Applied Catalysis B: Environmental 226 (2018) 403–411

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Nano-architectured CeO_2 supported Rh with remarkably enhanced catalytic activity for propylene glycol reforming reaction in microreactors

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ARTICLE INFO

Keywords:
Ceria
Morphology
Alumina
Rhodium
Steam reforming
Propylene glycol

ABSTRACT

The influence of morphology and crystalline facets of nanoshaped ceria oxide support in Rh/CeO_2 and $Rh/CeO_2/Al_2O_3$ catalysts have been investigated by oxidative steam reforming of propylene glycol in microreactors at 630 °C at $S/C = 3.5$ and $O/C = 0.15$. First, well − defined ceria nanorods (NRs) and nanocubes (NCs) have been successfully synthesized by a facile hydrothermal method and then they are deposited on to $\alpha - Al_2O_3$. The result of transmission electron microscopy indicates that the ceria nanorods exposed (110) and (100) planes but nanocubes possess only (100) planes. The developed shape controlled ceria nanocrystals and they are mixed with alumina have been used as supports for the preparation of highly dispersed and size controlled Rh nanoparticles of Rh/CeO_2 and $Rh/CeO_2/Al_2O_3$ catalysts. Their performance was tested for the propylene glycol reforming reaction in microreactors, which provide high surface of the catalyst coatings, heat and mass transfer rate and controllability. The XPS and TEM results indicate that the CeO_2 morphology shows the selective exposure of different crystal planes which has a significant impact on the dispersion of Rh nanoparticles that influenced in the reforming reaction. The steam reforming reaction experiments show that the ceria nanorods supported Rh catalyst was achieved significantly better activity and stability for 100 h of time on stream than for the all other catalysts. This could be related to the better dispersion of Rh species and the higher surface oxygen vacancies associated with the exposed (100) and (110) crystal planes favor the stabilization of Rh nanoparticles against sintering and elimination of carbon deposition on active Rh nanoparticles during reforming reaction.

1. Introduction

Hydrogen production by steam reforming of polyalcohols has emerged as a promising alternative reaction in recent years. Especially propylene glycol is an attractive fuel for specific mobile applications in the aerospace environment owing to its non-toxicity and inflammability [1]. Because of the oxidative steam reforming is an endothermic catalytic reaction, a microreactor (MR) arranged as plate heat-exchanger is the most efficient and compact reactor design for conducting this reaction on-board a vehicle to circumvent any heat transfer problems through combustion of unconverted hydrogen from the fuel cell anode in the second pass of the heat-exchanger. Owing to the high surface to volume ratio, microreactors achieve high heat and mass transfer rates, good phase contacting and thus seem to be particularly well suited for the production of hydrogen by steam reforming reactions [2–7]. Cai et al. [8] studied the hydrogen production by steam reforming of ethanol in microchannel reactors and concluded that the activity of their catalyst was higher in the case of the microchannel reactors when comparing their performance with a packed bed reactor. Görke and coauthors [9] investigated the kinetics of steam reforming of ethanol in microreactors and confirmed that the performance of their catalyst was not affected by mass and heat transfer resistances.

In order to achieve high fuel conversion and high hydrogen yield through the application of microreactors, highly active and stable catalyst is required. Among the noble and non-noble metal catalysts studied to- date, rhodium has been found to be one of the most suitable metal for the steam reforming reaction of hydrocarbons and higher (poly)alcohols [10–12], as it shows the highest stability, activity and selectivity towards hydrogen due to its capability to break the C—C bond [13]. Most importantly, the catalyst support materials should generally possess adequate chemical and mechanical properties to provide the required stability under the steam reforming conditions at high temperatures. From the viewpoint of increasing advantages, ceria is an important support material for promoting the dispersion of the active metal nanoparticles and increasing the metal–support interaction which can enhance the catalytic performance in reforming reactions

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https://doi.org/10.1016/j.apcatb.2017.12.062
Received 21 September 2017; Received in revised form 13 December 2017; Accepted 23 December 2017

[14–17]. Moreover, ceria can improve the catalyst stability due to its high oxygen storage capacity (OSC) and the oxygen exchange capacity, which is associated with its ability to reversibly change oxidation states between $Ce^{4+}$and Ce^{3+} [18,19]. Recently, we reported that the easily accessible oxygen from CeO_2 can react and eliminate the carbon species as soon as it forms and this process keeps the active metal surface free of carbon, thus inhibiting deactivation [20]. Thormann [21] et al. examined the hexadecane reforming in a microchannels coated with Rh/CeO_2 catalyst and observed the significant impact of the ceria support on the reformate composition. Steam reforming of ethanol was studied over $Rh/CeO_2/Al_2O_3$ catalysts in a microchannel reactor and their results are compared with the performance of a packed bed reactor [22]. No carbon formation was observed on the Rh/CeO_2 during dry methanol reforming due to a higher surface fugacity of oxygen species adsorbed on the ceria support that react to remove carbon [23]. Montini et al. [24] synthesized the $Rh@Ce_xZr_{1-x}O_2–Al_2O_3$ nanocomposites by direct sol-gel method for efficient hydrogen production from ethanol steam reforming reaction. The authors reported that the presence of ceria-zirconia mixed oxides in the nanocomposites play a key role to reduce carbon formation and facilitate its removal. Recently, Roh et al. [25] reported that $Rh/CeO_2–ZrO_2$ is very active for ethanol steam reforming and the supports favor the oxidation of carbonaceous species. The CeO_2 addition to Al_2O_3 support shows distinct impact on the catalytic activity of Rh catalysts for steam reforming of propane [26]. The addition of ceria stabilizes the structure of alumina by forming $CeAlO_3$ and to maintain the dispersion of rhodium [18].

However, the structure-sensitive behavior of shape controlled ceria oxide has attracted significant attention owing to its unique catalytic properties, and fruitful results have been achieved in catalytic applications [27–30]. For example, the crystal facets of the CeO_2 support play an important role in dispersion of active metal and stabilization of metal particles against sintering under high temperature reaction condition. In general, CeO_2 nanorods preferentially expose four (110) and two (100) planes, while the CeO_2 nanocubes expose six (100) planes [31]. According to the theoretical calculations, the surface energy and catalytic activity indicate that the (110) and (100) faces are more active, which means to increase the fraction of reactive (110) and (100) planes, than the (111) planes of CeO_2 nanoparticles [32–35]. On the other hand, ceria nanorods and nanocubes exhibit a greater capacity to store oxygen than ceria nanoparticles that could resist the carbon deposition on active metal. The effect of the morphology of nanocrystalline CeO_2 supported Rh catalyst was studied on the ethanol reforming reaction [27,36,37]. The influence of nano-architectured CeO_2 supports in $RhPd/CeO_2$ for the catalytic ethanol steam reforming reaction was reported by Divins et al. [38]. The crystal plane effect of CeO_2 nanostructures on the catalytic activity of Ni/CeO_2 and Ru/CeO_2 has been studied on different reactions [39,30]. The morphology effect of CeO_2 catalyst is mainly dependent on the reaction system and the nature of the metal dispersed on the CeO_2 support. For example, the catalysts based on CeO_2 nanorods were more active and selective in NO reduction [40] and CO oxidation [41,42], while catalysts based on CeO_2 nanocubes exhibit superior properties in soot combustion [43] and hydrogen oxidation [44]. Moraes et al. [45] and Soykal et al. [36] found that ceria nanocube possess good reducibility and oxygen mobility and improved the dispersion of metals, leading to superior performance of steam reforming of ethanol. Rh/CeO_2 catalysts with CeO_2 nanocrystals of rod and cubic shape exhibit satisfactory catalytic activity on steam reforming of ethanol [27]. Wang et al. [28] reported that Ni/CeO_2 nanorods exhibited excellent catalytic behavior in catalytic activity in methane dry reforming. Although many works have been reported on the catalytic activity of nanoshaped CeO_2 supported catalysts in reforming reaction [27,28,36–39], there is no report dealing with the effect of CeO_2 morphology on the catalytic performance in the reforming of propylene glycol in microreactors. We here present the influence of the morphology and crystal plane of ceria for the first time on catalytic efficiency of steam reforming of propylene glycol in microreactors and discussed the role of crystal plane and oxygen vacancy in ceria.

2. Experimental

2.1. Catalyst preparation

Shape controlled CeO_2 nanorods and nanocubes were prepared by a facile hydrothermal method as reported previously [30]. First, 3.47 g of $Ce(NO_3)_3·6H_2O$ dissolved in 40 mL of deionized water. Then, 38.4 g of NaOH dissolved in 120 mL of water were added into ceria solution and stirred for 15 min for the formation of a milky suspension. Subsequently, the suspension was transferred into a Teflon-lined stainless steel autoclave and then the autoclave was sealed and heated for 24 h at 100 °C for NRs and 180 °C for NCs. After the hydrothermal treatment, the precipitates were separated by centrifugation process. Then, the precipitates were re-suspended in water under ultra-sonication for 10 min, and then separated again using centrifugation. This process was repeated three times. The solids were then washed in ethanol and recovered by centrifugation using the same procedure, which was also repeated three times to remove completely possible sodium ionic remnants. The solids obtained were dried at 100 °C overnight and then calcined at 450 °C for 5 h in presence of air. 20% of obtained CeO_2 nanocrystals were mixed with $\alpha-Al_2O_3$ in aqueous medium and stirred for 3 h. The mixtures were dried at 100 °C for 12 h and followed by calcination at 450 °C for 5 h. For comparison, the CeO_2/Al_2O_3 was also prepared by direct impregnation of $Ce(NO_3)_3·6H_2O$ precursor on to $\alpha-Al_2O_3$ and the solids were dried at 100 °C for 12 h and calcined at 450 °C for 5 h in air. Subsequently, 5 wt% of Rh was impregnated separately on to CeO_2 and CeO_2/Al_2O_3 using $RhCl_3·xH_2O$ as a precursor and calcined at 450 °C for 3 h. The catalysts prepared are hereafter denoted as Rh/CeO_2–NR, Rh/CeO_2–NC, Rh/CeO_2–NR/Al_2O_3, Rh/CeO_2–NC/Al_2O_3 and $Rh/CeO_2/Al_2O_3$ (prepared by direct impregnation of ceria on alumina). The quantitative analysis of Rh and Ce was determined by XRF and their results are presented in the results and discussion Section 3.1. The obtained catalysts were coated onto microchannels of stainless steel mircoreactors by applying our previously reported wash coating technique [20,46].

2.2. Catalyst characterization

The TEM images were acquired on a FEI Tecnai microscope operating at 200 kV. For TEM observations, the catalyst samples were coated into the copper grids by suspending a small amount of the catalyst in ethanol under ultra-sonication (Branson, 100 W42 kHz) for 1 h. A drop of catalyst suspension was then placed on to the copper grids with holey carbon films, followed by drying at room temperature. Rigaku multipurpose X-ray diffraction instrument with Ni-filtered Cu Kα radiation was used to collect the powder X-ray diffraction (XRD) patterns. XPS measurements were carried out on a Thermo Scientific K–Alpha spectrometer equipped with a monochromatic small–spot X–ray source and a 180° double focusing hemispherical analyzer with a 128–channel delay line detector. Spectra were obtained for all the calcined catalyst using an aluminum anode ($AlK_\alpha = 1486.6$ eV) operated at 72 W and a spot size of 400 µm. Survey scans were measured at constant pass energy of 200 eV, and high–resolution scans of the separate regions were measured at 50 eV. The background pressure of the ultra–high vacuum (UHV) chamber was 2×10^{-8} mbar. All of the binding energies that are reported have been calibrated to the C 1 s transition at 284.5 eV. The surface area of all catalysts was measured at 77 K on a Micromeritics Tristar II analyzer. The catalysts were degassed at 150 °C for 2 h before measurements. The Brunauer-Emmett-Teller (BET) method in the relative pressure range of $P/P_0 = 0.0–0.4$ was employed to obtain specific surface areas. The H_2-TPR measurements were carried out for calcined catalysts in a quartz tube reactor equipped with a thermal conductivity detector (TCD). The catalysts were