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Transfer hydrogenation over sodium-modified ceria: Enrichment of redox sites active for alcohol dehydrogenation

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Transfer hydrogenation over sodium-modified ceria: Enrichment of redox sites active for alcohol dehydrogenation

Abstract

Ceria (CeO₂) and sodium-modified ceria (Ce-Na) were prepared through combustion synthesis. Palladium was deposited onto the supports (Pd/CeO₂ and Pd/Ce-Na) and their activity for the aqueous-phase transfer hydrogenation of phenol using 2-propanol under liquid flow conditions was studied. Pd/Ce-Na showed a marked increase (6×) in transfer hydrogenation activity over Pd/CeO₂. Material characterization indicated that water-stable sodium species were not doped into the ceria lattice, but rather existed as subsurface carbonates. Modification of ceria by sodium provided more adsorption and redox active sites (i.e. defects) for 2-propanol dehydrogenation. This effect was an intrinsic property of the Ce-Na support and independent of Pd. The redox sites active for 2-propanol dehydrogenation were thermodynamically equivalent on both supports/catalysts. At high phenol concentrations, the reaction was limited by 2-propanol adsorption. Thus, the difference in catalytic activity was attributed to the different numbers of 2-propanol adsorption and redox active sites on each catalyst.

Keywords

Transfer hydrogenation, Ceria, Sodium, Alcohol dehydrogenation, Redox, Defect sites, Oxidation, Flow chemistry

Disciplines

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1 Transfer hydrogenation over sodium-modified ceria: enrichment
2 of redox sites active for alcohol dehydrogenation

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22 **Abstract**

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24 Palladium was deposited onto the supports (Pd/CeO_2 and Pd/Ce-Na) and their activity for the
25 aqueous-phase transfer hydrogenation of phenol using 2-propanol under liquid flow conditions
26 was studied. Pd/Ce-Na showed a marked increase (6x) in transfer hydrogenation activity over
27 Pd/CeO_2 . Material characterization indicated water-stable sodium species were not doped into
28 the ceria lattice, but rather existed as sub-surface carbonates. Modification of ceria by sodium
29 provided more adsorption and redox active sites (i.e. defects) for 2-propanol dehydrogenation.
30 This effect was an intrinsic property of the Ce-Na support and independent of Pd. The redox sites
31 active for 2-propanol dehydrogenation were thermodynamically equivalent on both
32 supports/catalysts. At high phenol concentrations, the reaction was limited by 2-propanol
33 adsorption. Thus, the difference in catalytic activity was attributed to the different number of 2-
34 propanol adsorption and redox active sites on each catalyst.

35 **Keywords**

36 Transfer hydrogenation, ceria, sodium, alcohol dehydrogenation, redox, defect sites, oxidation,
37 flow chemistry

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45 **1. Introduction**

46 The inevitable depletion of fossil fuels and the controversy that surrounds their use makes it
47 imperative to develop sustainable, economical, and efficient alternatives to petrochemicals. Plant
48 biomass is the most recognized alternative and is widely regarded as the most promising
49 renewable resource to replace petroleum feedstocks.[1] Of plant biomass, lignin is the only
50 large-scale source of aromatics. As such, there has been a significant amount of effort devoted
51 and progress made to efficiently harvest the aromatics in a cost-competitive manner.[2] The
52 obvious and urgent needs for more sustainable chemical processes will likely lead to the
53 development of lignin-based technologies and allow it to become a significant source of
54 renewable aromatics.[3] However, to take full advantage of renewable aromatic feedstocks,
55 sustainable and economical downstream processes that convert the depolymerization products
56 into high-value commodity chemicals need to be developed.[4]

57 Lignin is a phenolic-based polymer and therefore a significant portion of the depolymerization
58 products are phenolics.[5, 6] Phenol finds its major use as a precursor for plastics often by
59 reaction with other compounds or molecules. For example, phenol can be reduced to afford
60 cyclohexanone and/or cyclohexanol. The ketone (K) and alcohol (A) products, either separately
61 or in a mixture (KA oil), are predominantly used as precursors for nylon.[7] Industrial processes
62 that convert phenol to precursors used in nylon production rely on high pressure molecular
63 hydrogen as the reductant.[8] Therefore, it is advantageous to develop catalysts and catalytic
64 systems that lower the hydrogen pressure needed for phenol reduction or eliminate the need for
65 molecular hydrogen all together. Recently, there have been several catalytic systems developed
66 for phenol reduction at or near atmospheric hydrogen pressures.[9] Far fewer systems have been
67 developed that eliminate the need for molecular hydrogen through transfer hydrogenation.[10-

68 13] Thus, there is a present and forecasted need to develop catalytic transfer hydrogenation
69 systems that can transform biomass platform molecules into high-value commodity chemical
70 precursors and lessen our reliance on petroleum-based feedstocks for downstream processing of
71 biomolecules.

72 In recent years there has been a surge in the development of heterogeneous transfer
73 hydrogenation catalytic systems.[14] Oftentimes, these systems contain two components: one to
74 activate the donor molecule for hydrogen liberation and the other to activate the liberated
75 hydrogen for reduction of the unsaturated functionality. Noble metals are widely used to promote
76 the latter, while homogenous inorganic or organic bases (e.g. NaOH, K-O^tBu) have traditionally
77 been used for the former. From an advanced catalyst design standpoint, it is beneficial to
78 incorporate the necessary promoters within the solid catalyst to achieve the desired activity and
79 avoid the undesired homogeneous components. In a previous study, we showed that ceria
80 supported palladium was active for room temperature phenol hydrogenation with molecular
81 hydrogen at atmospheric pressure.[15] Ceria is a mildly basic, redox active metal oxide and as
82 such, a seemingly good candidate for transfer hydrogenation reactions. Considering its potential,
83 ceria has been poorly studied for transfer hydrogenation catalysis. Catalytic systems involving
84 iridium oxide,[16] gold,[17, 18] and nickel[19] supported on ceria have been reported for
85 transfer hydrogenation of ketones and aldehydes without the use of a base promoter. Shimizu et
86 al.[19] studied the transfer hydrogenation of ketones over Ni/CeO₂ catalyst using 2-propanol as
87 the hydrogen donor. The catalyst showed good activity for aromatic and aliphatic ketone
88 reduction. Although a base metal was used, the catalyst was not stable in air and thermal
89 regenerative treatments were needed between recycling experiments.

90 Ceria and ceria-based materials are best known for their redox properties, which are related to
91 the number and type of oxygen vacancies within the material.[20-31] The significant effort and
92 progress made to understand the role of oxygen vacancies during catalytic processes has enabled
93 the design of defect-engineered ceria-based materials.[32-38] Perhaps most notable are ceria
94 materials with well-defined shapes that expose specific crystallographic planes, which dictate the
95 amount and type of defect sites present.[39-43] The redox properties of these materials are
96 oftentimes probed with short-chain alcohols, whose adsorption, reactions, and product
97 distribution/desorption temperature are believed to depend on the defect sites present.[44-48]
98 Typically, the more defect-rich ceria materials give rise to higher yields of dehydrogenation
99 products. With this in mind, the development of ceria-based materials with high concentrations
100 of defect sites should translate into high dehydrogenation activities and therefore be excellent
101 candidates for transfer hydrogenation reactions. Herein, we report the combustion synthesis of
102 ceria and sodium-modified ceria using cerium nitrate and cerium/sodium nitrate precursors,
103 respectively. Sodium modification was found to increase the number of redox active sites on the
104 surface that lead to 2-propanol dehydrogenation. Palladium was supported on both materials and
105 their activity for phenol transfer hydrogenation using potentially renewable 2-propanol[49] is
106 reported. Keeping along the lines of sustainable biomass upgrading, the reactions were run in
107 liquid flow mode, which has the added advantages of high throughput and catalyst recycling
108 efficiency.[50]

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113 **2. Results and discussion**

114 *2.1 Catalysis*

115 Ceria (CeO_2) and the cerium-sodium oxide material (Ce-Na) with nominal 20 at. % Na loading
116 were prepared using a modified solution combustion synthesis (SCS) with Pluronic polymer as
117 fuel and metal nitrate salts. The SCS method was chosen due to its precedence for forming
118 homogeneous multi-metal oxide composites.[51] Palladium was deposited onto Ce-Na (Pd/Ce-
119 Na) and CeO_2 (Pd/ CeO_2) through impregnation with palladium(II) acetate, followed by oxidative
120 and reductive thermal treatments at 350 °C. The physicochemical properties of the as-
121 synthesized supports and catalyst are summarized in Table S1.

122 The liquid flow transfer hydrogenation of phenol using 2-propanol as the sacrificial hydrogen
123 donor with Pd/Ce-Na and Pd/ CeO_2 catalysts proceeded through the formation of cyclohexanone
124 and cyclohexanol in various proportions depending on reaction conditions (Table 1). Both
125 catalysts displayed outstanding stability during 7-day continuous catalytic runs (Fig. 1a).
126 However, Pd/Ce-Na showed a marked increase in transfer hydrogenation activity over Pd/ CeO_2 .
127 For instance, under the conditions given in Table 1 for Entries 2 and 7, the rate of phenol
128 conversion was nearly five times higher over Pd/Ce-Na than Pd/ CeO_2 and about six times as
129 high for Entries 5 and 10. As evident from Table 1, Pd/Ce-Na showed higher phenol conversion
130 rates under all the reaction conditions tested. Both catalysts showed initial deactivation attributed
131 to decreased surface area and/or Pd dispersion with TOS (Table S2). Pd/ CeO_2 showed a higher
132 initial deactivation than Pd/Ce-Na likely owing to operation of the latter near equilibrium
133 conversion (83 % conversion) and better catalyst stability (Table S2). For Pd/Ce-Na, the ketone
134 to alcohol yield ratio (K:A) varied from about 10:90 to 40:60 through control of the flow rate and
135 phenol concentration (Table 1, Entries 1-5). The ketone yield was more or less constant when

136 varying these parameters, while the alcohol yield was more sensitive to these variations (Table 1,
137 Entries 1-5). For Pd/CeO₂, the K:A ratio was larger than for Pd/Ce-Na, giving almost exclusively
138 the ketone (Table 1, Entries 6-10). Both catalysts showed a higher conversion rate as the 2-
139 propanol-water ratio was increased. Interestingly, neat 2-propanol resulted in a monotonic, yet
140 significant decrease of conversion rate as a function of time over both catalysts which was not
141 observed in the presence of water (Fig. S1). Washing the catalysts with water overnight at 140
142 °C after the reaction in neat 2-propanol resulted in regeneration of the original activity. This
143 suggests the decreased activity may be related to hydroxyl disproportionation, which results in
144 the removal of lattice oxygen through water formation.[52-55] In absence of water, the hydroxyl
145 disproportionation equilibrium lies to the right in Scheme S1, giving oxygen deficient ceria,
146 which is a poor oxidation catalyst.[52] The regeneration data implies that water is able to
147 dissociatively adsorb on partially reduced ceria,[55-57] and shift the equilibrium in Scheme S1 to
148 the left. Thus, water appears to be a necessary component to maintain hydroxyl
149 disproportionation equilibrium in a way that favors the redox process. Arrhenius plots were
150 constructed for [phenol] = 0.1 M and the apparent activation barriers for phenol conversion over
151 Pd/CeO₂ and Pd/Ce-Na were $115 \pm 3 \text{ kJ mol}^{-1}$ and $48 \pm 2 \text{ kJ mol}^{-1}$, respectively (Fig. 1b).

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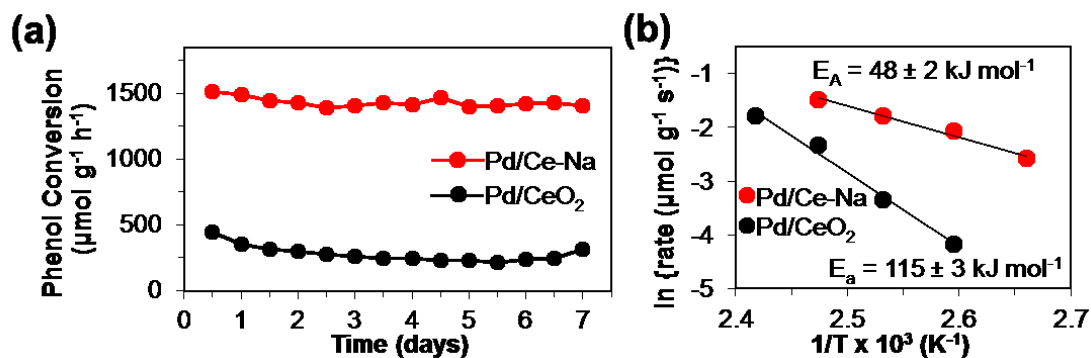
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158 **Table 1.** Reaction conditions and catalytic results for transfer hydrogenation of phenol with 2-
 159 propanol.^a

Entry	Catalyst	Phenol (M)	Flow Rate ($\mu\text{L min}^{-1}$)	Conversion Rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	Yield (%)		K:A
					C=O	C-OH	
1	Pd/Ce-Na	0.150	44.1 ^b	759 \pm 6	13 \pm 1	82 \pm 1	14:86
2	Pd/Ce-Na	0.150	95.6 ^c	1390 \pm 40	26 \pm 1	54 \pm 2	33:67
3	Pd/Ce-Na	0.150	191 ^d	1410 \pm 20	16 \pm 1	25 \pm 1	40:60
4	Pd/Ce-Na	0.200	44.1	905 \pm 16	19 \pm 1	67 \pm 2	22:78
5	Pd/Ce-Na	0.200	95.6	1360 \pm 60	18 \pm 1	41 \pm 3	30:70
6	Pd/CeO ₂	0.150	44.1	266 \pm 9	31 \pm 4	2 \pm 1	93:7
7	Pd/CeO ₂	0.150	95.6	287 \pm 8	16 \pm 1	<1	96:4
8	Pd/CeO ₂	0.150	191	279 \pm 3	8 \pm 1	0	100:0
9	Pd/CeO ₂	0.200	44.1	215 \pm 4	20 \pm 2	<1	97:3
10	Pd/CeO ₂	0.200	95.6	217 \pm 5	10 \pm 2	0	100:0

160 ^a0.5g of catalyst was used for all reactions. Water was flowed over the catalyst at room
 161 temperature for 2 h before beginning the initial run (Entries 1, 6). After that, the reactions were
 162 run sequentially (Entries 2-5, 7-10). 90 v/v % aqueous 2-propanol was used for all reactions.
 163 Column temperature was 140 °C. Catalyst bed volume (V_{bed}) was 0.4 mL. Errors are reported as
 164 one standard deviation away from the mean. ^bFor a flow rate of $\sim 0.05 \text{ mL min}^{-1}$, 72 mL of
 165 reagent was used with 12 mL sample composite intervals generating 6 data points over 24 h. ^cFor
 166 a flow rate of $\sim 0.10 \text{ mL min}^{-1}$, 144 mL of reagent was used with 24 mL sample composite
 167 intervals generating 6 data points over 24 h. ^dFor a flow rate of $\sim 0.20 \text{ mL min}^{-1}$, 168 mL of
 168 reagent was used with 24 mL sample composite intervals generating 7 data points over 14 h.

169



170
 171 **Fig. 1.** (a) Phenol conversion rate for Pd/CeO₂ and Pd/Ce-Na during 7 day time-on-stream (TOS)
 172 study. Conditions: 0.15 M phenol in 90 v/v % aqueous 2-propanol, 0.5 g catalyst, $\sim 0.1 \text{ mL min}^{-1}$,
 173 $T = 140 \text{ }^\circ\text{C}$, $V_{\text{bed}} = 0.4 \text{ mL}$. Each data point corresponds to 72 mL product stream composite. (b)
 174 Arrhenius plots of phenol conversion over Pd/CeO₂ ($E_A = 115 \text{ kJ mol}^{-1}$) and Pd/Ce-Na ($E_A = 48$

175 kJ mol⁻¹). Conditions: 0.1 M phenol in 90 v/v % aqueous 2-propanol, 0.5 g catalyst, ~0.1 mL
176 min⁻¹, V_{bed} = 0.4 mL. Each data point (at each temperature) corresponds to the average of 6 rate
177 measurements collected at 4 h sampling intervals (24 mL composite) over 24 h.

178 Physicochemical properties are often invoked to explain differences in activity and were found
179 to be similar for both catalysts after the reaction (Table S3). That is, the specific surface area of
180 Pd/CeO₂ decreased by an order of magnitude over the course of the reaction, which made it
181 comparable to Pd/Ce-Na. Likewise, the Pd dispersion value on both catalysts decreased to about
182 10 % during time-on-stream, suggesting Na does not enhance Pd dispersion.[58, 59] Both
183 catalysts showed the same Pd loadings before and after reaction, which is consistent with the
184 long-term catalyst stability. The similar post-reaction physicochemical properties between the
185 catalysts suggest that sodium modification was able to promote transfer hydrogenation activity.
186 In order to understand the role of sodium promotion more clearly, preferential attention was
187 given to support characterization. The role of palladium was studied where deemed relevant.

188 *2.2 Materials Characterization*

189 Elemental analysis of as-synthesized Ce-Na support confirmed sodium was present at 18 at. %
190 and agreed well with nominal loading of 20 at. % (Table 2, Entry 1). DRIFT (Fig. S2-S4) and
191 XPS (Fig. S5) analysis showed sodium was present as a carbonate. ICP analysis of Ce-Na after
192 continuous-flow aqueous treatment at room temperature for twelve hours showed a drastic
193 reduction of sodium content from 18 to 4.0 at. % (Table 2, Entries 1, 3), with most soluble
194 sodium species removed after two hours during washing (Fig. S6). The data presented in Fig. S6
195 was obtained after washing the material at catalytic temperatures (i.e. 140 °C) and showed a
196 further decrease in sodium loading to 2.6 at. % (Table 2, Entry 4). Quite surprisingly, sodium
197 was retained even after 7 days on stream (Table 2, Entry 5). While ICP analysis confirmed the

198 presence of sodium after washing, XPS (Fig. S5g) indicated that there were minimal amounts of
 199 sodium on the surface, suggesting that sodium species are contained within the material. Bearing
 200 in mind the aqueous conditions used during catalysis, all Ce-Na and Pd/Ce-Na characterization
 201 was performed after aqueous washing at room temperature (Table 2, Entry 3).

202

203 **Table 2.** Physicochemical properties of supports and catalysts under varying conditions.

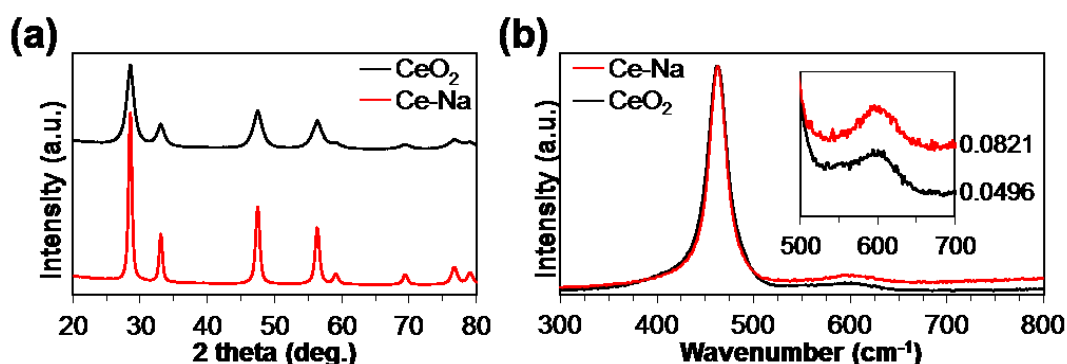
Entry	Sample	Surface Area (m ² g ⁻¹) ^a	Na Loading (at. %) ^b	Lattice Constant (Å) ^c
1	Ce-Na	29	18 ± 1 ^d	5.412
2	CeO ₂	210	0	5.412
3	Ce-Na ^e	42	4.0 ± 0.2 ^f	5.412
4	Ce-Na ^g	40	2.6 ± 0.1 ^h	---
5	Pd/Ce-Na ⁱ	20	2.7 ± 0.2 ^j	---

204 ^aDetermined by nitrogen physisorption using BET approximation. ^bDetermined by ICP-OES
 205 and is relative to Ce. ^cDetermined using HighScore software. ^dMeasured across three batches.
 206 ^eWashed with flowing water (0.1 mL min⁻¹) for 12 h at room temperature. ^fMeasured across two
 207 batches with two sample preps in duplicate (i.e. 8 data points). ^gWashed with flowing water (0.1
 208 mL min⁻¹) for 12 h at 140 °C. ^hMeasured for one batch with two sample preparations in duplicate
 209 (i.e. 4 data points). ⁱResults after 7 d reaction. ^jMeasured in duplicate with two sample
 210 preparations (i.e. 4 data points).

211

212 The PXRD pattern of the supports (Fig. 2a) and catalysts (Fig. S7) exhibited diffraction peaks
 213 that could be indexed to the fluorite structure of ceria, with no other reflections observed. The
 214 absence of sodium-containing reflections (e.g. Na₂O, Na₂CO₃, etc.) in the diffraction pattern
 215 suggests sodium species could be amorphous or have a crystallite size below the detection limit
 216 of the instrument. Since XPS analysis indicated that sodium was not present on or near the
 217 surface, it is also possible that sodium was doped into the ceria matrix. Rietveld analysis showed
 218 no significant difference in lattice constant between Ce-Na and CeO₂ (Table 2, Entries 1-3). The

219 identical lattice constants between Ce-Na and CeO₂ could be an indication that residual sodium
220 species were not contained within the bulk ceria lattice. Alternatively, it could reflect the similar
221 sizes of Ce⁴⁺ (0.97 Å)[60] and Na⁺ (0.99 Å)[60], which has been observed for Pr- (0.99 Å)[60]
222 doped ceria.[61, 62]. The identical lattice parameters from PXRD analysis were also supported
223 by HR-TEM imaging for several crystallites of Ce-Na that gave an average d-spacing of 0.31 ±
224 0.03 nm (Fig. S8). This value corresponds to the (111) surface termination and is also the
225 predominant facet observed for CeO₂ (Fig. S9).[15] The result rules out structural promotion (i.e.
226 surface termination) for the higher rate of phenol turnover and lower activation barrier for
227 conversion.



228 **Fig. 2.** (a) PXRD patterns for CeO₂ and Ce-Na showing cubic fluorite phase. (b) Raman spectra
229 using 488 nm excitation for CeO₂ and Ce-Na. Inset shows band associated with intrinsic defects
230 (D-band). The numbers represent the ratio ($A_D:A_{F_{2g}}$) of the peak areas for the D-band (600 cm⁻¹)
231 and the F_{2g}-band (462 cm⁻¹).
232

233 Given the comparable size of sodium and cerium (IV) cations, PXRD may not be suitable for
234 determining whether sodium was doped into the ceria lattice. In direct contrast to PXRD, which
235 primarily gives information related to the cationic sublattice, Raman spectra of fluorite-type
236 oxides are sensitive to bulk oxygen lattice vibrations, which are related to M-O bond symmetry
237 and defects. The Raman spectra for CeO₂ and Ce-Na are shown in Fig. 2b. Both samples

238 exhibited Raman bands around 462 cm^{-1} and were attributed to the F_{2g} triply degenerate Raman-
239 active phonon of the cubic CeO_2 -fluorite phase.[41, 63, 64] This band can be viewed as a
240 symmetrical stretching vibration of the oxygen atoms surrounding a cerium cation (i.e. CeO_8).
241 Thus, the location of the band is sensitive to the M-O bond lengths and symmetry present in
242 ceria-based materials.[62, 64] The band positions for the two materials were identical suggesting
243 similar bond lengths in accordance with the lattice constants obtained from PXRD analysis. Both
244 samples also exhibited bands around 600 cm^{-1} that have been suggested to result from the
245 presence of intrinsic oxygen defects.[41] The ratio between the defect band (D-band) and the F_{2g}
246 band (i.e. $A_D:A_{F_{2g}}$) is used to compare the amounts of intrinsic defects between different ceria-
247 based materials.[41, 65] Ce-Na showed a higher $A_D:A_{F_{2g}}$ ratio ($1.7\times$) indicating more defects
248 compared to CeO_2 even with the former having a larger crystallite size.[64] However, the exact
249 nature of these defects, either vacancy-interstitial (Frenkel) or Ce^{3+} substitutional in an
250 octahedral environment, is still debated.[41, 63] Another defect band around 570 cm^{-1} has been
251 observed for ceria during thermal treatment under reducing environments and is attributed to
252 oxygen vacancies formed during reduction (i.e. extrinsic oxygen vacancies).[44] The same band
253 has also been observed upon substitutional doping of cerium cations with aliovalent metals and is
254 thought to result from charge compensation and is thus associated with extrinsic oxygen
255 vacancies.[62] The absence of this band in Ce-Na suggests sodium is not acting as a
256 substitutional dopant that exhibits charge-compensation. Charge compensation through
257 formation of $\text{Na}^+ \text{-Ce}^{3+}$ cationic pairs could also be possible and would not involve formation of
258 oxygen vacancies. However, this motif would be expected to result in differences of lattice
259 constant between the two materials due to the larger ionic radius of Ce^{3+} , which was not

260 observed in PXRD analysis. Thus, the PXRD and Raman data together suggest sodium was not
261 acting as a dopant.

262 Structural analysis of the Ce-Na support indicated that sodium was not contained within the
263 ceria lattice, but it was shown through chemical analysis that sodium species are still present
264 even after washing with water at elevated temperatures for extended periods of time (Table 2).
265 Considering that the predominant sodium species before washing were carbonates, the residual
266 sodium may be in the form of carbonates that are trapped at the grain boundaries within the bulk
267 of the particles (Table S1, Fig. S8). Fig. S10 shows the CO₂-TPD profile while monitoring the
268 heat flow and weight loss for the Ce-Na support. The TGA-DSC-MS analysis showed two high
269 temperature CO₂ desorption peaks around 700-800 °C and 900-1100 °C. The former CO₂
270 desorption peak was exothermic while the latter was endothermic. The exothermic transition
271 with evolution of CO₂ suggests carbonate decomposition and likely arises from sodium
272 carbonate decay. Anhydrous sodium carbonate is known to decompose at temperatures higher
273 than 800 °C, but metal oxide additives have been shown to lower the decomposition
274 temperature.[66] Furthermore, the decomposition of sodium carbonate is an exothermic process
275 in agreement with the thermal data and is expected to result in the formation of sodium oxide.
276 The endothermic CO₂ evolution peak could be due to CO₂ desorbing from sodium oxide. The
277 total weight loss from the onset of the exothermic transition to the end of the endothermic
278 transition (i.e. 700-1100 °C), assuming sodium carbonate decomposition, allowed an estimation
279 of residual sodium to be 3.8 at. %. This result is in excellent agreement with that obtained from
280 elemental analysis (Table 2, Entry 3). Furthermore, XPS depth-profiling experiments showed the
281 Na 1s binding energy was characteristic of sodium carbonate (Fig. S11).[67] Thus, it appears that

282 the insoluble sodium fraction was sodium carbonate and that it was largely inaccessible to water
283 (Table 2).

284 ^{23}Na solid-state NMR (SSNMR) spectroscopy was also performed on the Ce-Na support. ^{23}Na
285 is a 100% naturally abundant $I = 3/2$ quadrupolar nucleus which normally gives rise to relatively
286 narrow solid-state NMR spectra. The ^{23}Na spin echo SSNMR spectrum of Ce-Na support
287 possessed a relatively broad, featureless resonance (Fig. S12A). A 2D triple quantum multiple
288 quantum magic angle spinning (MQMAS) experiment suggested that the broadening of the ^{23}Na
289 SSNMR spectrum was primarily due to a distribution of isotropic ^{23}Na chemical shifts in the
290 range of 10 to -10 ppm; broadening from the second order quadrupolar interaction was minimal
291 (Fig. S12A). This suggests that there are many distinct sodium sites/environments, and within
292 these sites the sodium ions must reside at sites of relatively high spherical symmetry (i.e.,
293 pseudo-octahedral coordination environments). A $^{23}\text{Na}\{^1\text{H}\}$ rotational echo double resonance
294 (REDOR) experiment was performed to assess the spatial proximity of the Na ions to protons.
295 The REDOR experiment indicates that ca. 60% of the Na ions are proximate (within 5 Å) of ^1H
296 nuclei (Fig. S12B and Fig. S12C). This would suggest that the majority of the sodium carbonate
297 is present as a hydrated phase or nearby to sorbed water. This is perhaps to be expected since the
298 Ce-Na support was thoroughly washed to remove excess Na. Several distinct crystalline
299 anhydrous and hydrated sodium carbonate phases have previously been reported.[68, 69]
300 Therefore, the range of isotropic ^{23}Na chemical shifts most likely arises from the presence of a
301 variety of hydrated and anhydrous sodium carbonate phases/environments. Keeping the XPS
302 results in mind, these sodium carbonate phases are likely trapped in between the ceria grains.

303 The role of residual sodium carbonate during catalysis remains unclear. The insolubility under
304 aqueous conditions at elevated temperatures for 7 days suggests that it is not accessible to the

305 environment and thus should not participate directly in the catalysis. To better understand the
306 role of sodium carbonate a control sample was prepared through impregnation of CeO₂ with
307 aqueous NaNO₃ (20 at. %) followed by calcination at 450 °C (Na/CeO₂). Pd was then deposited
308 on the support (Pd/Na/CeO₂). It is expected that decomposition of the sodium precursor should
309 yield surface sodium carbonate species that are easily removed with water and thus clarify the
310 role of sodium carbonate. Quite remarkably, the control catalyst was slightly more active than
311 Pd/Ce-Na (Fig. S13). ICP analysis revealed that Pd/Na/CeO₂ contained 1.1 Na-at. % after
312 reaction, which is about a 60 % decrease of Na content compared to Pd/Ce-Na (Table 2, Entry
313 5). XPS depth profiling experiments showed the Na 1s binding energy for Na/CeO₂ (washed
314 with water at room temperature) was consistent with sodium carbonate (Fig. S14). The result
315 suggests that the physical amount of sodium carbonate during catalysis does not affect activity,
316 at least from about 1-3 Na-at. %. Although the results provide some insight into the role of
317 sodium carbonate, they are not conclusive.

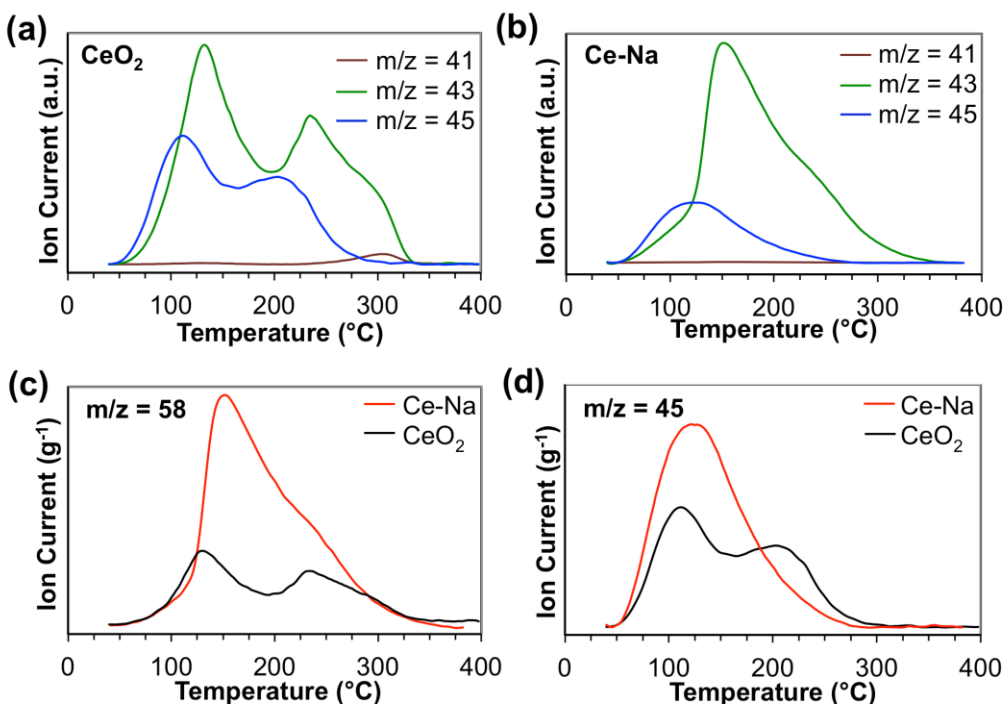
318 Considering that bulk characterization techniques did not support the formation of sodium-
319 doped ceria and that the physical amount of sodium carbonate doesn't appear to correlate with
320 activity, it is possible that sodium modification affects the surface properties of the material. XPS
321 analysis was conducted on both supports to probe possible electronic structure differences that
322 could provide insight into the different catalytic activity. The Ce 3d spectral region (Fig. S15a)
323 showed characteristic peaks attributed to Ce(IV), [70-73] with no obvious difference between the
324 two supports. The O 1s spectral region shown in Fig. S15b displayed subtle differences between
325 CeO₂ and Ce-Na. The O 1s spectrum peak maximum, assigned to lattice oxygen, shifted from
326 529.5 eV (CeO₂) to 529.3 eV (Ce-Na). The shift signifies, on average, a more electron-rich
327 environment of lattice oxygens. Since sodium is present it would seem plausible that the

328 apparent increased oxygen electron density for Ce-Na could be due to higher material basicity,
329 which has been observed for other metal oxides modified with sodium[74, 75] and could explain
330 the different reaction rates observed. However, the basic properties and C-H activating
331 ability[76] of the two materials were found to be identical by testing with basicity probes and
332 base-catalyzed reactions (Fig. S16-S18, Table S4-S5). For completeness, the acidic properties
333 were also found to be unmodified (Fig. S19-20). This data indicates that the acid-base properties
334 for Ce-Na were unaltered relative to CeO₂ and that these reactivity descriptors are not relevant
335 for the activity difference observed during phenol transfer hydrogenation.

336 2.3 Redox Properties and Kinetic Analysis

337 The most notable reactivity descriptor for ceria-based materials is the redox property. The
338 redox property of ceria correlates to the number of defects within the material, especially as they
339 relate to oxygen vacancies.[20, 35, 41, 42, 44, 77] Since 2-propanol oxidation is a prerequisite
340 for phenol turnover, the 2-propanol reactivity over both CeO₂ and Ce-Na were studied. The
341 temperature programmed surface reaction (TPSR) of 2-propanol was used to determine the
342 relationship between acetone formation and the transfer hydrogenation activity of the two
343 materials. At this point it should be noted that 2-propanol was adsorbed dissociatively[52, 78-80]
344 on both materials as evidenced by two $\nu(\text{C-O})$ stretching bands at 1162 and 1132 cm⁻¹
345 corresponding to end-on and bridging coordination of isopropoxide to cerium cations,
346 respectively (Fig. S21). The materials were saturated *ex situ* with 2-propanol and heated under
347 Ar while monitoring evolved 2-propanol ($m/z = 45$), acetone ($m/z = 43, 58$), and propylene (m/z
348 = 41). The characteristic acetone signal at $m/z = 58$, whose intensity is weak relative to the
349 somewhat uncharacteristic signal at $m/z = 43$, was monitored to ensure the signal at $m/z = 43$ is
350 primarily due to acetone desorption. The identical profiles observed for all samples at $m/z = 43$

351 and $m/z = 58$ indicates that the intensity of the $m/z = 43$ signal is primarily due to evolved
 352 acetone (Fig. S22). Fig. 3a, b shows the 2-propanol, acetone, and propylene signal intensity
 353 profile versus temperature for CeO_2 and Ce-Na, respectively. For CeO_2 , acetone desorption
 354 occurred over a broad temperature range. Onset desorption occurred around 50°C and continued
 355 to about 320°C . There were two major desorption maxima centered at 133°C and 237°C , with
 356 a significant shoulder around 300°C . Unreacted 2-propanol also desorbed over a broad
 357 temperature range spanning $50\text{-}275^\circ\text{C}$, with two maxima observed at 105°C and 208°C slightly
 358 below the acetone maxima. A small propylene desorption was found at 307°C . For Ce-Na, onset
 359 desorption also occurred around 50°C with a dominant acetone desorption maximum at 150°C
 360 and a significant shoulder at 228°C . Unreacted 2-propanol desorbed over $50\text{-}250^\circ\text{C}$ with single
 361 maximum at 120°C . There were negligible amounts of propylene observed.



362
 363 **Fig. 3.** TPD-MS profile for TPSR of adsorbed 2-propanol on (a) CeO_2 and (b) Ce-Na. The m/z
 364 $=41, 43,$ and 45 signals correspond to propylene, acetone, and 2-propanol, respectively. Mass

365 normalized TPD-MS profile for TPSR of adsorbed 2-propanol on Ce-Na and CeO₂ while
366 monitoring (c) $m/z = 58$ and (d) $m/z = 45$ which correspond to acetone and 2-propanol,
367 respectively.

368 The signal corresponding to acetone ($m/z = 58$) for Ce-Na and CeO₂ were normalized to the
369 material mass and are shown in Fig. 3c. The formation rate of acetone is clearly higher on Ce-Na
370 indicated by the increased slope before the first maximum. Curiously, the temperature at
371 maximum acetone desorption were similar for Ce-Na and CeO₂. In addition, both materials
372 showed an acetone desorption shoulder around 240 °C. Typically, the desorption maximum is
373 proportional to the activation energy for the rate limiting step. This implies that the higher rate of
374 acetone formation observed for TPSR of 2-propanol on Ce-Na was not due to a reduced
375 activation barrier during an elementary reaction step. This result also indicates that the higher
376 rate can be attributed to more active sites present on the surface of Ce-Na in spite of the large
377 difference in surface area between the two materials. According to Redhead,[81, 82] the
378 activation energy of acetone formation on the two materials using the first desorption maximum
379 was $106 \pm 21 \text{ kJ mol}^{-1}$ and $101 \pm 20 \text{ kJ mol}^{-1}$ for Ce-Na and CeO₂, respectively. Considering that
380 formation of adsorbed isopropoxide occurs at room temperature (Fig. S21) and that acetone
381 shows little affinity for the surface of ceria above room temperature,[52] it seems likely the
382 observed activation barrier is due to C-H scission of adsorbed isopropoxide to form acetone. This
383 elementary reaction step is a redox process implying that there are more redox active centers on
384 Ce-Na and that these redox centers are equivalent. The relative areas of the mass-normalized
385 acetone TPD-MS profiles on the two supports showed $2.9\times$ more acetone evolving from Ce-Na,
386 suggesting this support had about three times more 2-propanol dehydrogenation sites than CeO₂.

387 Additionally, the 2-propanol desorption profile for the two supports indicated a higher amount of
388 desorbed 2-propanol on Ce-Na (Fig. 3d).

389 TPSR of adsorbed 2-propanol clearly showed the rate of acetone formation is higher for Ce-Na
390 than for CeO₂, but the actual catalytic conditions are quite different and the reactant-limited
391 TPSR results of the supports may not be representative during catalysis. Therefore, the rate of
392 acetone formation under catalytic conditions was monitored by trapping with 2,4-
393 dinitrophenylhydrazine and quantified using ¹H-NMR. The acetone formation rate was
394 monitored at 140 °C under liquid flow conditions with 90 v/v % aqueous 2-propanol. For CeO₂
395 and Ce-Na the rates were 7 μmol g⁻¹ h⁻¹ and 13 μmol g⁻¹ h⁻¹, respectively (Table 3, Entries 1, 2).
396 For Pd/CeO₂ and Pd/Ce-Na, the average acetone formation rate observed over three trials was
397 2920 ± 80 μmol g⁻¹ h⁻¹ and 6270 ± 40 μmol g⁻¹ h⁻¹, respectively (Table 3, Entries 3, 4). The
398 increased 2-propanol dehydrogenation rate of both catalysts was likely due to the activity of Pd
399 for 2-propanol dehydrogenation.[83] The TPSR study of adsorbed 2-propanol over the supports
400 indicated the average acetone formation rate (i.e. from 40-400 °C) was about three times higher
401 over Ce-Na, which was more than observed with the catalysts under catalytic conditions (2.1x).
402 However, the TPSR study spanned a much broader temperature range than the catalytic study
403 and is an average over each temperature within that range. Comparing the two y-maxima (130-
404 150 °C) from the TPSR TPD-MS curve for evolved acetone (Fig. 3c) should indicate the relative
405 dynamic acetone formation rate under reaction conditions (Table 3, Entries 3, 4). The relative
406 maxima for evolved acetone between the two materials from TPSR of 2-propanol (2.4x) was in
407 good agreement for the relative rates under dynamic liquid conditions using the catalysts (2.1x).
408 Thus, given the acetone formation rates for the supports, it appears that palladium increases the
409 acetone formation rate over both catalysts more or less equally, but the support largely dictates

410 the difference in the observed acetone formation rate. The similar 2-propanol dehydrogenation
 411 rate ratios between the supports and catalysts (Table 2, Entry 3 and 5, respectively) indicate that
 412 the amount of sodium species does not significantly affect dehydrogenation activity and that
 413 sodium carbonates are mere spectators in the reaction. This is also consistent with sodium
 414 species residing below the surface.

415

416 **Table 3.** Acetone formation rates over supports and catalysts in absence and presence of phenol.^a

Entry	Catalyst	[Phenol] (M)	Acetone Rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	C=O Rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$) ^b	C-OH Rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$) ^b	Expected Acetone Rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$) ^c
1	CeO ₂	0	7 ± 0.7^e	---	---	---
2	Ce-Na	0	13 ± 1.3^e	---	---	---
3	Pd/CeO ₂	0	2920 ± 80^d	---	---	---
4	Pd/Ce-Na	0	6270 ± 40^d	---	---	---
5	Pd/CeO ₂	0.15	576 ± 58^e	288	12	612
6	Pd/Ce-Na	0.15	3680 ± 368^e	476	974	3874

417 ^aConditions: 90 v/v % aqueous 2-propanol, 0.5g of catalyst, 0.1 mL min⁻¹, T = 140 °C, V_{bed} =
 418 0.4 mL. ^bRates obtained from data found in Table 1, Entries 2, 7. ^cCalculated assuming 2 moles
 419 of acetone per mole of cyclohexanone and 3 moles of acetone per mole of cyclohexanol.
 420 ^dAverage rate from three separate reactions. Errors represent one standard deviation from the
 421 mean. ^eRate from one reaction. Errors represent average relative error determined during method
 422 validation (see experimental).

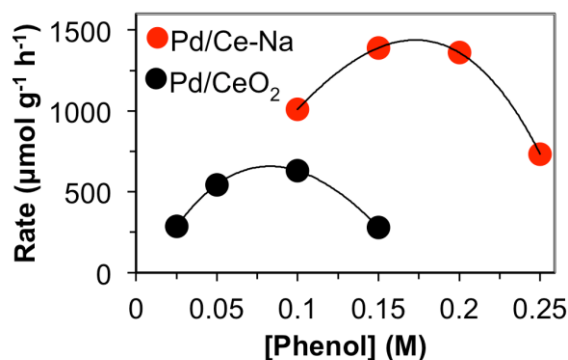
423

424 Although there was a clear enhancement in the rate of evolved acetone for Pd/Ce-Na, it did not
 425 represent the difference in phenol transfer hydrogenation rates observed (3-6x), which should
 426 correlate to the amount of acetone formed. To ensure that our assumption of a one-to-one
 427 acetone to molecular hydrogen stoichiometric relationship was valid, the amount of acetone
 428 formed during phenol transfer hydrogenation was measured under the conditions found in Table
 429 1, Entries 2, 7. The evolved acetone for Pd/Ce-Na and Pd/CeO₂ were 3680 $\mu\text{mol g}^{-1} \text{h}^{-1}$ and 576

430 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively (Table 3, Entries 5, 6). These results agree well with the expected
431 amount of acetone that should be formed considering the yield of products (Table 3).

432 A series of kinetic experiments were run to understand the cause of the lower activation barrier
433 for Pd/Ce-Na (Fig. 1b) since 2-propanol TPSR suggests there should be no difference. The
434 experimental data showed that the acetone formation rate over both catalysts decreased in
435 presence of phenol, likely due to their affinity for the same adsorption sites.[15, 52] However,
436 the relative percent decrease was much more severe over Pd/CeO₂ (80 %) than over Pd/Ce-Na
437 (33 %) (Table 3). In addition, the difference between phenol conversion rates for the two
438 catalysts increased with phenol concentration (Table 1). These results suggest the difference in
439 apparent activation barrier may be related to the barrier for 2-propanol adsorption in the presence
440 of phenol. Here, we are assuming that the surface kinetics follow Langmuir-Hinshelwood
441 mechanism for competitive binding. That is, increasing the phenol concentration should lead to
442 higher binding site occupancy, which would hinder 2-propanol adsorption and limit turnover.
443 Evidence for this type of behavior was obtained by monitoring the phenol conversion rate as a
444 function of phenol concentration (Fig. 4). Both materials showed a non-linear dependence of rate
445 versus phenol concentration at conversions less than unity. The reaction rate profiles are
446 characteristic for competitive adsorption.[82] The rate data also suggests there are more 2-
447 propanol/phenol adsorption sites that lead to phenol turnover on Pd/Ce-Na shown by the up and
448 rightward shift of the rate profile relative to Pd/CeO₂. That is, if the amount of 2-propanol/phenol
449 adsorption sites were equal, the curve would be expected to shift straight up due to the increased
450 number of redox active sites previously shown. This was supported through phenol adsorption
451 isotherms that showed there were more phenol/2-propanol adsorption sites on the Ce-Na support
452 even with the surface area of CeO₂ being five times greater (Fig. 5a). The y-intercept of the

453 linear region was taken as the approximate monolayer coverage and gave $77 \mu\text{mol g}^{-1}$ and 36
454 $\mu\text{mol g}^{-1}$ for Ce-Na and CeO_2 , respectively. This ratio (2.1) agrees well with the mass normalized
455 area summation of all monitored reactants and products from the TPSR-MS profiles for Ce-Na
456 and CeO_2 (2.4) (Fig. 3c, d). Furthermore, the ratio is identical to the ratio of acetone formation
457 rates observed over the two catalysts in the absence of phenol (Table 3, Entries 3, 4). Although
458 the latter comparison is made between the supports and catalysts, it does suggest that the phenol
459 adsorption sites are the same as 2-propanol and that these adsorption sites are active for 2-
460 propanol dehydrogenation.



461
462 **Fig. 4.** Phenol conversion rate versus phenol concentration over Pd/CeO₂ and Pd/Ce-Na.
463 Conditions: 90 v/v % aqueous 2-propanol, 0.5 g catalyst, $\sim 0.1 \text{ mL min}^{-1}$, $T = 140 \text{ }^\circ\text{C}$, $V_{\text{bed}} = 0.4$
464 mL.

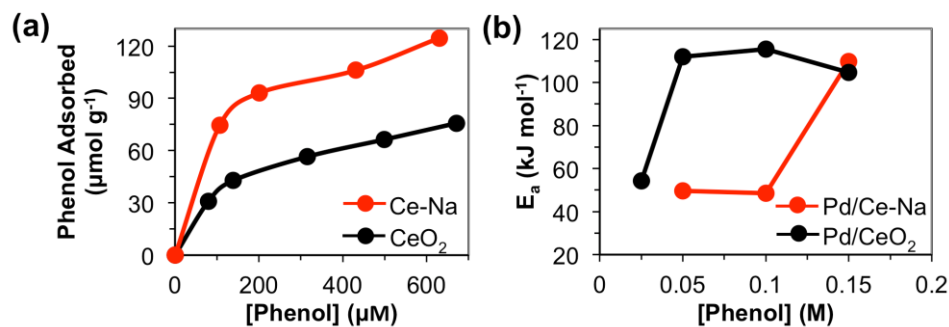
465 Further evidence for the apparent activation barrier arising from the barrier for 2-propanol
466 adsorption in presence of phenol was obtained by monitoring the phenol conversion rate as a
467 function of aqueous 2-propanol concentration. Under the reaction conditions shown in Fig. S23,
468 the apparent order for 2-propanol during the transfer hydrogenation of phenol over Pd/CeO₂ and
469 Pd/Ce-Na were 3.7 and 0.9, respectively. The dependence of phenol conversion rate on the 2-
470 propanol concentration over both catalysts indicates that water competes for the same binding

471 sites as 2-propanol/phenol. The higher dependence of conversion rate on 2-propanol
472 concentration for Pd/CeO₂ is consistent with phenol blocking a larger percentage of 2-propanol
473 adsorption sites (i.e. Langmuir-Hinshelwood competitive binding) since all other conditions are
474 equal. This was also made apparent by the drastic color change of CeO₂ in the presence of a 2-
475 propanol/phenol solution (Fig. S24).[15] If the observed activation barrier for phenol transfer
476 hydrogenation reflects the adsorption barrier for 2-propanol, the apparent activation energy
477 should be a function of phenol concentration. Thus, Arrhenius plots were constructed to
478 determine the variation of activation energy as a function of phenol (Fig. 5b). Indeed, at high
479 concentrations of phenol, Pd/Ce-Na showed an apparent activation barrier of 110 kJ mol⁻¹ while
480 at low concentrations Pd/CeO₂ gave 54 kJ mol⁻¹. The transition from low to high activation
481 barrier occurs at higher phenol concentrations for the Pd/Ce-Na catalyst. This is consistent with
482 the Ce-Na support having more hydroxyl group binding sites than the CeO₂ support and suggests
483 that the high activation barrier over both catalysts is due to the 2-propanol adsorption barrier in
484 the presence of phenol. The higher amount of phenol/2-propanol adsorption and redox sites is
485 likely related to the higher amount of O-vacancies observed from Raman studies (Fig. 2b).[46,
486 47, 54]

487

488

489



490
 491 **Fig. 5.** (a) Phenol adsorption isotherms for Ce-Na and CeO₂. (b) Plot showing the apparent
 492 activation energy for the transfer hydrogenation of phenol as a function of phenol concentration.

493
 494 **3. Conclusions**

495 The 2-propanol dehydrogenation activity of ceria is enhanced through modification with
 496 sodium by increasing the number of adsorption and redox active sites. This effect was an
 497 intrinsic property of the Ce-Na support and independent of Pd. Sodium is neither on the surface
 498 of the active material nor is it doped into ceria, but exists likely as a subsurface carbonate species
 499 of varying degrees of hydration. Deposition of palladium onto ceria and sodium-modified ceria
 500 provides catalysts active for the transfer hydrogenation of phenol using 2-propanol. The catalytic
 501 transfer hydrogenation of phenol was conducted in flow mode and required water for stability.
 502 The higher activity of the sodium-modified catalyst was attributed to the higher amount of 2-
 503 propanol/phenol adsorption sites and redox sites active for 2-propanol dehydrogenation. The
 504 apparent activation energy transitioned from low to high upon increasing phenol concentration
 505 over both catalysts and was attributed to the barrier for 2-propanol adsorption. This transition
 506 occurred at higher phenol concentrations for Pd/Ce-Na owing to the higher amount of substrate
 507 adsorption sites. Additional studies are in progress to determine the precise location of Na in the
 508 catalyst and the mechanism by which it increases the number of adsorption and redox-active sites

509 on ceria. Nonetheless, the enhancement of hydroxyl adsorption and redox active sites on ceria
510 through facile sodium modification is expected to be broadly applicable to other ceria-based
511 catalysis.

512

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517 by Iowa State University under Contract No. DE-AC02-07CH11358.

518

519 **Appendix A. Supplementary material**

520 Supplementary data (Experimental, physicochemical properties of all materials, reaction data,
521 schemes, DRIFT spectra, XPS spectra, XRD diffractograms, TEM, TGA/DSC/MS data, CO₂-
522 TPD data, kinetic data, adsorption data) associated with this article can be found, in the online
523 version, at

524

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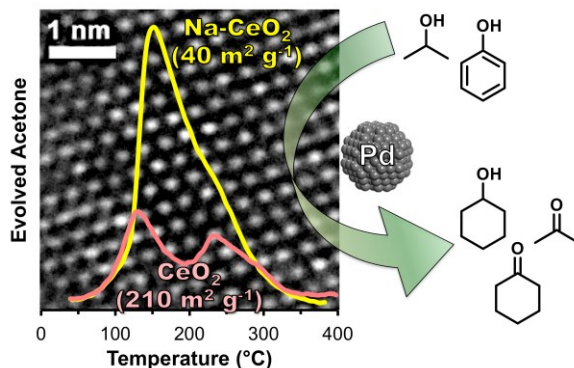
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644

645

646 **Graphical abstract**



647

648 **Highlights**

649 • Liquid flow transfer hydrogenation of phenol performed over Pd/CeO₂ and Pd/Ce-Na.

650 • Pd/Ce-Na shows 6x higher activity than Pd/CeO₂.

651 • Water-stable sodium species seemingly exist as subsurface carbonate spectators.

652 • Na-modification increases the number of substrate adsorption and redox active sites

653 • High apparent activation energies reflect propanol adsorption barrier in presence of
654 phenol.

655

656 **List of tables**

657 **Table 1.** Reaction conditions and catalytic results for transfer hydrogenation of phenol with 2-
658 propanol.

659 **Table 2.** Physicochemical properties of supports and catalysts under varying conditions.

660 **Table 3.** Acetone formation over catalysts in the absence and presence of phenol.

661

662 **Table 1.** Reaction conditions and catalytic results for transfer hydrogenation of phenol with 2-
 663 propanol.^a

Entry	Catalyst	Phenol (M)	Flow Rate ($\mu\text{L min}^{-1}$)	Conversion Rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	Yield (%)		K:A
					C=O	C-OH	
1	Pd/Ce-Na	0.150	44.1 ^b	759 \pm 6	13 \pm 1	82 \pm 1	14:86
2	Pd/Ce-Na	0.150	95.6 ^c	1390 \pm 40	26 \pm 1	54 \pm 2	33:67
3	Pd/Ce-Na	0.150	191 ^d	1410 \pm 20	16 \pm 1	25 \pm 1	40:60
4	Pd/Ce-Na	0.200	44.1	905 \pm 16	19 \pm 1	67 \pm 2	22:78
5	Pd/Ce-Na	0.200	95.6	1360 \pm 60	18 \pm 1	41 \pm 3	30:70
6	Pd/CeO ₂	0.150	44.1	266 \pm 9	31 \pm 4	2 \pm 1	93:7
7	Pd/CeO ₂	0.150	95.6	287 \pm 8	16 \pm 1	<1	96:4
8	Pd/CeO ₂	0.150	191	279 \pm 3	8 \pm 1	0	100:0
9	Pd/CeO ₂	0.200	44.1	215 \pm 4	20 \pm 2	<1	97:3
10	Pd/CeO ₂	0.200	95.6	217 \pm 5	10 \pm 2	0	100:0

664 ^a0.5g of catalyst was used for all reactions. Water was flowed over the catalyst at room
 665 temperature for 2 h before beginning the initial run (Entries 1, 6). After that, the reactions were
 666 run sequentially (Entries 2-5, 7-10). 90 v/v % aqueous 2-propanol was used for all reactions.
 667 Column temperature was 140 °C. Catalyst bed volume (V_{bed}) was 0.4 mL. Errors are reported as
 668 one standard deviation away from the mean. ^bFor a flow rate of $\sim 0.05 \text{ mL min}^{-1}$, 72 mL of
 669 reagent was used with 12 mL sample composite intervals generating 6 data points over 24 h. ^cFor
 670 a flow rate of $\sim 0.10 \text{ mL min}^{-1}$, 144 mL of reagent was used with 24 mL sample composite
 671 intervals generating 6 data points over 24 h. ^dFor a flow rate of $\sim 0.20 \text{ mL min}^{-1}$, 168 mL of
 672 reagent was used with 24 mL sample composite intervals generating 7 data points over 14 h.

673

674 **Table 2.** Physicochemical properties of supports and catalysts under varying conditions.

Entry	Sample	Surface Area (m ² g ⁻¹) ^a	Na Loading (at. %) ^b	Lattice Constant (Å) ^c
1	Ce-Na	29	18 ± 1 ^d	5.412
2	CeO ₂	210	0	5.412
3	Ce-Na ^e	42	4.0 ± 0.2 ^f	5.412
4	Ce-Na ^g	40	2.6 ± 0.1 ^h	---
5	Pd/Ce-Na ⁱ	20	2.7 ± 0.2 ^j	---

675 ^aDetermined by nitrogen physisorption using BET approximation. ^bDetermined by ICP-OES
676 and is relative to Ce. ^cDetermined using HighScore software. ^dMeasured across three batches.
677 ^eWashed with flowing water (0.1 mL min⁻¹) for 12 h at room temperature. ^fMeasured across two
678 batches with two sample preps in duplicate (i.e. 8 data points). ^gWashed with flowing water (0.1
679 mL min⁻¹) for 12 h at 140 °C. ^hMeasured for one batch with two sample preparations in duplicate
680 (i.e. 4 data points). ⁱResults after 7 d reaction. ^jMeasured in duplicate with two sample
681 preparations (i.e. 4 data points).

682

683

684

685 **Table 3.** Acetone formation rates over supports and catalysts in absence and presence of phenol.^a

Entry	Catalyst	[Phenol] (M)	Acetone Rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	C=O Rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$) ^b	C-OH Rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$) ^b	Expected Acetone Rate ($\mu\text{mol g}^{-1} \text{h}^{-1}$) ^c
1	CeO ₂	0	7 ± 0.7 ^e	---	---	---
2	Ce-Na	0	13 ± 1.3 ^e	---	---	---
3	Pd/CeO ₂	0	2920 ± 80 ^d	---	---	---
4	Pd/Ce-Na	0	6270 ± 40 ^d	---	---	---
5	Pd/CeO ₂	0.15	576 ± 58 ^e	288	12	612
6	Pd/Ce-Na	0.15	3680 ± 368 ^e	476	974	3874

686 ^aConditions: 90 v/v % aqueous 2-propanol, 0.5g of catalyst, 0.1 mL min⁻¹, T = 140 °C, V_{bed} =
687 0.4 mL. ^bRates obtained from data found in Table 1, Entries 2, 7. ^cCalculated assuming 2 moles
688 of acetone per mole of cyclohexanone and 3 moles of acetone per mole of cyclohexanol.
689 ^dAverage rate from three separate reactions. Errors represent one standard deviation from the
690 mean. ^eRate from one reaction. Errors represent average relative error determined during method
691 validation (see experimental).

692

693

694 **List of figures**

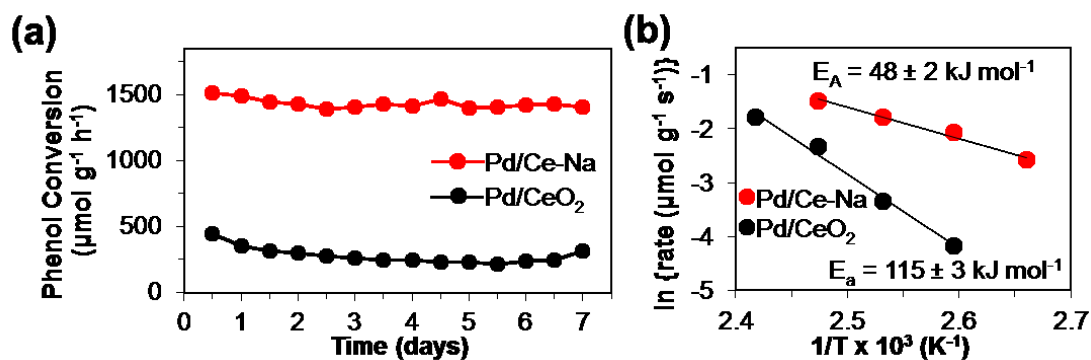
695 **Fig. 1.** (a) Phenol conversion rate for Pd/CeO₂ and Pd/Ce-Na during 7 day time-on-stream (TOS)
696 study. Conditions: 0.15 M phenol in 90 v/v % aqueous 2-propanol, 0.5 g catalyst, ~0.1 mL min⁻¹,
697 T = 140 °C, V_{bed} = 0.4 mL. Each data point corresponds to 72 mL product stream composite. (b)
698 Arrhenius plots of phenol conversion over Pd/CeO₂ (E_A = 115 kJ mol⁻¹) and Pd/Ce-Na (E_A = 48
699 kJ mol⁻¹). Conditions: 0.1 M phenol in 90 v/v % aqueous 2-propanol, 0.5 g catalyst, ~0.1 mL
700 min⁻¹, V_{bed} = 0.4 mL. Each data point (at each temperature) corresponds to the average of 6 rate
701 measurements collected at 4 h sampling intervals (24 mL composite) over 24 h.

702 **Fig. 2.** (a) PXRD patterns for CeO₂ and Ce-Na showing cubic fluorite phase. (b) Raman spectra
703 using 488 nm excitation for CeO₂ and Ce-Na. Inset shows band associated with intrinsic defects
704 (D-band). The numbers represent the ratio (A_D:A_{F_{2g}}) of the peak areas for the D-band (600 cm⁻¹)
705 and the F_{2g}-band (462 cm⁻¹).

706 **Fig. 3.** TPD-MS profile for TPSR of adsorbed 2-propanol on (a) CeO₂ and (b) Ce-Na. The m/z
707 =41, 43, and 45 signals correspond to propylene, acetone, and 2-propanol, respectively. Mass
708 normalized TPD-MS profile for TPSR of adsorbed 2-propanol on Ce-Na and CeO₂ while
709 monitoring (c) m/z = 58 and (d) m/z = 45 which correspond to acetone and 2-propanol,
710 respectively.

711 **Fig. 4.** Phenol conversion rate versus phenol concentration over Pd/CeO₂ and Pd/Ce-Na.
712 Conditions: 90 v/v % aqueous 2-propanol, 0.5 g catalyst, ~0.1 mL min⁻¹, T = 140 °C, V_{bed} = 0.4
713 mL.

714 **Fig. 5.** (a) Phenol adsorption isotherms for Ce-Na and CeO₂. (b) Plot showing the apparent
715 activation energy for the transfer hydrogenation of phenol as a function of phenol concentration.



716

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719 $T = 140 \text{ }^\circ\text{C}$, $V_{\text{bed}} = 0.4 \text{ mL}$. Each data point corresponds to 72 mL product stream composite. (b)

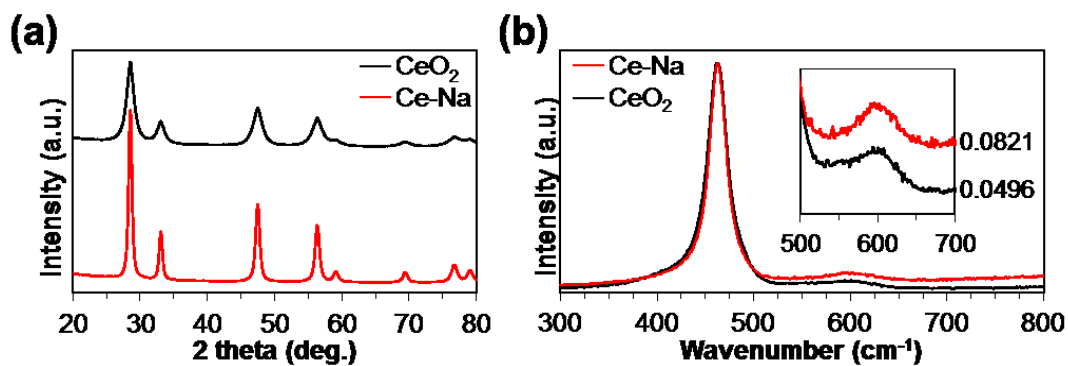
720 Arrhenius plots of phenol conversion over Pd/CeO₂ ($E_A = 115 \text{ kJ mol}^{-1}$) and Pd/Ce-Na ($E_A = 48$

721 kJ mol^{-1}). Conditions: 0.1 M phenol in 90 v/v % aqueous 2-propanol, 0.5 g catalyst, $\sim 0.1 \text{ mL}$

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723 measurements collected at 4 h sampling intervals (24 mL composite) over 24 h.

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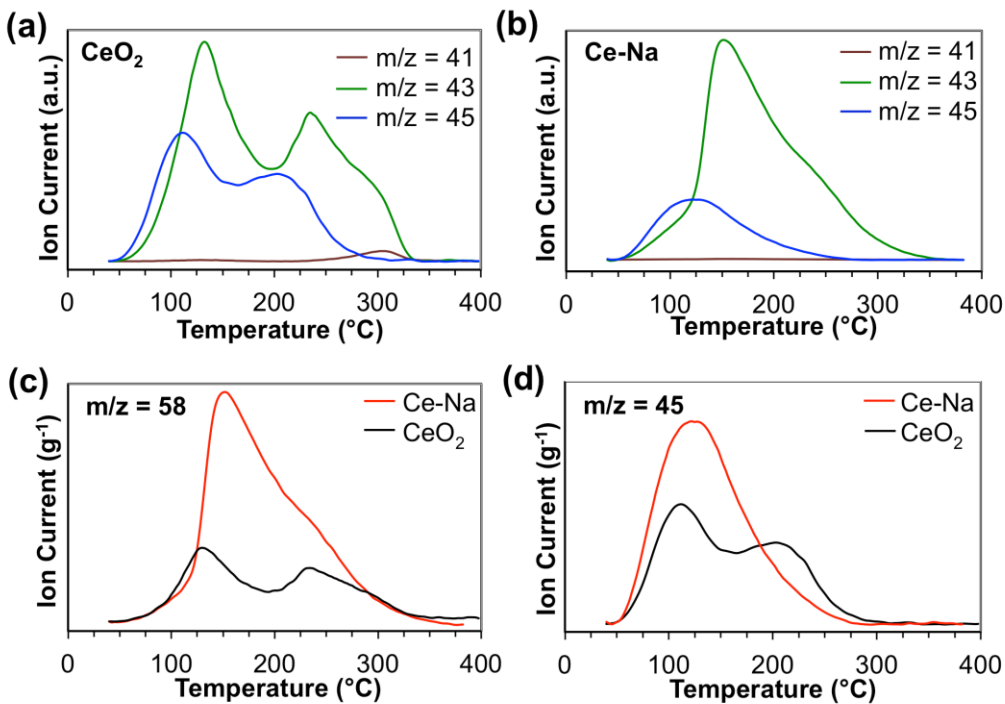
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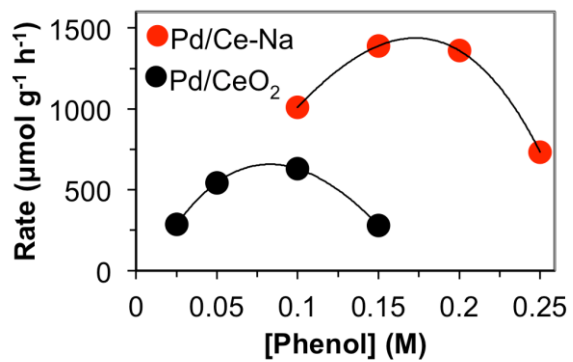
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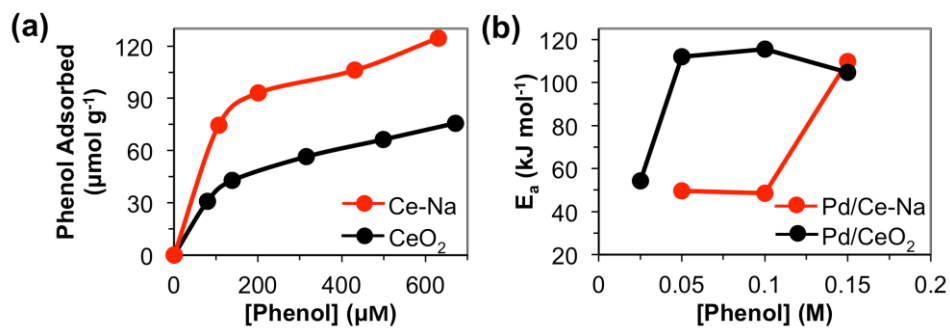
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744 **Fig. 4.** Phenol conversion rate versus phenol concentration over Pd/CeO₂ and Pd/Ce-Na.

745 Conditions: 90 v/v % aqueous 2-propanol, 0.5 g catalyst, $\sim 0.1 \text{ mL min}^{-1}$, $T = 140 \text{ }^\circ\text{C}$, $V_{\text{bed}} = 0.4$

746 mL.

747



748

749 **Fig. 5.** (a) Phenol adsorption isotherms for Ce-Na and CeO₂. (b) Plot showing the apparent
 750 activation energy for the transfer hydrogenation of phenol as a function of phenol concentration.

751