



Role of palladium crystallite size on CO oxidation over CeZrO₄₋₈ supported Pd catalysts

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ABSTRACT

Photodeposited palladium on nanocrystalline CeZrO₄₋₈ support was evaluated for CO oxidation, as a function of particle size and pre-treatment. All the catalysts were well characterized by XRD, SEM, EDX, TEM, CO chemisorption and Raman spectroscopy. It was observed that change in photodeposition time alters the average crystallite size of Pd, and the same was confirmed by CO chemisorption. 7 nm average crystallite size of Pd exhibited excellent catalytic activity for CO oxidation. In order to understand the effect of support and metal-support interaction, 1 wt% Pd was deposited deliberately onto reduced and oxidized CeZrO₄₋₈ support. The reduced support with anionic vacancies and more Ce³⁺ species exhibited an improvement in CO oxidation at onset temperature. Detailed analysis shows that Pd-deposition occurs preferentially at oxygen-vacancy sites and subsequent metal-support interaction influences the catalysis.

1. Introduction

Carbon monoxide is a poisonous gas and has toxic effects on human health at concentration above 35 ppm [1]. CO oxidation has received much attention in the last few decades because of its importance in automotive exhaust treatment, fuel cells, air purification as well as in gas sensors [2–4]. Variety of materials like metal oxides [5–7], mixed metal oxides [8,9] and metal supported materials [10], etc. have been reported as catalysts for the CO oxidation in the literature. Among various oxides, ceria (CeO₂) was one of the major components of automotive catalysts since its crystal structure does not change during storage and release process of oxygen i.e. oxygen storage capacity (OSC) and thus added to three way catalysts (TWC) as an OSC material [11]. OSC is one of the key requirements for TWC to remove NO_x, CO and HCs.

Ceria exists as redox material Ce³⁺/Ce⁴⁺ and oxygen (anionic) vacancies, where cerium bears +4 and +3 oxidation states under oxygen-rich and oxygen-lean conditions, respectively. To improve OSC of pure ceria, effect of addition of other oxides to it, was well studied. It was observed that addition of zirconia (forming solid solution) to ceria not only improves OSC but also its thermal stability [12]. To develop automotive catalysts, ceria zirconia (CZ) solid solutions were further developed to second and third generation CZ materials [12]. There are

various ceria-zirconia based materials including solid solutions, mixed oxides, physical mixtures, exists; among them, mixed metal oxides are the most popular class of materials. It was observed that when ZrO₂ is incorporated in the lattice of the ceria, it enhances OSC and thermal stability [12]. Ceria based noble metal catalysts for CO oxidation reported in the literature mainly includes Pt/CeO₂ [13,14], Au-CeO₂ composite [15,16] while other than ceria comprise Pt/SnO₂, Pd/SnO₂, Au supported on γ-Fe₂O₃, MnO_x and Co₃O₄ [17–20]. Materials for TWC, particularly for the total oxidation of volatile organic compounds (VOCs) and CO, supported palladium (Pd) based catalyst is considered as an active ingredient. Though there are noble metals other than palladium, like Pt, Rh, they have a serious disadvantage that they become passive (specifically Rh and Pt) in oxygen rich atmosphere due to formation of oxides when subjected to elevated temperatures [21–24]. Pd/CeO₂ catalysts, with 0.25 – 2.0% Pd loading exhibited the significant low temperature activity for CO oxidation [25] while with 1 wt % Pd loading catalysts like Pd/CeO₂-TiO₂ [26] and Pd/Al₂O₃, Pd/CeO₂-Al₂O₃ [27], etc. are also reported in the literature. These ceria based catalysts showed significant CO conversion, however, the role of Pd crystallite size and support on CO oxidation is not thoroughly evaluated.

Recently, CeZrO₄₋₈, a new material was explored for oxidative dehydrogenation of ethylbenzene to styrene [28] and Pd/CeZrO₄₋₈ for

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Suzuki cross coupling reaction in water [29]. CeZrO_{4.8} has robust fluorite structure and exhibits high redox properties [28]. Exploitation of new materials in catalysis is always an arena of great interest for researchers worldwide. In continuation of our efforts in exploring new materials in catalysis [29–31], herein an attempt was made to explore Pd/CeZrO_{4.8} for carbon monoxide oxidation reaction. Present manuscript, mainly emphasizes on effect of crystallite size of metal (Pd) dispersion and role of defects present on the support on catalytic activity. In the present work, Pd catalyst was synthesized wherein; Pd was deposited onto CeZrO_{4.8} support by photo-deposition technique with varying irradiation time. Change in irradiation time affects the crystallite size and thereafter the catalytic activity for the said reaction. In the present work, we tried to find out the optimum Pd crystallite size for CO oxidation reaction with 1% Pd loading over CeZrO_{4.8} support. The effect of oxidation state of cerium from the support on the catalytic activity was also investigated.

2. Experimental section

2.1. Materials and methods

All the chemicals were procured from Sigma Aldrich and used for the catalyst preparations without further purification.

For XPS analysis, X-ray photoelectron spectrum (XPS) with custom built APPEs unit equipped with R3000HP (VG Scienta) analyzer was used. Transmission Electron Microscopy (TEM) imaging was done using TECNAI 20 s-twin electron microscope. Raman spectra of the samples were carried out using Horiba JY LabRAM HR 800 Raman spectrometer (microscope in reflectance mode). CO chemisorption analysis; analysis of average crystallite size of palladium samples were carried out by using autosorb iQ instrument.

2.2. Preparation of support CeZrO_{4.8}

CeZrO_{4.8} was prepared by gel-combustion method using cerium nitrate and zirconyl nitrate as metal precursors and glycine as a fuel. In a typical catalyst preparation method, desired amount of both the precursors were added in distilled water and to this glycine (60% fuel-deficient ratio) was added and further evaporated to dryness on hot plate to yield a transparent gel. The obtained transparent gel was heated further to give a fluffy powder which was further calcined at 600 °C for 6 h (4°/min ramping rate) to give CeZrO_{4.8} [28].

2.3. Preparation of support Pd/CeZrO_{4.8}

Palladium (1 wt% loading) was deposited onto CeZrO_{4.8} support by photo-deposition technique [32]. In a typical catalyst preparation method, palladium nitrate was first dissolved in 120 mL of methanol to this desired amount of CeZrO_{4.8} and 30 mL water was added. The formed mixture was further purged with Argon with continuous stirring for 90 min for degassing. Finally the mixture was kept for photo-deposition by irradiating it with 400W UV light for different times. Catalysts prepared by 20, 40 and 60 min irradiation time are designated as PCZ-20, PCZ-40 and PCZ-60 respectively (where P stands for palladium and CZ for CeZrO_{4.8}).

2.4. Reduction and oxidation of the support (CeZrO_{4.8})

To investigate the effect of reduced and oxidized support on catalytic activity, the said support was reduced in a tubular furnace under H₂ atmosphere at 550 °C for 1 h with flow rate of 50 mL/min and ramping rate of 5°/min.

For oxidation, material CeZrO_{4.8} was kept in tubular furnace using air flow at 500 °C with 50 mL/min, 4°/min, flow rate and ramping rate, respectively for 1 h. On as prepared, reduced and oxidized support, 1 wt % Pd was photo-deposited and their activity was further evaluated for

the CO oxidation reaction.

2.5. General procedure for CO oxidation

The evaluation of catalytic activity of various prepared catalyst samples was performed using fixed bed reactor with 14 mm diameter at atmospheric pressure. The activity was evaluated for CO oxidation at various temperatures from room temperature to 300 °C. CO, O₂ and N₂ gases were used and their flow rate was controlled by using mass flow controller (MFC). In this set up, vertical reactor was kept in tubular furnace having uniform temperature zone of 4 cm equipped with radix 4000 temperature controller. The catalyst bed temperature was measured by using K-type thermocouple. The reaction was carried out with 50 mL/min flow rate (CO: O₂: N₂ = 1:5:19). The conversion was measured by gas chromatography (GC) equipped with online gas sampling valve, molecular sieve column and thermal conductivity detector (TCD) in a steady state with a ramping rate of 2°/min, kept at different temperatures used for analysis for 10 min for the equilibration. CO oxidation to CO₂ was calculated by formula $CO_{in} - CO_{out}/CO_{in} \times 100$.

3. Results and discussion

3.1. Characterization of catalysts

The X-ray diffraction pattern was recorded for the as prepared, reduced as well as oxidized CeZrO_{4.8} support. All the peaks could be indexed for the fluorite structure and no impurity phases were observed [28,29]. After reduction (refer section 2.4) of the said support, the decrease in the line broadening was observed which attributed to the increase in the average crystallite size and release of micro-strain in the support to some extent. XRD patterns of PCZ-20, PCZ-40 and PCZ-60 catalysts also showed prominent peaks of above said fluorite support with undetectable Pd phases (Fig. 1b). The presence of Pd was confirmed by EDX and XPS analysis well discussed below.

On reduction of CeZrO_{4.8} anionic vacancies/defects are generated due to partial reduction of Ce⁴⁺ to Ce³⁺. Reduced and unreduced CeZrO_{4.8} showed clearly distinct Raman spectra from each other (SI Fig. 6). In case of reduced CeZrO_{4.8} large broadening was observed along with shifts near ~ 460 and 610 cm⁻¹ due to generated anionic vacancies. It was observed that upon reduction, the colour of CeZrO_{4.8} became bluish (cyan) from yellow due to decrease in the band gap as well as partial filling of Ce 4f orbital [29].

PCZ-40 and PCZ-60 reduced catalyst were further analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). SEM image of PCZ-40 showed layered morphology and can be clearly seen in SI Fig. 1(a). EDX (energy dispersive X-ray analysis) and TEM image is shown for reduced PCZ-40 material in SI Fig. 1c and d, respectively. From the TEM analysis, all the particles are of the order of 20 nm (SI Fig. 1b). TEM analysis (SI Fig. 4) shows the presence of micro and mesoporous morphology of the material which is an essential factor for diffusion and mass transfer of reactants as well as products. On cursory look at various TEM images (see SI), nano size particles with random shapes with spherical to ellipsoidal geometry were observed. Random polygonal morphology was observed in case of PCZ-40 reduced (SI Fig. 1b) whereas in case of PCZ-60, hexagonal morphology was also evidenced from TEM (SI Fig. 1d). Elemental composition obtained from EDX was in accordance with the expected nominal input concentration. BET surface area of this material was observed to be 48 m²/g (refer supplementary information).

After the deposition of palladium onto the support by changing time of irradiation, average palladium crystallite size, % metal dispersion and active metal surface area were calculated by CO chemisorptions method. The data of CO chemisorptions is well tabulated in Table 1 below. It was observed that for all the catalysts the average crystallite size was in the range of 6.6–8.5 nm where 17% maximum metal dispersion was achieved in case of a catalyst PCZ-40 and PCZ-60 (Table 1,

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