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Ethanol steam reforming over Co/CeO_2 catalysts: Investigation of the effect of ceria morphology

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ABSTRACT

Co catalysts supported on ceria supports with different morphologies such as nano-rods (NR) and nano-cubes (NC) were investigated in regard to their activity for ethanol steam reforming. Ceria supports were prepared using the hydrothermal method where the particle shape is manipulated by controlling the pH and pressure of the precipitation environment. Structural characterization with TEM and XRD showed the two morphologies to be similar in particle size, but different in the exposure of different crystal planes. The nano-cubes had a higher exposure of the (1 1 0) plane, which is known to have a higher affinity for creating anion vacancies and surface defects. Controlled atmosphere X-ray absorption fine structure analysis, temperature programmed reduction/oxidation, dispersion measurements and steady-state reaction performance tests showed significant differences between the two catalysts. Co catalysts supported on nanocubes showed higher reducibility compared to those supported on nanorods or commercial supports of similar particle size. These catalysts also showed high H_2 and CO_2 yields in the 400–500 °C range whereas Co/CeO_2(NR) had limited carbon cleavage activity and were only active for dehydrogenation and dehydration. The superior performance of Co/CeO_2(NC) catalysts is thought to be due to a combination of factors, including improved metal dispersion, increased reducibility and higher oxygen mobility.

1. Introduction

Hydrogen is a promising energy carrier with a high gravimetric energy density and a potential to be the fuel for fuel cells. With the increasing demand on developing renewable energy technologies with a minimal carbon footprint, it is evermore important to investigate clean hydrogen production methods. Use of hydrogen produced from bio-derived liquids would have a closed carbon loop due to the potential of sequestering CO_2 produced during reforming via photosynthesis in plant growth [1]. Ethanol steam reforming (ESR) is a cost-effective and efficient technology, which is widely investigated as reported in a number of reviews [2–5]. Non-noble metals that are active for this reaction include Ni, Cu, and Co. Although high activities in a wide temperature range for relatively high space velocities were reported for the supported noble metal catalysts, such as Ru, Re, Pd, Pt and Rh [6–15], high cost associated with such catalytic systems limits their application. Cobalt catalysts supported on metal-oxide supports, such as zirconia, magnesia and ceria have been found to have high C—C bond cleavage activity and hydrogen yields for ESR reaction in the temperature range of 300–500 °C [16,17]. Effect of catalyst preparation techniques such as reverse-micro-emulsion and solvothermal decomposition was found to increase activity by improving the contact between support and active metal [18]. Nature of the metal oxide support has been found to play a significant role in ESR, with previous work focusing on increasing the oxygen storage capacity and enabling more efficient delivery of oxygen to ethoxy species on the surface by using CeO_2 supports [19]. Introduction of a divalent cation such as Ca was seen to improve oxygen mobility further by increasing the number of oxygen vacancies on the catalyst surface [20]. In both cases, improvements in H_2 yields were reported as well as lower selectivity values for liquid by-products.

Effect of different crystal morphologies on catalytic performance has been reported previously for bulk oxides [26–29] as well as for supports. Different morphologies of ceria were used for a variety of reactions, such as water-gas shift [30,31], NO oxidation [32], methanol steam reforming [33,34] and CO oxidation [35–37] as well as ethanol steam reforming with Rh as the active metal [38]. Godinho et al. [39] reported Ga doped ceria nanorods to be significantly superior when compared to Ga doped on commercial ceria samples for ESR. There have also been several molecular

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