Reaction Sensitivity of Ceria Morphology Effect on Ni/CeO$_2$ Catalysis in Propane Oxidation Reactions

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Introduction

A Ceria (CeO$_2$) has been extensively studied as catalysts and catalyst supports in a wide array of catalytic reactions, particularly in catalytic oxidation reactions, due to its high oxygen storage capacity (OSC) and Ce^{4+}/Ce^{3+} redox cycle.[1] Recently, morphology engineering of catalyst nanoparticles is emerging as a novel strategy to tune their catalytic performances without changing catalyst compositions and meanwhile to establish their structure-performance relations.[2,3] Ni/CeO$_2$ catalysts have been studied as catalysts for water-gas shift reaction, selective catalytic reduction of NO with NH$_3$, preferential CO oxidation in excess H$_2$, methane combustion, oxidative dehydrogenation of light alkanes and reforming reactions. The CeO$_2$ morphology effect on NiO/CeO$_2$ catalysts were previously examined in several reactions.[4,5] However, systematic studies still lack, especially for CeO$_2$ rods whose surface structures were found to vary with calcination temperatures.[6] We employed CO and CO$_2$ chemisorption to probe the surface structures of various CeO$_2$ nanocrystals, in which CeO$_2$ rods calcined at 500 and 700 °C were found to mainly expose {110}+{100} and {111}+{110} facets, respectively.[7]

Materials and Methods

CeO$_2$ nanocube and nanorod were prepared by the hydrothermal method and the The CeO$_2$ nanoparticles were purchased from Sigma-Aldrich. Ni/CeO$_2$ catalysts were prepared by the wet impregnation method. Compositions of catalysts were analyzed with a Perkin Elmer Optima 7300 DV inductively coupled plasma-atomic emission spectrometer (ICP-AES). X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250 high-performance electron spectrometer using monochromatized Al Kα radiation (hν = 1486.7 eV). H$_2$-temperature programmed reduction (H$_2$-TPR) experiments were performed on a Micromeritics Autochem 2920 apparatus equipped with TCD detector and an online mass spectrometer (HIDEN QIC-20).

Results and Discussion

We performed peak deconvolution analysis of all H$_2$ TPR profiles, from which the H$_2$ consumption of α1, α2, β and γ peaks were acquired (Figure 1). In addition to the α1, α2, β and γ reduction peaks, Ni/c-CeO$_2$ catalysts exhibit another reduction peak (labelled as the γ' peak) while other Ni/CeO$_2$ catalysts do not. The γ' reduction peak lies between the β and γ reduction peaks and its H$_2$ consumption amount does not change much with the Ni loadings of Ni/c-CeO$_2$ catalysts. The above XPS results show that Ni/c-CeO$_2$ catalysts exhibit the Ni-O-Ce species with the strongest Ni-CeO$_2$ interaction among all Ni/CeO$_2$ catalysts. We thus assign the γ' reduction peak to the reduction of CeO$_2$ activated by the very strongly-interacting Ni-O-Ce structure of Ni/c-CeO$_2$ catalysts. Likely correlations between the calculated C$_3$H$_8$ combustion rates at 250 °C in C$_3$H$_8$ combustion and the C$_3$H$_6$ formation rates at 300 °C in ODHP reaction

of various Ni/CeO$_2$ catalysts and the amount of different oxygen species estimated from H$_2$ TPR results were comprehensive examined (Figure 2). Among the investigated Ni/CeO$_2$ catalysts, 2.5Ni/r-CeO$_2$-500 catalysts exhibit the largest amount of strongly-activated oxygen species and the highest C$_3$H$_8$ combustion rate in C$_3$H$_8$ combustion reaction while 2.6Ni/c-CeO$_2$ catalyst exhibits the largest amount of the weakly-activated oxygen species and the highest C$_3$H$_6$ formation rate in ODHP reaction. Thus, the CeO$_2$ morphology engineering strategy is effective in finely tuning the metal-CeO$_2$ interaction and the reactivity of oxygen species to meet the requirements of different types of catalytic oxidation reactions.[8]

Significance

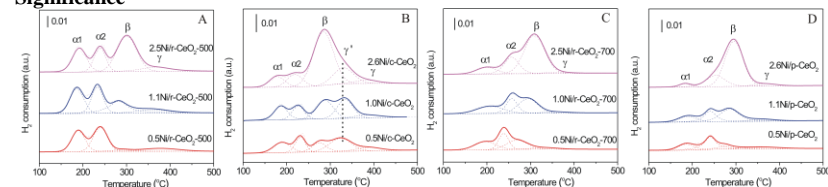
Figure 1. H$_2$-TPR profiles with peak fitting of (A) Ni/r-CeO$_2$-500, (B) Ni/c-CeO$_2$, (C) Ni/r-CeO$_2$-700 and (D) Ni/p-CeO$_2$ catalysts.
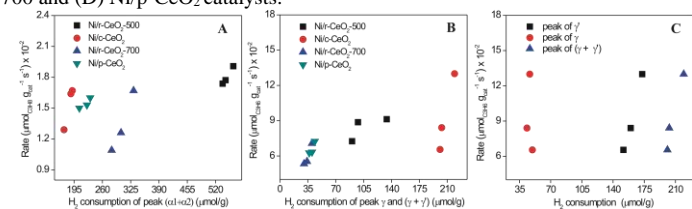

Figure 2. (A) Relationship between the propane oxidation rate at 250 °C in the propane combustion reaction and the H$_2$-consumption values of (α1+α2) peak for various Ni/CeO$_2$ catalysts (B) Relationship between the propene formation rate in the ODHP reaction at 300 °C and the H$_2$-consumption values of γ and (γ + γ') peaks for various Ni/CeO$_2$ catalysts. (C) Relationship between the propene formation rate at 300 °C in the ODHP reaction and the H$_2$-consumption values of peak γ', γ, (γ' + γ) for various Ni/c-CeO$_2$ catalysts.

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