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Support structure and reduction treatment effects on CO oxidation of SiO_2 nanospheres and CeO_2 nanorods supported ruthenium catalysts

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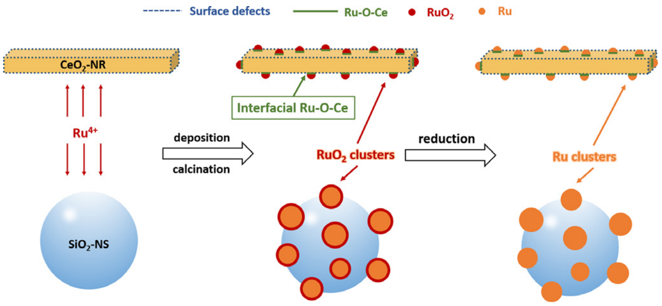
GRAPHICAL ABSTRACT



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ABSTRACT

The effects of support structure and reducibility, oxidation and reduction treatment and ruthenium loading amount were studied in SiO_2 nanospheres and CeO_2 nanorods supported ruthenium catalysts on CO oxidation. 0.4, 1.0 and 5.0 wt% Ru were impregnated on SiO_2 nanospheres and CeO_2 nanorods using precipitation method and then the samples were oxidized in air. Half of the oxidized samples were also further reduced under hydrogen atmosphere to compare the effect of reduction treatment on the catalytic activity. Detailed XRD, Raman, TEM, H_2-TPR, and CO oxidation analyses were carried out to understand the effects of RuO_x-support interaction, oxidation and reduction treatment and ruthenium loading amount on the catalytic performance. Compared to SiO_2 nanospheres supported ruthenium catalysts, both the oxidized and reduced RuO_x/CeO_2 catalysts exhibited superior catalytic performance in terms of CO conversion and low-temperature hydrogen consumption. After the reduction treatment in H_2, the RuO_x/CeO_2 catalysts is further activated for low-temperature CO conversion. Especially, the 5.0 wt% Ru/CeO_2-reduction sample can achieve ~9% CO conversion at near room temperature. The enhanced low-temperature activity of CeO_2 nanorods supported ruthenium catalysts was correlated strongly to the surface defects on CeO_2 nanorods, dispersion of RuO_x, and interfacial structures between CeO_2 and RuO_x.

1. Introduction

Low-temperature or near room temperature oxidation of carbon monoxide (CO) has been one of the most extensively studied catalytic conversion reactions from the viewpoint of industry and environment protection, especially for cleaning the air, purification of hydrogen through preferential oxidation in polymer electrolyte membrane fuel cells, and lowering pollutant automotive exhaust emissions [1–3]. The development of noble metals such as Pt, Au, and Pd [4–6] and transitional metal oxides such as CuO and Co_3O_4 [7,8], as catalysts for low-temperature CO oxidation has

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been widely reported in the literature and this research field continues to be very active. Recently, supported ruthenium (Ru)-based catalysts were employed in many gas-solid reactions because of their excellent activities under low temperature and pressure conditions, including the catalytic oxidation of volatile organic compounds (VOCs) [9,10], preferential oxidation of CO (PROX) [11], synthesis of ammonia [12], oxidation of HCl (the Deacon process) [13] and partial oxidation of CH_4 [14]. For example, Kim et al. [15] examined γ-Al_2O_3-supported noble metal (Ru, Rh, and Pt) catalysts with the metal content (5 wt% or 0.5 wt%) at different reaction temperatures. They found that 100% CO conversion could be achieved over 5 wt% Ru/γ-Al_2O_3 at 60 °C due to the easily reducible Ru species during the PROX reaction. Over et al. [16] reported that in excess O_2 at atmospheric pressure, an ultrathin RuO_2 (110) (1–2 nm thick) formed on the Ru (0001) surface exposes bridging oxygen atoms and ruthenium atoms not capped by oxygen characterized by scanning tunneling microscopy (STM) and low-energy electron diffraction (LEED). Their results indicate that the coordinately unsaturated Ru sites in RuO_2 (110) account for the superior activity for CO oxidation compared to the metallic Ru surface.

In supported metal catalysts, the primary function of supports is to enhance the dispersion and thermal stability of metal atoms/nanoclusters, but the interactions between the metal atoms/nanoclusters catalyst and the underlying support are thought to be critical for some important catalytic reactions. For example, these interactions could help trap or bond catalyst atoms/clusters on the support surface, trigger mass transfer (diffusion and electron transfer) between catalyst and support, and create various defects and strain at the interface during sample preparation and under reaction conditions (reducing and oxidizing environment) at elevated temperature. It has been widely reported that reducible oxide supports (i.e. CeO_2 and TiO_2) can promote the catalyst activity and selectivity via a synergistic effect or strong catalyst-support interaction, for example in CeO_2, mainly due to a reversible valence change ($2Ce(IV)O_2 \rightleftharpoons Ce_2(III)O_3 + 1/2O_2$) of the cerium ions with formation or elimination of oxygen vacancies [17–19]. This support promoting effect was also discovered in CeO_2-supported RuO_x catalysts. Okal et al. [20] found that VOCs oxidation reactions occur at much lower temperatures over Ru/CeO_2 (~150 °C) compared to those over Ru/Al_2O_3 (~170 °C) and Ru/$ZnAl_2O_4$ (~180 °C) due to the redox species of ruthenium on CeO_2 easily reacting with the lattice oxygen of CeO_2. Wang et al. [21] substantiated that Ru/CeO_2 with oxygen vacancy in CeO_2 has a much lower activation temperature for CO_2 methanation compared with Ru surface in Ru/α-Al_2O_3 without oxygen vacancy using operando XANES, IR, and Raman. Other and our results revealed that the reducibility and oxygen storage capacity of CeO_2 nanoparticles is in accordance with their CO oxidation activity, following the sequence: rods > cubes > octahedra. The higher activity of rods was attributed to more exposed reactive crystal planes {1 1 0} and {1 0 0} and/or defected {1 1 1} [22,23]. Huang et al. [24] reported that Ru supported on CeO_2 nanorods is more active than that on CeO_2 octahedra and nanocubes for the catalytic oxidation of chlorobenzene, which was explained by a larger number of Ru—O—Ce bonds, higher content of Ru^{4+}, easy surface oxygen mobility, and reducibility of CeO_2 nanorods support.

Based on the above observations, the selection of support type and understanding the catalyst-support interactions are vital for further enhancing the activity of supported ruthenium catalysts. In addition, thermal treatments of catalysts also play a critical role in the formation of catalyst-support interfacial structure and influencing the catalyst-support interactions. So in this work, a comparative study was conducted on irreducible SiO_2 nanospheres and highly reducible CeO_2 nanorods supported ruthenium catalysts to understand the effect of support reducibility/oxygen storage capacity (OSC) and thermal treatments (oxidation and reduction treatments) on the catalytic performance of CO oxidation. The results will further improve our understanding of the interfacial interactions between catalyst and oxide supports, and possible synergistic effect in RuO_x-CeO_2 for low-temperature CO conversion.

2. Experimental

2.1. Preparation of supports

Silica (SiO_2) nanospheres were synthesized according to a modified Stöber method [25]. 158 mL absolute ethanol, 7.8 mL ammonium hydroxide (28% NH_3 in H_2O) and 2.8 mL distilled water were introduced in a 250 mL round-bottom flask and heated to 50 °C under stirring, then 5.8 mL tetraethyl orthosilicate (TEOS) was added to the solution and stirred at 50 °C for 24 h. SiO_2 nanospheres were obtained by drying the white solution at 70 °C for 24 h. CeO_2 nanorods were synthesized using a hydrothermal method as reported previously [23]. The 88 mL of 0.1 M $Ce(NO_3)_3 \cdot 6H_2O$ and 8 mL of 6.0 M NaOH solutions were added in a Teflon liner of 200 mL capacity. The mixture was stirred for about 15 s, and then the lid of Teflon liner was closed. After putting the Teflon liner into a stainless-steel autoclave, it was heated and kept at 90 °C for 48 h. Finally, the sample was filtered and then was washed with 500 mL DI water and 50 mL ethanol. CeO_2 nanorods were obtained by drying at 60 °C for 12 h.

2.2. Preparation of RuO_x/SiO_2 and RuO_x/CeO_2 catalyst

0.4, 1.0 and 5.0 wt% Ruthenium were loaded onto CeO_2 nanorods and SiO_2 nanospheres by impregnating CeO_2 and SiO_2 with an aqueous solution containing a required amount of $Ru(NO)(NO_3)_3$ and tuning the pH value of the solution to ca. 9. Then the precipitates were initially heated at 80 °C under stirring for 4 h. In the end, the precipitates were continuously heated at 100 °C to vaporize water and transferred into a drying oven kept overnight for further drying. After that, the as-prepared dry samples were calcined in air at a rate of 10 °C/min up to 300 °C and maintaining this temperature for 5 h. xRu/CeO_2-o and xRu/SiO_2-o (o refers to the oxidized sample) catalysts were obtained (x = 0.4, 1.0 and 5.0, where x is the ruthenium content in weight percentage ($x = [Ru/(Ru + CeO_2)]_{wt} \times 100\%$ or $x = [Ru/(Ru + SiO_2)]_{wt} \times 100\%$). Finally, part of samples was reduced by heating up in a 5% H_2/Ar flow (200 mL min^{-1}) at a rate of 10 °C/min up to 300 °C and maintaining this temperature for 5 h. After cooling down to room temperature under H_2 atmosphere, xRu/CeO_2-r and xRu/SiO_2-r (r refers to the reduced sample) catalysts were obtained.

2.3. Catalyst characterizations

Powder X-ray diffraction (XRD) analysis was executed in a Philips X'Pert MPD diffractometer and the diffraction patterns were recorded using Cu Kα source (λ = 0.154 nm) in the range of 2θ between 10° and 90° with a step size of 0.05°/min. JADE software was used to determine the lattice constant and average crystallite sizes by use of Scherer's formula from the recorded patterns.

Scanning electron microscope (SEM; JEOL 7000 FE) coupled with an Oxford Instruments energy dispersive X-ray spectrometer (EDS) was used to determine the chemical composition. Transmission electron microscope (TEM, FEI Tecnai F20) operated at 200 kV was used to characterize the particle shape/size and morphology of the prepared catalyst samples.

Horiba Labram HR 800 Raman Spectrometer with a 532 nm laser module was used to collect Raman spectra of the catalysts. The Raman scattering in the 100–1200 cm^{-1} region was collected.