



Catalytic oxidation of *n*-octane over cobalt substituted ceria ($\text{Ce}_{0.90}\text{Co}_{0.10}\text{O}_{2-\delta}$) catalysts

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ABSTRACT

Catalytic oxidative activation of octane was carried out in the presence of Co substituted ceria catalysts of the type $\text{Ce}_{1-x}\text{Co}_x\text{O}_{2-\delta}$ ($\text{Ce}_{0.90}\text{Co}_{0.10}\text{O}_{2-\delta}$). The catalysts were synthesized by the solution combustion method and the surface characteristics were determined by BET, powder XRD, structural refinement and XPS. The synthesized catalyst crystallizes with a fluorite structure, the crystallinity was confirmed by bright-field images of TEM. Hydrogen uptake studies show a strong reduction peak at 425 °C and it proves substitution of cobalt ions inside the matrix of the lattice system. X-ray photoelectron spectroscopy (XPS) clarified that even though under reduction conditions, the cerium ions were slightly oxidized because of the sequence of standard reduction potentials of both cerium and cobalt ions. The catalytic activity of the catalyst was investigated between the temperature range from 350 to 550 °C, in a continuous flow fixed bed reactor at GHSV 4000 h⁻¹ with varying *n*-octane to oxygen molar ratios from 1:0.5 to 1:2.5. Results show that the conversion and selectivity of products (alkenes, oxygenates, aromatics, carbon oxides and cracked products) from the *n*-octane varies consequently with *n*-octane to oxygen molar ratio. The product selectivity at iso-conversion for C₈ products, aromatics, oxygenates and octenes was determined. The catalyst shows higher activity with respect to an increase in the *n*-octane to oxygen molar ratio and reaction temperature.

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1. Introduction

Cerium oxide has been widely investigated due to its multiple applications; as a catalyst, an electrolyte material of solid oxide fuel cells, a material of high refractive index, etc. [1–3]. Due to the special and favorable properties of ceria such as redox, acid–base and oxygen storage capacity [4,5], it has considerable significance in the area of industrial catalysis for the oxidation of hydrocarbons [6–8] and these properties of ceria either alone or with transition metals are important parameters in facilitating several organic reactions [9].

Due to the high effectiveness of ceria oxide used as a support and the low cost of cobalt, these materials can form a highly active and selective catalytic system [10–16]. These materials are used in the field of CO oxidation [17], hydrogenation reactions [18], formation of hydrogen peroxide from oxygen and hydrogen [19], the water gas shift reaction [20] and automotive catalysis [21–23].

Ceria has the fluorite structure, with cerium ions at the corners and face center of the cube and the oxygen atoms in tetrahedral positions, but the activity of ceria-based catalyst depends greatly on its structure and nanosized ceria shows higher activity than

bulk-phase ceria, because of the easier reduction of the surface oxygen species on ceria nanoparticles [24]. Ceria can be employed as an oxide carrier or a mixed oxide carrier with a transition metal oxide providing unique catalytic properties [25,26]. A number of ceria-based systems such as, $\text{CeO}_2/\text{Al}_2\text{O}_3$, CuO/CeO_2 , $\text{CeO}_2/\text{SiO}_2$, Pt/CeO_2 , Rh/CeO_2 , $\text{CeO}_2/\text{ZrO}_2$, Pd/CeO_2 and Au/CeO_2 have been studied for their catalytic properties [27–36].

Substitution of transition metals or noble metals in sites of cerium in the CeO_2 matrix by solid–solid reaction to give $\text{Ce}_{1-x}\text{M}_x\text{O}_{2-\delta}$ (M=Cu, Fe, Mn, Pt, Pd, Rh, Ru, Cr, Ni) has been reported [37]. Ceria influences the catalytic activity of the supported metal by the metal–support interaction. In addition to the metal support interaction the supported metal can also influence the physicochemical properties of the ceria support such as the oxygen storage capacity, $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple, and the defect sites such as anionic vacancies at the metal–ceria interface can directly contribute to the catalytic activity of the ceria-supported metals [31,38,39]. The enhancement in the catalytic activity of ceria supported materials is also due to the redox potential of $\text{Ce}^{4+}/\text{Ce}^{3+}$ (1.61 V), which is higher than some of the reduction potentials of 3d transition metals like $\text{Cr}^{6+}/\text{Cr}^{3+}$ (1.33 V), $\text{Fe}^{3+}/\text{Fe}^{2+}$ (0.77 V), $\text{Mn}^{3+}/\text{Mn}^{2+}$ (1.51 V) or $\text{Cu}^{2+}/\text{Cu}^0$ (0.34 V) and it has been shown that substituted transition metal ions remain in the oxidized form in the CeO_2 matrix [37]. In the cobalt substituted ceria matrix, the redox potential of $\text{Co}^{3+}/\text{Co}^{2+}$ (1.81 V) is higher than the reduction

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