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One-step synthesis of nanostructured Pd-doped mixed oxides MO_x-CeO_2 (M = Mn, Fe, Co, Ni, Cu) for efficient CO and C_3H_8 total oxidation

Jin-Yong Luo, Ming Meng *, Jin-Song Yao, Xin-Gang Li, Yu-Qing Zha, Xitao Wang, Tian-Yong Zhang

Tianjin Key Laboratory of Applied Catalysis Science and Engineering, Department of Catalysis Science and Technology, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China

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ABSTRACT

A series of nanostructured Pd-doped mixed oxides MO_x-CeO_2 (M = Mn, Fe, Co, Ni, Cu), with uniform mesoporous structure and large surface area exceeding 115 $m^2\ g^{-1}$, were synthesized in one step by a surfactant-assisted co-precipitation. Their catalytic performance was investigated using total oxidation of CO and C_3H_8 as the model reactions. The results show that, a synergism exists between even trace amounts of exposed Pd and 3d-transition metal oxides for CO oxidation, whereas such an effect is absent for C_3H_8 oxidation. In situ diffuse reflectance infrared spectroscopy (DRIFTS) study reveals that the synergistic essential for CO oxidation should be the interaction-assisted generation of active oxygen species between Pd and MO_x, which react readily with CO, forming bidentate carbonate (1587 and 1285 cm^{-1}) as intermediates. Moreover, structural characterization results indicate that a solid solution is formed between CeO_2 and Mn_2O_3 or Fe_2O_3, resulting in the very strong interaction between Pd and MO_x, as well as the greatly improved CO oxidation. The light-off temperatures for Pd-doped Mn and Fe-containing catalysts, as compared with the Pd-free catalysts, are decreased by more than 70 and 100 °C, respectively. In particular, a CO conversion as high as 80% can be achieved even at room temperature on Pd-doped Mn-containing catalyst. While for C_3H_8 oxidation, the C–H bond activation, but not the oxygen activation, plays a crucial role. The C–H bond activation ability of the catalysts is largely determined by the d-electron configurations of the M cations. A 'double-peak' phenomenon can be derived with the increase of d-electron number.

1. Introduction

The control of noxious emissions from automobiles is one of the most urgent and compelling problems faced by nearly every country in the world. It has been reported that during the cold-start transients, a considerable amount (50–80%) of CO and hydrocarbons (HCs) is released into the air despite the application of the three-way catalysts (TWCs) [1]. It is therefore highly recommended to explore catalysts with excellent low-temperature oxidation activity for the removal of CO and HCs.

Currently, noble metal catalysts, especially platinum group catalysts, represent the state-of-art in internal combustion engine emission technology, but the high price and low availability limit their application. In such situation, some base metal oxides attract much attention since they are very active as well. For example, it has been reported that Co_3O_4 catalysts can exhibit high activity for CO oxidation as low as -63 °C and for propane activation even under ambient conditions [2,3]. However, the stability presents a challenge. Due to the depletion of the active oxygen species, these catalysts suffer from relatively quick deactivation. In order to lower the catalyst cost and maintain the sustainable high activity at the same time, some researchers found that, promotion of base metal oxides with even a small amount of noble metals can greatly improve their steady-state oxidation activities, such as in the supported Pd-(CrO_x, MnO_x, Fe_2O_3, Co_3O_4, $LaCoO_3$) [4–11], Pt(-Pd)-Co_3O_4 [12–14]. The support selection is another important aspect. For the most frequently used support–Al_2O_3 with high surface area, the strong metal oxide–support interaction, like the formation of the M–O–Al linkage, is detrimental to the propane oxidation [15]. As regarding CeO_2, its strong interaction with metal oxides MO_x can weaken the M–O bond [16], which is favorable to the oxidation activity by contrast. On this basis, it is desirable to develop mixed oxides MO_x-CeO_2 promoted by a small amount of noble metals.

Recently, Co_3O_4-CeO_2 catalysts with high surface area and mesoporous structure were prepared, using a template method or co-precipitation in the presence of surfactant cetyltrimethyl ammonium bromide (CTAB) as described elsewhere [17]. After conventional impregnation with Pd, its surface area is remarkably

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* Corresponding author. Tel.: +86 22 2789 2275; fax: +86 22 2789-2275.
E-mail address: mengm@tju.edu.cn (M. Meng).

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decreased because of the partial pore blocking and the enhanced CeO_2 crystallization. So what about the synthesis of the Pd-containing mixed oxides by one-step co-precipitation? In this case, the preparation procedures can be reduced, and more importantly, the high surface area can be maintained. The main concern is probably the encapsulation of the precious metals in the volume, which may result in the inefficient utilization of these metals. But some new observations indicate that even the totally-encapsulated catalysts exhibit excellent catalytic activity, such as the Pt-in-CeO_2 [18,19] and Ir-in-CeO_2 catalysts [20]. In these catalysts, the encapsulation structure can generate very strong or even maximum metal–ceria interaction, weakening the surface Ce–O bond and forming more reactive oxygen species. On the basis of enhanced component interaction, it seems promising to prepare excellent low-temperature oxidation catalysts by one-step co-precipitation.

Consequently in this work, a series of Pd-promoted mixed oxide catalysts MO_x-CeO_2 (M = Mn, Fe, Co, Ni, Cu) were synthesized in the presence of CTAB by one-step co-precipitation. The structural properties, redox behaviors and catalytic performance of the catalysts for CO and C_3H_8 oxidation were carefully investigated and correlated. The goal of present study was to explore new preparation method and to gain some insights into the reaction mechanisms for CO and C_3H_8 oxidation, in order to design optimal oxidation catalysts used for the removal of cold-start emission.

2. Experimental

2.1. Catalyst preparation

The Pd-promoted MO_x-CeO_2 mixed oxides (atomic ratio: M/Ce = 3/7, M = Mn, Fe, Co, Ni or Cu) were prepared by the one-step co-precipitation in the presence of CTAB, as described elsewhere [17]. Appropriate amounts of $PdCl_2$, $MCl_x{\cdot}yH_2O$ ($MnCl_2{\cdot}4H_2O$, $FeCl_3{\cdot}6H_2O$, $CoCl_2{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$, $CuCl_2{\cdot}2H_2O$), $CeCl_3{\cdot}7H_2O$ (Shanghai Chemical Reagents), and CTAB (Fuchen Chemical Reagents Factory) were dissolved in distilled water (molar ratio: CTAB/(M + Ce) = 0.8), then aqueous solution of NaOH (2 M) was added dropwise until the pH arrived at ca. 11. After continuous stirring for 2 h, the obtained suspension was transferred to a Teflon-sealed autoclave and hydrothermally aged at 120 °C for 48 h. After filtration, washing and drying, the powder was calcined in air at 500 °C for 4 h. The catalysts were denoted as PdCeM. For comparison, the non-promoted mixed oxides, Pt or Au-promoted Co_3O_4-CeO_2 (precursor: $H_2PtCl_6{\cdot}6H_2O$ or $HAuCl_4{\cdot}3H_2O$), and Pd-CeO_2 catalysts were prepared by the same method as well. All the precious metals have a 0.5% weight loading. The actual composition of the catalyst was analyzed by atomic absorption spectroscopy (AAS, Hitachi 180-80).

2.2. Catalyst characterization

Surface area, pore volume and pore size distribution were measured by nitrogen adsorption/desorption at 77 K using a Quantachrome QuadraSorb SI instrument. The samples were degassed at 300 °C for 8 h before experiments. The specific surface area (S_{BET}) was determined from the linear part of the adsorption curve. The pore diameter distribution was calculated from the desorption branch using the BJH formula.

X-ray diffraction (XRD) patterns were recorded on an X'pert Pro rotatory diffractometer (PANAlytical Company) using Co K_α radiation (λ = 0.1790 nm) at 40 kV and 40 mA. The average crystallite size of CeO_2 was calculated by using Scherrer equation from the line broadening corresponding to crystal plane (1 1 1) without incorporating microstrain effects.

X-ray photoelectron spectra (XPS) were recorded on a PHI-1600 ESCA spectrometer using Mg-K_α radiation (1653.6 eV). The binding energies were calibrated using C1s peak of contaminant carbon (B.E. = 284.6 eV) as standard.

TEM images were obtained by using a Philips Tecnai G^2F20 system operating at 200 kV. The sample was ultrasonically suspended and deposited on a carbon film supported on a copper grid.

Temperature programmed reduction by H_2 (H_2-TPR) was performed on a Thermo-Finnigan TPDRO 1100 instrument with a thermal conductivity detector (TCD). Before detection, the gas was purified by a solid trap containing CaO + NaOH materials in order to remove the H_2O and CO_2. The quartz tube reactor was loaded with 50 mg sample in powder form and heated from room temperature to 900 °C in 5% H_2/N_2 mixture with a flow rate of 20 ml min^{-1}. By replacing the 5% H_2/N_2 with 5% CO/He, the CO-TPR tests were also carried out. After the sample was reduced by 5% H_2/N_2 from room temperature to 500 °C and held for 10 min, temperature programmed oxidation (TPO) tests were performed from room temperature to 900 °C in 6% O_2/He flow at a rate of 20 ml min^{-1}.

In situ diffuse reflectance infrared spectroscopy (DRIFTS) measurement was performed on a Nicolet Nexus spectrometer equipped with a MCT detector cooled by liquid nitrogen. First, the sample powder (30 mg) was treated in situ at 300 °C in 6% O_2/He with a flow rate of 50 ml min^{-1}. After cooling to room temperature in 6% O_2/He, a background spectrum was collected for spectra correction. Subsequently, pure CO was further introduced to the in situ chamber for 5 min adsorption, accounting for a concentration of 3% in the gas mixture. The spectra were collected accumulating 32 scans at a resolution of 2 cm^{-1}, and displayed in Kubelka–Munk unit.

2.3. Catalytic activity measurement

The catalytic activity measurement was carried out in a continuous fixed-bed quartz tubular reactor (i.d. 8 mm) mounted in a tube furnace. The temperatures of both the furnace and the catalyst bed were measured by thermocouples. The feed gas mixture, consisting of 1% CO and 5% O_2, or 0.5% C_3H_8 and 5% O_2, balanced by N_2, was fed to the catalyst bed (20–60 mesh, 600 mg) without diluent at a weight hourly space velocity (WHSV) of 15,000 ml g^{-1} h^{-1}. The effluent gas from the reactor was analyzed by a gas chromatograph (BFS SP-3430) equipped with a thermal conductivity detector and a flame ionization detector (FID). The conversion was determined by the differences between the inlet and outlet concentrations. For C_3H_8 oxidation, the products almost completely belong to CO_2. And the CO_2 concentration was measured by FID (before detection, it was converted to CH_4 by a Ni-based catalyst mounted in a furnace), leading to a well-matched carbon balance.

3. Results

3.1. Textural and structural properties by physical characterization

The nitrogen adsorption/desorption isotherms and the corresponding BJH pore size distributions of the catalysts are shown in Fig. 1. It can be seen that the isotherms of all the catalysts exhibit typical IV shape, with the P/P_0 position of the inflection point corresponding to a diameter in the mesoporous range. The hysteresis loops belong to the H_2 type, suggesting that the mesopores are randomly distributed, possibly formed by the surfactant-assisted nanoparticles assembly [21]. The pore diameters are narrowly centered ranging from 4 to 8 nm, indicating that these oxides possess mesoporous structure in good homo-