solutions were preheated at 363 K for 24 h prior to kinetic study. Reaction conditions: glucose 1 wt %, Al to glucose molar ratio 9:100, 363 K.