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SUPPLEMENTARY INFORMATION

for

*Integrated Low Carbon H₂ Conversion with In-Situ Carbon
Mineralization from Aqueous Biomass Oxygenate Precursors by
Tuning Reactive Multiphase Chemical Interactions*

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1 *Extent of carbon mineralization*

2 In this study, the estimation of the extent of carbonation was done using both TGA (Thermo
3 Gravimetric Analysis) and TCA (Total Carbon Analysis). The TGA method provided an insight
4 into the presence of different solid phases (e.g., carbonate and hydrate phases as well as organic
5 carbon with distinct decomposition temperature) and the quantification of each phase in the
6 analyzed sample. The TGA technique can be difficult for samples with overlapping weight drop
7 curves. Thus, the TGA method should be used for samples with clear distinction between weight
8 drop curves, and this was the case for carbonated samples in this study. The total carbon reported
9 from the TCA [g of C/g of carbonated solids] was converted into the extent of carbonation by
10 comparing the TCA data with the theoretical carbon capture capacity of the minerals.

11 The determination of the extent of the carbon mineralization with the ladle slag was challenged by
12 the heterogeneous compositions of slag samples. Thus, the extent of mineral carbonation is
13 calculated and estimated based on a careful determination of the chemical phases. First, only Ca-
14 and Mg- based oxides and silicates which make up > 65 wt.% of NuLD (**Table 1**) are considered
15 to react and produce Ca- and Mg-carbonates, while other metals such as Fe and Al are considered
16 unlikely to dissolve at pH greater than 7.5 and react to produce respective carbonates. For example,
17 Iron oxides can react with CO₂ to form siderite (FeCO₃), however, it has been reported that the
18 formation of siderite is inhibited by the low solubility of iron oxide .⁴³ Second, only non-
19 carbonated Ca and Mg species are considered for carbon mineralization. The pH of NuLD in
20 solution used in this study was measured to be 12.17. Dissolution of solid calcium and magnesium
21 carbonate at pH greater than 7.5 in material systems bearing alkaline industrial residues and
22 solvents is negligible.⁴⁰ Based on the above assumptions, the extent of carbon mineralization was

1 calculated. Where the TGA method was used to analyze the carbonated solids, Eq. (2) was used to
2 determine the extent of carbon mineralization. On the other hand, Eq. (3) was used when TCA was
3 used for the solid analysis.

$$4 \text{ Extent of carbon mineralization (\%)} = \frac{\frac{TGA}{(1-TGA)}}{\text{theoretical maximum CO}_2 \text{ storage capacity}} \times 100(\%) \quad (\text{S1})$$

$$5 \text{ Extent of carbon mineralization (\%)} = \frac{\frac{3.67 \cdot TCA}{(1-3.67 \cdot TCA)}}{\text{theoretical maximum CO}_2 \text{ storage capacity}} \times 100(\%) \quad (\text{S2})$$

6 TGA in **Eq. (S1)** represents the percent weight change of the carbonated solid at its calcination
7 temperature, and TCA in **Eq. (S2)** represents the weight fraction of carbon in the carbonated
8 sample with a unit of (weight of carbon/ weight of sample). The coefficient 3.67 is introduced
9 into **Eq. (S2)** to account for the ratio of the molecular weights of CO₂ to carbon. In reactions
10 where ladle slag was used as the alkaline sorbent, the theoretical maximum CO₂ capacity was
11 calculated after subtracting the initial amount of residual CO₂ which was estimated to be 0.02 g (±
12 2%) CO₂ per g of NuLD.

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1 **Table S1.** Reactions involved with complete conversions of various biomass oxygenates with
 2 and without an alkaline sorbent. *M* represents either Ca or Mg metal.

Biomass Oxygenates	Reaction stoichiometry
Methanol (CH ₃ OH)	$\text{CH}_4\text{O}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{CO}_{2(\text{g})} + 3\text{H}_{2(\text{g})}$
Ethylene glycol (C ₂ H ₆ O ₂)	$\text{C}_2\text{H}_6\text{O}_{2(\text{aq})} + 2\text{H}_2\text{O}_{(\text{l})} \rightarrow 2\text{CO}_{2(\text{g})} + 5\text{H}_{2(\text{g})}$
Glycerol (C ₃ H ₈ O ₃)	$\text{C}_3\text{H}_8\text{O}_{3(\text{aq})} + 3\text{H}_2\text{O}_{(\text{l})} \rightarrow 3\text{CO}_{2(\text{g})} + 7\text{H}_{2(\text{g})}$
Acetate Sodium (C ₂ H ₃ O ₂ Na)	$\text{C}_2\text{H}_3\text{O}_2\text{Na}_{(\text{aq})} + 3\text{H}_2\text{O}_{(\text{l})} \rightarrow \text{CO}_{2(\text{g})} + 4\text{H}_{2(\text{g})} + \text{NaHCO}_{3(\text{aq})}$
Formate (CH ₂ O ₂ Na)	$\text{CHO}_2\text{Na}_{(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow \text{H}_{2(\text{g})} + \text{NaHCO}_{3(\text{aq})}$

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Biomass Oxygenates	Reaction stoichiometry with in-situ CO ₂ capture
Methanol (CH ₃ OH)	$\text{CH}_4\text{O}_{(\text{aq})} + \text{M}(\text{OH})_{2(\text{aq})} \rightarrow \text{MCO}_{3(\text{s})} + 3\text{H}_{2(\text{g})}$
Ethylene glycol (C ₂ H ₆ O ₂)	$\text{C}_2\text{H}_6\text{O}_{2(\text{aq})} + 2\text{M}(\text{OH})_{2(\text{aq})} \rightarrow 2\text{MCO}_{3(\text{s})} + 5\text{H}_{2(\text{g})}$
Glycerol (C ₃ H ₈ O ₃)	$\text{C}_3\text{H}_8\text{O}_{3(\text{aq})} + 3\text{M}(\text{OH})_{2(\text{aq})} \rightarrow 3\text{MCO}_{3(\text{s})} + 7\text{H}_{2(\text{g})}$
Acetate Sodium (C ₂ H ₃ O ₂ Na)	$\text{C}_2\text{H}_3\text{O}_2\text{Na}_{(\text{aq})} + 2\text{M}(\text{OH})_{2(\text{aq})} + \text{H}_2\text{O}_{(\text{l})} \rightarrow 2\text{MCO}_{3(\text{s})} + 4\text{H}_{2(\text{g})} + \text{NaOH}_{(\text{aq})}$
Formate (CH ₂ O ₂ Na)	$\text{CHO}_2\text{Na}_{(\text{aq})} + \text{M}(\text{OH})_{2(\text{aq})} \rightarrow \text{MCO}_{3(\text{s})} + \text{H}_{2(\text{g})} + \text{NaOH}_{(\text{aq})}$

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Table S2. Gas product yields for hydrothermal conversion of biomass oxygenates with and without an alkaline sorbent.

Oxygenate	Catalyst	Reactor Mode	Time (hours)	Yield H ₂	Yield CO ₂	Yield CH ₄	Yield CO	Yield MCO ₃
Methanol	No Catalyst	NA	1	0.05(±0.01)	0.1(±0.01)	0.0(±0.0)	0.00(±0.00)	0.00(±0.00)
Methanol	No Catalyst	NA	3	0.41(±0.05)	0.97(±0.11)	0.0(±0.0)	0.00(±0.00)	0.00(±0.00)
Methanol	No Catalyst	NA	6	0.97(±0.10)	2.39(±0.25)	0.0(±0.0)	0.00(±0.00)	0.00(±0.00)
Methanol	No Catalyst	M1	1	0.31(±0.05)	0.00(±0.00)	0.0(±0.0)	0.00(±0.00)	5.35(±1.13)
Methanol	No Catalyst	M1	3	0.88(±0.09)	0.01(±0.01)	0.0(±0.0)	0.00(±0.00)	5.89(±1.82)
Methanol	No Catalyst	M1	6	3.21(±0.35)	0.00(±0.00)	0.0(±0.0)	0.00(±0.00)	10.91(±0.68)
Methanol	No Catalyst	M2	1	0.11(±0.01)	0.00(±0.00)	0.0(±0.0)	0.00(±0.00)	4.79(±0.64)
Methanol	No Catalyst	M2	3	3.45(±0.39)	0.00(±0.00)	0.0(±0.0)	0.00(±0.00)	5.35(±1.40)
Methanol	No Catalyst	M2	6	4.82(±0.54)	0.40(±0.07)	0.0(±0.0)	0.00(±0.00)	10.58(±4.33)
Methanol	Pt/Al ₂ O ₃	NA	1	54.80(±8.08)	61.16(±8.53)	0.99(±0.14)	0.00(±0.00)	0.00(±0.00)
Methanol	Pt/Al ₂ O ₃	NA	3	56.85(±6.76)	59.00(±6.98)	1.08(±0.13)	0.00(±0.00)	0.00(±0.00)
Methanol	Pt/Al ₂ O ₃	NA	6	64.49(±6.92)	70.42(±7.49)	1.33(±0.14)	0.54(±0.69)	0.00(±0.00)
Methanol	Pt/Al ₂ O ₃	M1	1	67.97(±7.40)	0.03(±0.01)	0.04(±0.08)	0.00(±0.00)	77.35(±8.30)
Methanol	Pt/Al ₂ O ₃	M1	3	73.06(±8.48)	0.04(±0.01)	0.13(±0.01)	0.00(±0.00)	77.19(±8.49)
Methanol	Pt/Al ₂ O ₃	M1	6	76.23(±8.20)	0.11(±0.02)	0.19(±0.02)	0.00(±0.00)	88.37(±7.24)
Methanol	Pt/Al ₂ O ₃	M2	1	35.03(±3.94)	7.28(±2.41)	0.83(±0.10)	0.00(±0.00)	24.71(±2.10)
Methanol	Pt/Al ₂ O ₃	M2	3	70.96(±8.82)	2.51(±0.55)	0.44(±0.05)	0.00(±0.00)	62.83(±10.07)
Methanol	Pt/Al ₂ O ₃	M2	6	71.34(±6.07)	2.83(±1.67)	0.44(±0.02)	0.00(±0.00)	81.89(±1.35)

Methanol	Ni/Al ₂ O ₃	NA	1	18.31(±1.95)	32.26(±4.13)	20.79(±2.21)	0.00(±0.00)	0.00(±0.00)
Methanol	Ni/Al ₂ O ₃	NA	3	16.27(±2.59)	45.18(±6.23)	50.46(±7.38)	0.00(±0.00)	0.00(±0.00)
Methanol	Ni/Al ₂ O ₃	NA	6	12.59(±1.81)	44.15(±5.88)	57.89(±8.43)	0.00(±0.00)	0.00(±0.00)
Methanol	Ni/Al ₂ O ₃	M1	1	56.43(±6.11)	0.02(±0.01)	5.63(±0.64)	0.00(±0.00)	73.09(±4.74)
Methanol	Ni/Al ₂ O ₃	M1	3	59.47(±6.24)	0.02(±0.00)	5.43(±0.56)	0.00(±0.00)	78.86(±7.89)
Methanol	Ni/Al ₂ O ₃	M1	6	57.04(±6.08)	0.50(±0.16)	6.78(±1.41)	0.00(±0.00)	72.40(±11.41)
Methanol	Ni/Al ₂ O ₃	M2	1	20.88(±2.23)	1.16(±0.30)	3.95(±0.46)	0.00(±0.00)	60.93(±1.45)
Methanol	Ni/Al ₂ O ₃	M2	3	48.58(±4.84)	0.09(±0.01)	5.01(±0.46)	0.00(±0.00)	65.00(±2.08)
Methanol	Ni/Al ₂ O ₃	M2	6	74.77(±7.54)	0.59(±0.17)	2.95(±0.31)	0.00(±0.00)	79.98(±10.05)
Formate	Ni/Al ₂ O ₃	NA	3	44.74(±9.05)	7.14(±0.78)	4.50(±1.02)	0.00(±0.00)	0.00(±0.00)
Formate	Ni/Al ₂ O ₃	M2	3	65.21(±3.86)	0.04(±0.04)	1.15(±0.06)	0.00(±0.00)	63.52(±0.34)
Formate	Pt/Al ₂ O ₃	NA	3	71.36(±4.02)	15.11(±1.02)	0.22(±0.02)	0.00(±0.00)	0.00(±0.00)
Formate	Pt/Al ₂ O ₃	M2	3	73.05(±4.54)	2.26(±1.54)	0.2(±0.02)	0.00(±0.00)	72.28(±2.38)
Acetate	Ni/Al ₂ O ₃	NA	3	2.14(±0.57)	1.88(±0.32)	0.71(±0.21)	0.00(±0.00)	0.00(±0.00)
Acetate	Ni/Al ₂ O ₃	M2	3	8.34(±0.78)	1.14(±0.17)	13.83(±1.20)	0.00(±0.00)	19.55(±2.21)
Acetate	Pt/Al ₂ O ₃	NA	3	3.25(±0.30)	12.31(±1.05)	33.47(±2.96)	0.00(±0.00)	0.00(±0.00)
Acetate	Pt/Al ₂ O ₃	M2	3	9.34(±0.91)	0.83(±0.22)	13.57(±1.17)	0.00(±0.00)	36.52(±2.29)
Glycerol	Ni/Al ₂ O ₃	NA	3	15.15(±0.19)	44.11(±1.99)	32.14(±1.28)	0.00(±0.00)	0.00(±0.00)
Glycerol	Ni/Al ₂ O ₃	M2	3	73.38(±3.29)	0.12(±0.01)	7.09(±0.41)	0.00(±0.00)	73.94(±9.59)
Glycerol	Pt/Al ₂ O ₃	NA	3	49.88(±0.29)	61.89(±1.05)	15.74(±0.03)	0.00(±0.00)	0.00(±0.00)
Glycerol	Pt/Al ₂ O ₃	M2	3	68.59(±0.43)	1.86(±0.09)	6.64(±0.05)	0.00(±0.00)	77.06(±11.86)
Ethylene Glycol	Ni/Al ₂ O ₃	NA	3	19.16(±0.23)	46.33(±2.09)	30.18(±0.18)	0.00(±0.00)	0.00(±0.00)

Ethylene Glycol	Ni/Al ₂ O ₃	M2	3	90.90(±0.02)	0.48(±0.01)	3.68(±0.02)	0.00(±0.00)	85.27(±2.44)
Ethylene Glycol	Pt/Al ₂ O ₃	NA	3	79.48(±1.12)	90.32(±1.28)	2.11(±0.04)	0.00(±0.00)	0.00(±0.00)
Ethylene Glycol	Pt/Al ₂ O ₃	M2	3	85.50(±0.72)	1.10(±0.18)	0.43(±0.01)	0.00(±0.00)	97.52(±1.15)

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1 **Table S3.** Summary of the Reactions Representing water dissociation and CO₂ hydration

Phenomena	Reactions	Equilibrium Constant
Water dissociation	$\text{H}_2\text{O}_{(l)} \rightarrow \text{H}^+_{(aq)} + \text{OH}^-_{(aq)}$	$K_w = 10^{-13.997}$
	$\text{CO}_{2(aq)} + \text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{CO}_3^*_{(aq)}$	$k_1 = 10^{-1.46}$
CO₂ hydration	$\text{H}_2\text{CO}_3^*_{(aq)} \rightarrow \text{HCO}_3^-_{(aq)} + \text{H}^+_{(aq)}$	$k_2 = 10^{-6.33}$
	$\text{HCO}_3^-_{(aq)} \rightarrow \text{CO}_3^{2-}_{(aq)} + \text{H}^+_{(aq)}$	$k_3 = 10^{-10.33}$

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3 To calculate the partial pressure of CO₂ in this systems, the maximum possible concentration of
 4 CO₂ was obtained by assuming complete conversion of methanol in Reaction 1, S.I Table 1 . The
 5 concentrations of carbonic acid, bicarbonate (HCO³⁻), and carbonate (CO₃²⁻) species at total
 6 carbon supply between 0 – 1.05 M was computed using the equations below and the distribution
 7 is shown in S.I Figure 1.

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$$9 \quad [\text{HCO}_3^-_{(aq)}] = ([\text{H}_2\text{CO}_3^*_{(aq)}] * k_2) / [\text{H}^+_{(aq)}] \quad (\text{S.I } 1)$$

$$10 \quad [\text{CO}_3^{2-}_{(aq)}] = ([\text{HCO}_3^-_{(aq)}] * k_3) / [\text{H}^+_{(aq)}] \quad (\text{S.I } 2)$$

$$11 \quad C_{\text{TOT}} = [\text{H}_2\text{CO}_3^*_{(aq)}] + [\text{HCO}_3^-_{(aq)}] + [\text{CO}_3^{2-}_{(aq)}] \quad (\text{S.I } 3)$$

$$12 \quad [\text{H}_2\text{CO}_3^*_{(aq)}] = C_{\text{TOT}} / (1 + (k_2 / [\text{H}^+_{(aq)}]) + ((k_2 * k_3) / ([\text{H}^+_{(aq)}]^2)) \quad (\text{S.I } 4)$$

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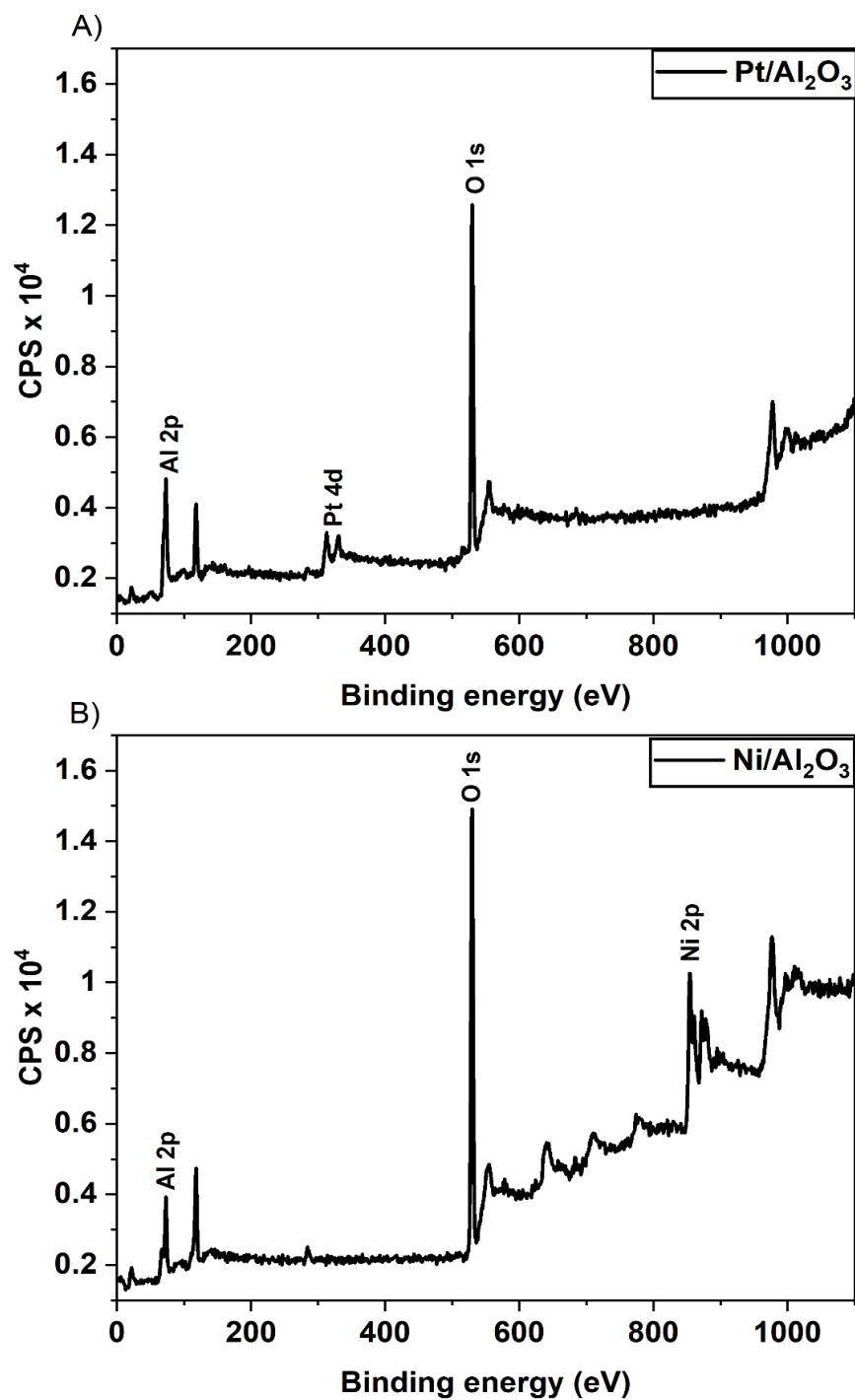
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Table S4. pH distribution of solutions.

Phenomena	pH of feedstock solution without Ca(OH)₂ in aqueous phase	pH of feedstock solution with Ca(OH)₂ in aqueous phase
Methanol (CH ₃ OH)	6.43	12.27
Ethylene glycol (C ₂ H ₆ O ₂)	4.88	12.25
Glycerol (C ₃ H ₈ O ₃)	5.09	12.25
Acetate Sodium (C ₂ H ₃ O ₂ Na)	7.67	12.27
Formate (CH ₂ O ₂ Na)	7.56	12.29

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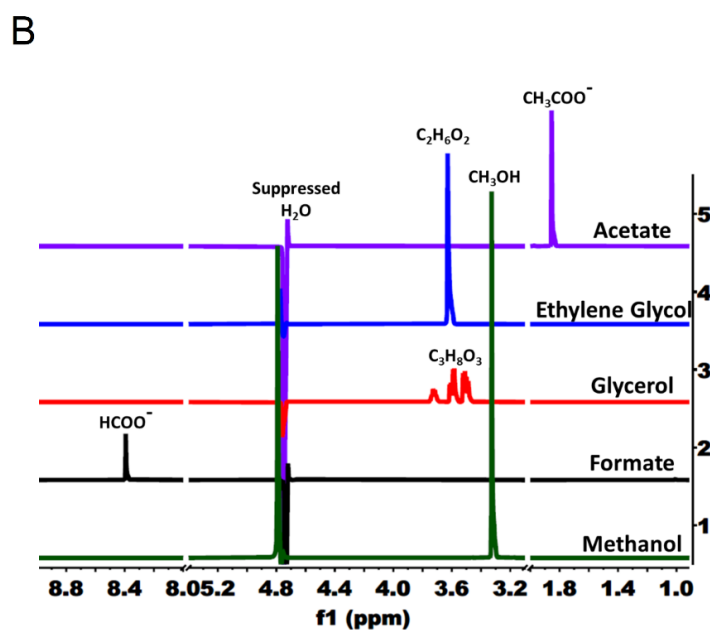
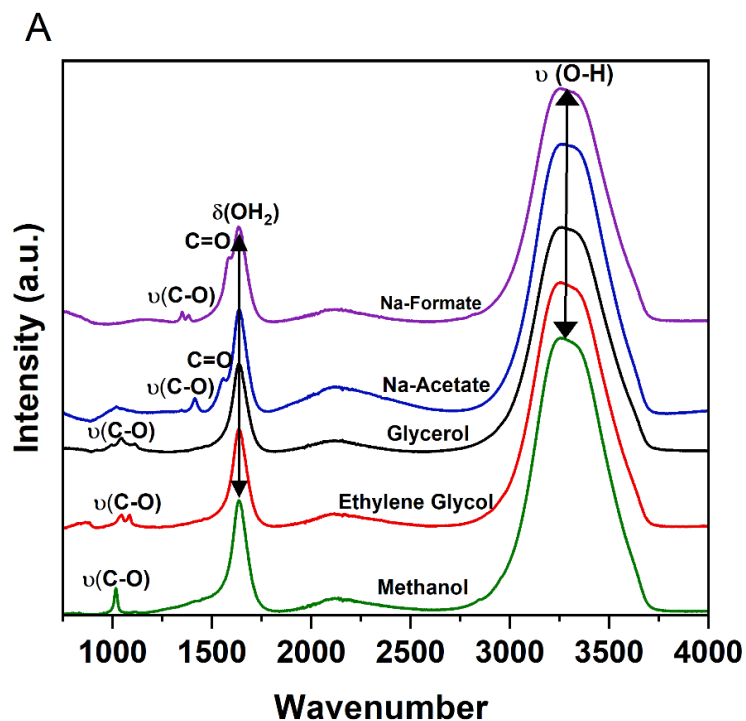


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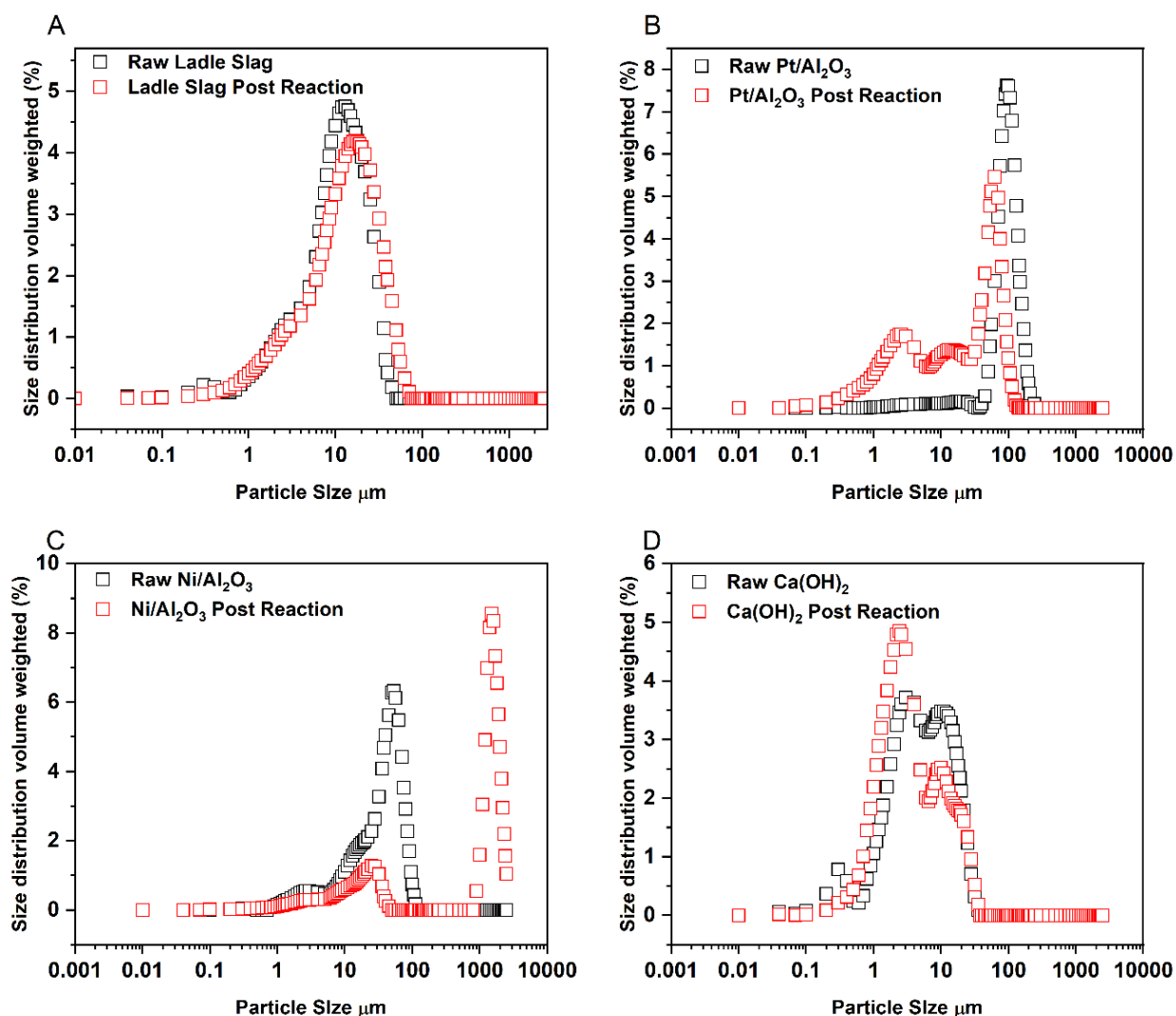
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Figure S1. XPS survey scan for a) Pt/Al₂O₃, and b) Ni/Al₂O₃.



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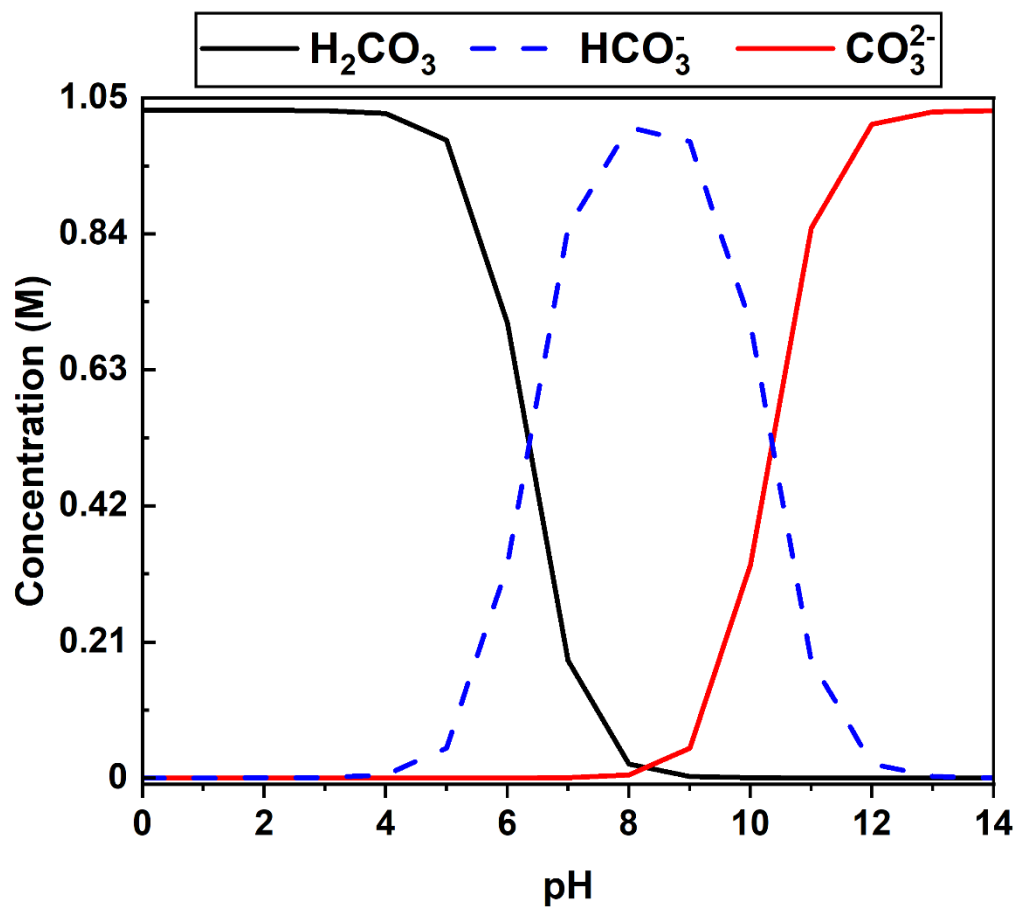
2 **Figure S2.** a) FTIR spectra of 3wt% methanol, formate glycerol, ethylene glycol and acetate
 3 feedstocks.) NMR spectra of 3wt% methanol, formate glycerol, ethylene glycol and acetate
 4 feedstocks.



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2 **Figure S3.** Volume weighted particle size distributions for: (a) Ladle Slag before and after reaction
 3 using 3wt% model oxygenate bearing wastewater as feedstock, (b) Pt/ Al_2O_3 , catalyst before and
 4 after reaction using 3wt% methanol as feedstock in the absence of an alkaline sorbent, (c) Ni/ Al_2O_3
 5 catalyst before and after reaction using 3wt% methanol as feedstock in the absence of an alkaline
 6 sorbent, and (d) $\text{Ca}(\text{OH})_2$ before and after reaction using 3wt% methanol as feedstock. Reactions
 7 were carried out at 50 bar and temperatures of 240 $^\circ\text{C}$.

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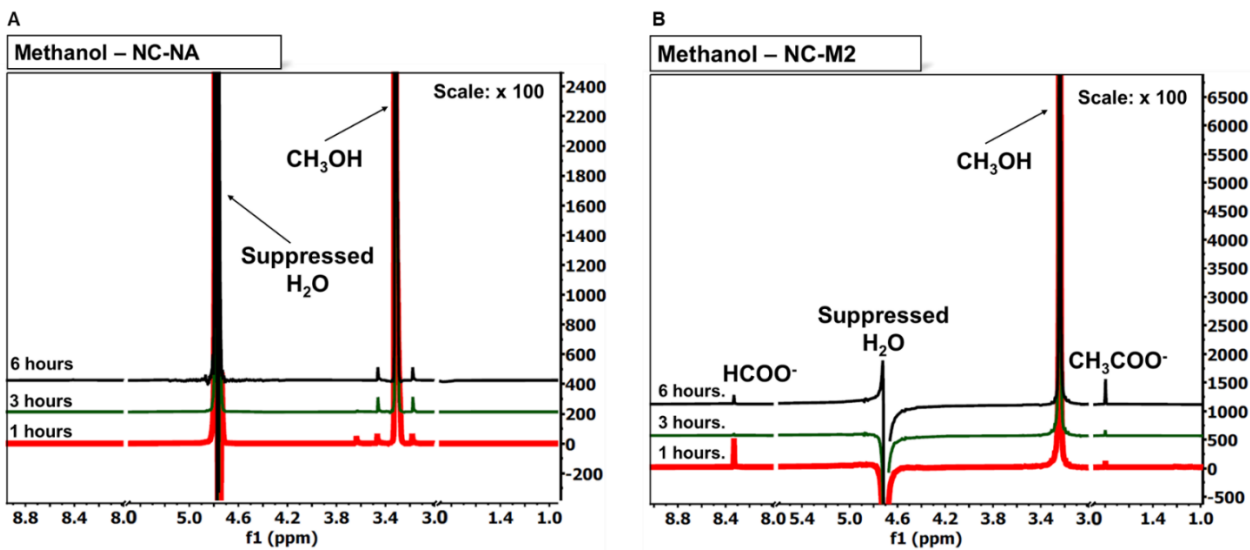


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2 **Figure S4.** The concentrations of [H₂CO₃*_(aq)], [HCO₃⁻_(aq)], and [CO₃²⁻_(aq)] as a function of pH in
 3 a closed system at maximum CO₂ concentration of ~ 1M.

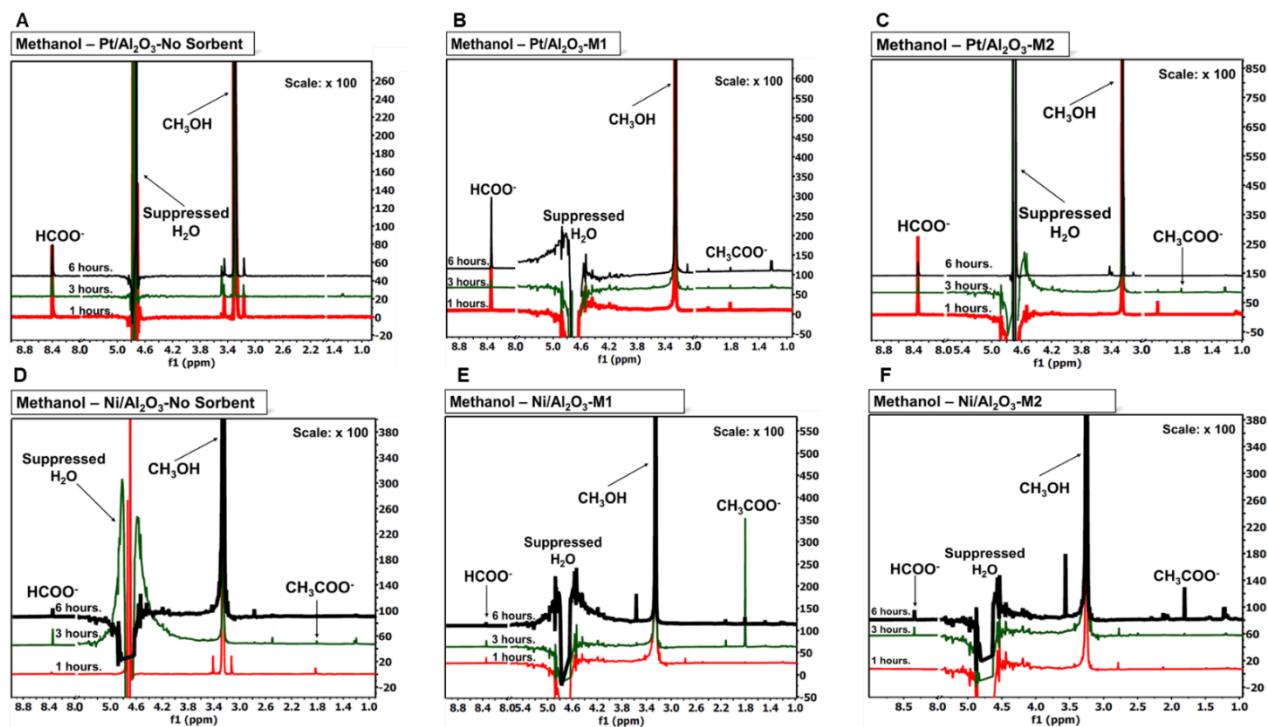
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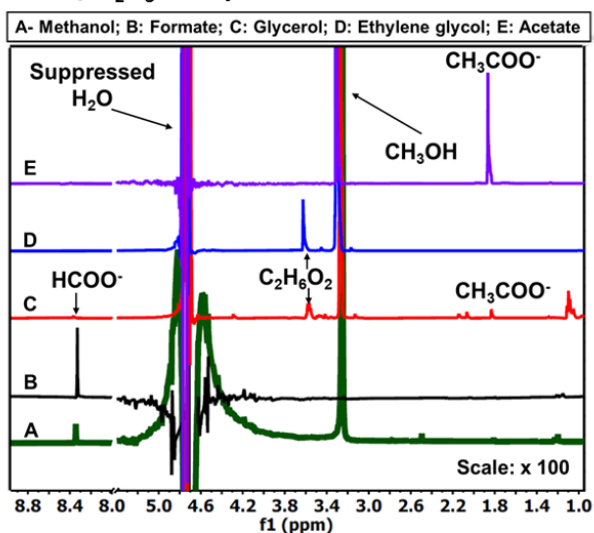
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Figure S5. NMR analysis for liquid product from reforming 3wt% methanol without a catalyst a) no catalyst and no alkaline sorbent, b) no catalyst with an alkaline sorbent using the mode 2 configuration. Reactions were carried out at 50 bar, and temperatures of 240⁰C.

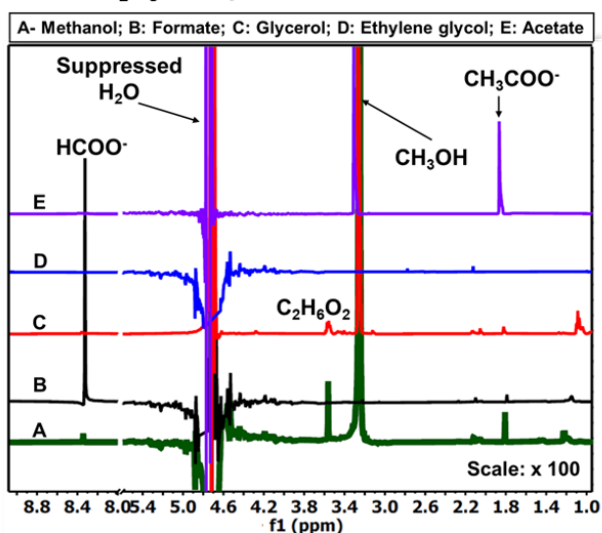


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 3 **Figure S6.** NMR analysis for liquid product from reforming 3wt% methanol in the presence of a
 4 catalyst a) reforming was carried out over Pt/Al₂O₃ catalyst without an alkaline sorbent. b)
 5 reforming was carried out using Pt/Al₂O₃ catalyst with an alkaline sorbent using the mode 1
 6 configuration c) reforming was carried out using Pt/Al₂O₃ catalyst with an alkaline sorbent using
 7 the mode 2 configuration. d) reforming was carried out over Ni/Al₂O₃ catalyst without an alkaline
 8 sorbent, e) reforming was carried out using Ni/Al₂O₃ catalyst with an alkaline sorbent using the
 9 mode 1 configuration f) reforming was carried out using Ni/Al₂O₃ catalyst with an alkaline sorbent
 10 using the mode 2 configuration Reactions were carried out at 50 bar, and temperatures of 240⁰C.

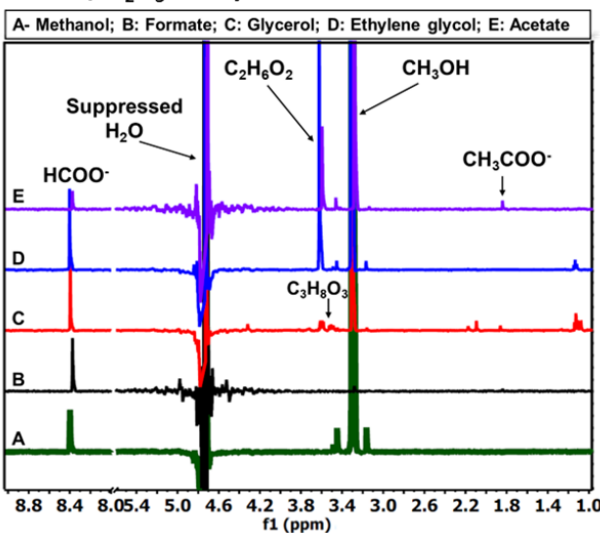
A: Ni/Al₂O₃ Catalyst - NA



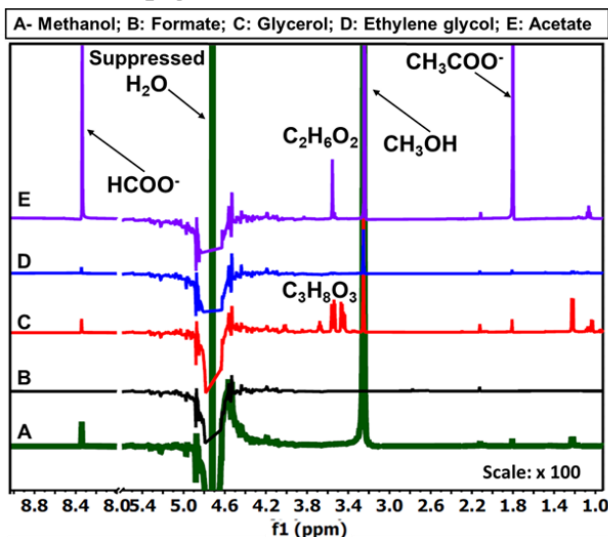
B: Ni/Al₂O₃ Catalyst – Alkaline Sorbent



C : Pt/Al₂O₃ Catalyst - NA



D : Pt/Al₂O₃ Catalyst – Alkaline Sorbent

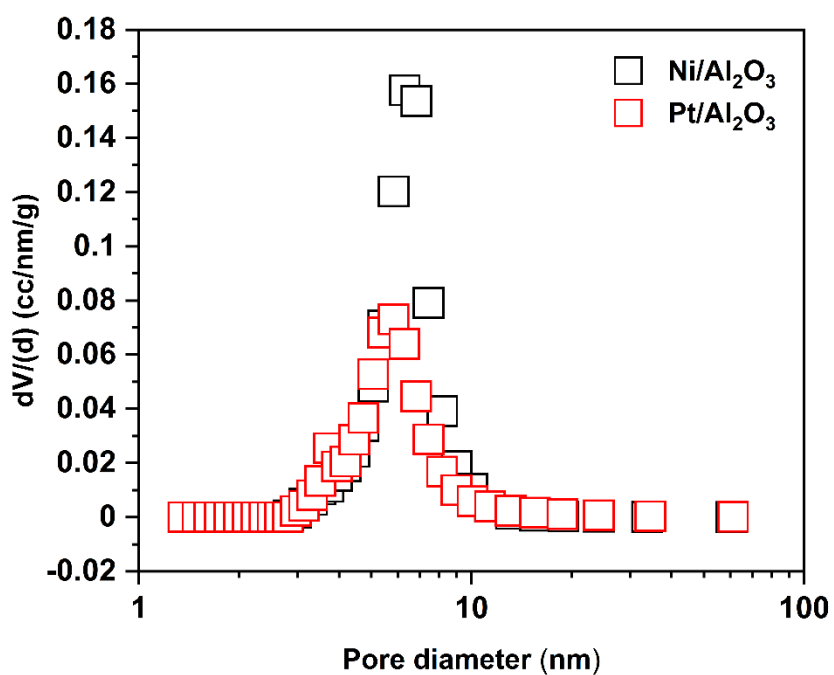
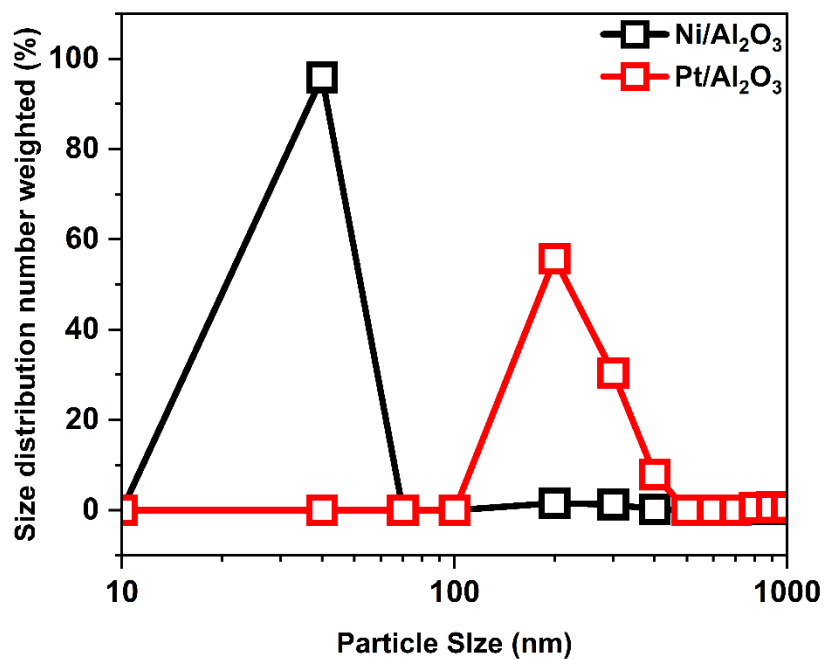


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2 **Figure S7.** NMR analysis for liquid product from reforming 3wt% methanol, formate, glycerol,
 3 ethylene glycol, and acetate over a catalyst a) reforming was carried out over Ni/Al₂O₃ catalyst
 4 without an alkaline sorbent. b) reforming was carried out using Ni/Al₂O₃ catalyst with an alkaline
 5 sorbent using the mode 2 configuration. c) reforming was carried out over Pt/Al₂O₃ catalyst
 6 without an alkaline sorbent. d) reforming was carried out using Pt/Al₂O₃ catalyst with an alkaline
 7 sorbent using the mode 2 configuration.

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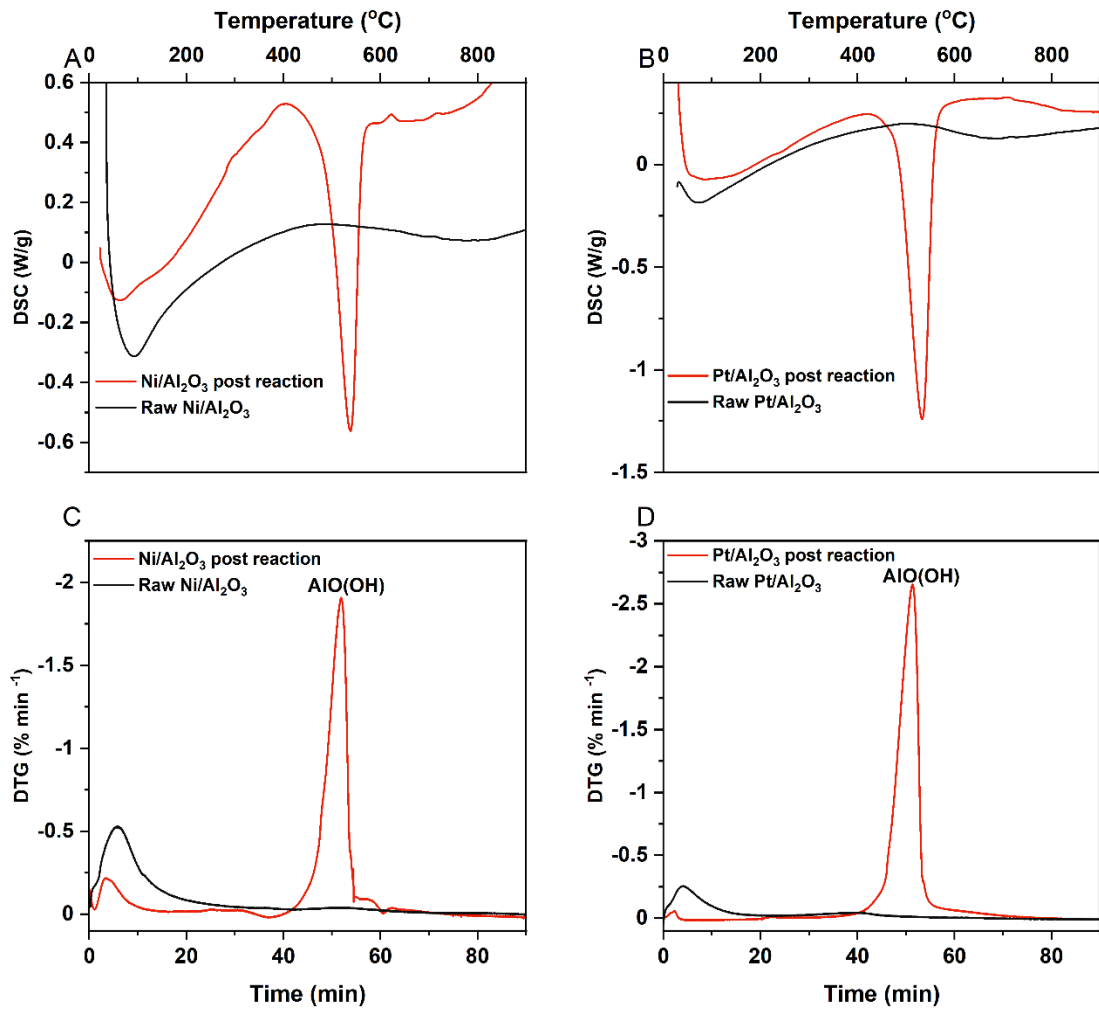
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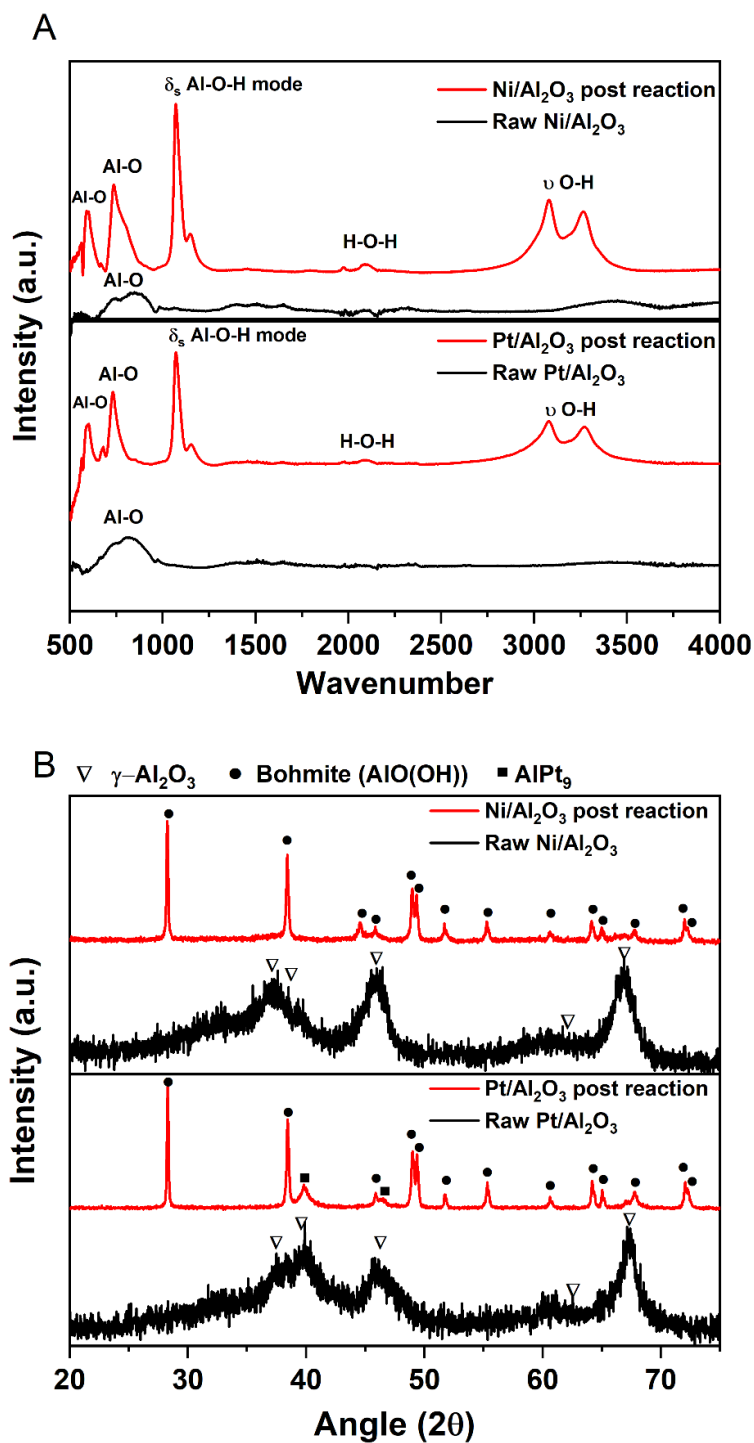
2 **Figure S8.** a) Number weighted particle size distributions and b) pore size distribution of catalysts
 3 used for experiments.

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Figure S9. DTG and DSC curve for Ni/Al₂O₃ and Pt/Al₂O₃ catalyst before and after reaction



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2 **Figure S10.** a) FTIR pattern for Ni/Al₂O₃ and Pt/Al₂O₃ before and after using 3 wt% methanol
 3 as feedstock.in the absence of an alkaline sorbent. b) XRD pattern for Ni/Al₂O₃ and Pt/Al₂O₃
 4 before and after using 3wt% methanol as feedstock.in the absence of an alkaline sorbent.

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