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

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ABSTRACT

Ceria (CeO_2) and sodium-modified ceria (Ce-Na) were prepared through combustion synthesis. Palladium was deposited onto the supports (Pd/CeO_2 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/CeO_2. 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.

1. Introduction

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

Lignin is a phenolic-based polymer and therefore a significant portion of the depolymerization products are phenolics [5,6]. Phenol finds its major use as a precursor for plastics often by reaction with other compounds or molecules. For example, phenol can be reduced to afford cyclohexanone and/or cyclohexanol. The ketone (K) and alcohol (A) products, either separately or in a mixture (KA oil), are predominantly used as precursors for nylon [7]. Industrial processes that convert phenol to precursors used in nylon production rely on high pressure molecular hydrogen as the reductant [8]. Therefore, it is advantageous to develop catalysts and catalytic systems that lower the hydrogen pressure needed for phenol reduction or eliminate the need for molecular hydrogen all together. Recently, there have been several catalytic systems developed for phenol reduction at or near atmospheric hydrogen pressures [9]. Far fewer systems have been developed that eliminate the need for molecular hydrogen through transfer hydrogenation [10–13]. Thus, there is a present and forecasted need to develop catalytic transfer hydrogenation systems that can transform biomass platform molecules into high-value commodity chemical precursors and lessen our reliance on petroleum-based feedstocks for downstream processing of biomolecules.

In recent years there has been a surge in the development of heterogeneous transfer hydrogenation catalytic systems [14]. Oftentimes, these systems contain two components: one to activate the donor molecule for hydrogen liberation and the other to activate the liberated hydrogen for reduction of the unsaturated functionality. Noble metals are widely used to promote the latter, while homogenous inorganic or organic bases (e.g. NaOH, K-O^{t}Bu)

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have traditionally been used for the former. From an advanced catalyst design standpoint, it is beneficial to incorporate the necessary promoters within the solid catalyst to achieve the desired activity and avoid the undesired homogeneous components. In a previous study, we showed that ceria supported palladium was active for room temperature phenol hydrogenation with molecular hydrogen at atmospheric pressure [15]. Ceria is a mildly basic, redox active metal oxide and as such, a seemingly good candidate for transfer hydrogenation reactions. Considering its potential, ceria has been poorly studied for transfer hydrogenation catalysis. Catalytic systems involving iridium oxide [16], gold [17,18], and nickel [19] supported on ceria have been reported for transfer hydrogenation of ketones and aldehydes without the use of a base promoter. Shimizu et al. [19] studied the transfer hydrogenation of ketones over Ni/CeO_2 catalyst using 2-propanol as the hydrogen donor. The catalyst showed good activity for aromatic and aliphatic ketone reduction. Although a base metal was used, the catalyst was not stable in air and thermal regenerative treatments were needed between recycling experiments.

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

2. Results and discussion

2.1. Catalysis

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

The liquid flow transfer hydrogenation of phenol using 2-propanol as the sacrificial hydrogen donor with Pd/Ce-Na and Pd/CeO_2 catalysts proceeded through the formation of cyclohexanone and cyclohexanol in various proportions depending on reaction conditions (Table 1). Both catalysts displayed outstanding stability during 7-day continuous catalytic runs (Fig. 1a). However, Pd/Ce-Na showed a marked increase in transfer hydrogenation activity over Pd/CeO_2. For instance, under the conditions given in Table 1 for Entries 2 and 7, the rate of phenol conversion was nearly five times higher over Pd/Ce-Na than Pd/CeO_2 and about six times as high for Entries 5 and 10. As evident from Table 1, Pd/Ce-Na showed higher phenol conversion rates under all the reaction conditions tested. Both catalysts showed initial deactivation attributed to decreased surface area and/or Pd dispersion with TOS (Table S2). Pd/CeO_2 showed a higher initial deactivation than Pd/Ce-Na likely owing to operation of the latter near equilibrium conversion (83% conversion) and better catalyst stability (Table S2). For Pd/Ce-Na, the ketone to alcohol yield ratio (K:A) varied from about 10:90 to 40:60 through control of the flow rate and phenol concentration (Table 1, Entries 1–5). The ketone yield was more or less constant when varying these parameters, while the alcohol yield was more sensitive to these variations (Table 1, Entries 1–5). For Pd/CeO_2, the K:A ratio was larger than for Pd/Ce-Na, giving almost exclusively the ketone (Table 1, Entries 6–10). Both catalysts showed a higher conversion rate as the 2-propanol-water ratio was increased. Interestingly, neat 2-propanol resulted in a monotonic, yet significant decrease in conversion rate as a function of time over both catalysts which was not observed in the presence of water (Fig. S1). Washing the catalysts with water overnight at 140 °C after the reaction in neat 2-propanol resulted in regeneration of the original activity. This suggests that the decreased activity may be related to hydroxyl disproportionation, which results in the removal of lattice oxygen through water formation [52–55]. In absence of water, the hydroxyl disproportionation equilibrium lies to the right in Scheme S1, giving oxygen deficient ceria, which is a poor oxidation catalyst [52]. The regeneration data imply that water is able to dissociatively adsorb on partially reduced ceria [55–57], and shift the equilibrium in Scheme S1 to the left. Thus, water appears to be a necessary component to maintain hydroxyl disproportionation equilibrium in a way that favors the redox process. Arrhenius plots were constructed for [phenol] = 0.1 M and the apparent activation barriers for phenol conversion over Pd/CeO_2 and Pd/Ce-Na were 115 ± 3 kJ mol^{-1} and 48 ± 2 kJ mol^{-1}, respectively (Fig. 1b).

Physicochemical properties are often invoked to explain differences in activity and were found to be similar for both catalysts after the reaction (Table S3). That is, the specific surface area of Pd/CeO_2 decreased by an order of magnitude over the course of the reaction, which made it comparable to Pd/Ce-Na. Likewise, the Pd dispersion value on both catalysts decreased to about 10% during time-on-stream, suggesting that Na does not enhance Pd dispersion [58,59]. Both catalysts showed the same Pd loadings before and after reaction, which is consistent with the long-term catalyst stability. The similar post-reaction physicochemical properties between the catalysts suggest that sodium modification was able to promote transfer hydrogenation activity. In order to understand the role of sodium promotion more clearly, preferential attention was given to support characterization. The role of palladium was studied where deemed relevant.

2.2. Materials characterization

Elemental analysis of as-synthesized Ce-Na support confirmed sodium was present at 18 at.% and agreed well with nominal loading of 20 at.% (Table 2, Entry 1). DRIFTS (Figs. S2–S4) and XPS (Fig. S5) analysis showed that sodium was present as a carbonate. ICP analysis of Ce-Na after continuous-flow aqueous treatment at room temperature for twelve hours showed a drastic reduction in sodium content from 18 to 4.0 at.% (Table 2, Entries 1, 3), with most soluble sodium species removed after two hours during