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ScienceDirect

Journal of Catalysis 254 (2008) 310–324

JOURNAL OF CATALYSIS

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Mesoporous Co_3O_4–CeO_2 and Pd/Co_3O_4–CeO_2 catalysts: Synthesis, characterization and mechanistic study of their catalytic properties for low-temperature CO oxidation

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Received 2 August 2007; revised 17 October 2007; accepted 4 January 2008

Available online 7 February 2008

Abstract

Several nanosized catalysts Co_3O_4–CeO_2 with varying compositions were synthesized by a surfactant-template method and further promoted by a small amount of Pd (0.5 wt%). These catalysts exhibit uniform mesoporous structure and high surface area (>100 $m^2\ g^{-1}$). The Co_3O_4 crystallites in these catalysts are encapsulated by nanosized CeO_2 with only a small fraction of Co ions exposing on the surface and strongly interacting with CeO_2. Such structure maximizes the interaction between Co_3O_4 and CeO_2 in three dimensions, resulting in unique redox properties. The introduction of Pd prominently enhances both the reduction and oxidation performance of the catalysts, due to hydrogen or oxygen spillover. These catalysts prepared by surfactant-template method exhibit excellent oxidation performance, especially the ones promoted with Pd, which show markedly enhanced CO oxidation activity even at room temperature. Based upon the results of structural properties, redox behaviors and *in situ* DRIFTS study, two different reaction pathways over Co_3O_4–CeO_2 and Pd/Co_3O_4–CeO_2 are proposed.

Keywords: Cobalt oxide; Ceria; Palladium; Mesoporous catalyst; CO oxidation; Structural characterization; Synergy; Mechanism

1. Introduction

Carbon monoxide (CO) is one of the main gaseous pollutants, which is generally produced and released from the combustion process of fossil fuel. For instance, during the cold start period of vehicles, a lot of carbon monoxide (CO) and hydrocarbons (HCs) are generated because of the incomplete combustion of fuel. At the moment, since the temperatures of emission and catalyst bed are very low, the three-way catalysts (TWCs) exhibit poor catalytic oxidation performance, which results in the release of a considerable fraction (50–80%) of emission into the air [1]. Therefore, it is highly necessary to explore low-temperature oxidation catalysts for the removal of CO and HCs. Recently, much attention has been attracted to the cobalt oxide catalysts (Co_3O_4, Co_3O_4/Al_2O_3) due to their unique activity for ambient CO oxidation [2,3]. It is reported that the light-off temperature (T_{50}) for CO oxidation over Co-based catalysts is as low as −63 °C [4]. Cerium oxide, as oxygen storage material, is often added to TWCs, since it not only possesses high oxygen storage capacity (OSC), but also enhances and stabilizes the dispersion of transition metal oxides. Consequently, it is feasible to develop oxidation catalysts mainly consisting of cobalt and cerium oxides.

As catalysts, Co–Ce mixed oxides have been applied in many reactions, such as low-temperature CO oxidation [5,6], methanol oxidation [7], CH_4 combustion [8,9], diesel soot oxidation [10], N_2O decomposition [11] and Fischer–Tropsch synthesis [12]. During these reactions, a catalytic synergistic effect between cobalt and cerium oxides is observed, especially for the oxidation reaction. It is well established that the preparation method could exert a basic influence on the structural properties of the catalysts, like surface area, component dispersion and

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doi:10.1016/j.jcat.2008.01.007

strength of interaction, which in turn determines the redox properties and reactivity of the final catalysts. Recently, by using surfactant cetyltrimethyl ammonium bromide (CTAB) as template, our group has successfully synthesized mesoporous La–Co–Ce–O and La–Co–Zr–O with large surface areas [13,14]. By using the same template, CuO–CeO_2 binary catalysts with high surface area have also been synthesized [15]. Due to the existence of more reactive sites, these catalysts show high catalytic activity for CO oxidation.

Moreover, it is believed that the oxidation activity of base metal oxide catalysts can be prominently enhanced by the addition of a small amount of Pd, sometimes to a great extent, which is called active-phase enhancement (APE) [16]. Nowadays, more and more studies are focusing on the catalysts with combination of noble metal and base metal oxides for oxidation applications, like Pd–(Cr, Cu)/(Ce, Zr)O_x/Al_2O_3 [17,18], Pt–(MnO_x, CoO_x)/SiO_2 [19], Co–(Pt, Pd, Rh)/Ce–Al–O(Al_2O_3) [20], Pd–(Fe, Mn, Co, Ni, Cu)–O_x/NaZSM-5 [21], Pd/(Mn_2O_3 + SnO_2) [22], and Pd(–Pt)/Co_3O_4(Co_3O_4–CeO_2) [23–26]. For CO oxidation, most researchers believe that noble metal is responsible for CO adsorption and base metal oxide for oxygen supply. The spillover of CO from noble metals to base metal oxides is a potential interpretation for the enhancement effect.

In this work, a series of mesostructured catalysts Co_3O_4–CeO_2 with high surface area were prepared by using a surfactant-template method, even with Co/(Co + Ce) atomic ratio up to 40%. These catalysts exhibit quite unique redox properties of cobalt phase, such as the low-temperature initiation for its reduction and oxidation, and especially the high-temperature extending for reduction completion. For CO oxidation, these catalysts display a volcano-type behavior as Co_3O_4 content increases. The catalyst with the best oxidation performance is further promoted by a small amount of palladium, and a remarkably improved CO oxidation activity is achieved even at room temperature (RT), compared with those of Co_3O_4–CeO_2 and Pd/CeO_2. The unique properties and the synergy effect between Pd and Co_3O_4–CeO_2 are interpreted in terms of structural information derived from physicochemical analysis. A novel pathway for CO oxidation over Pd/Co_3O_4–CeO_2 is proposed, which is quite different from the generally-believed one that noble metal is responsible for CO adsorption and base metal oxide, like Co_3O_4 and CeO_2, for oxygen supply.

2. Experimental

2.1. Catalyst preparation

The Co_3O_4–CeO_2 catalysts with different Co/(Co + Ce) atomic ratios (15%, 20%, 30%, 40%), denoted as CeCo15, CeCo20, CeCo30 and CeCo40, respectively, were prepared by surfactant-template method using CTAB (Fuchen Chemical Reagents Factory) as template. Appropriate amounts of $CoCl_2\cdot6H_2O$, $CeCl_3\cdot7H_2O$ (Shanghai Chemical Reagents Factory) and CTAB were dissolved in distilled water at room temperature and stirred for 15 min, then NaOH solution (2 M) was added slowly to the above solution under vigorous stirring until pH arrived at ca. 11. After stirring for 2 h, the obtained brown suspension was transferred to a Teflon-sealed autoclave and aged at 120 °C for 48 h. The obtained precipitate was filtered and washed, first with water and then with acetone in order to remove the surfactant thoroughly. The resulting black powder was dried at room temperature and calcined in air at 500 °C for 4 h. Then part of the CeCo30 catalyst was impregnated in the aqueous solution of $Pd(NO_3)_2$, giving a Pd loading of 0.5 wt%. The obtained precursor was then dried at 120 °C and calcined in air at 500 °C for 1 h. All these catalysts prepared by the surfactant-template method are denoted as ST catalysts.

For comparison, 0.5 wt% Pd/CeO_2 catalyst was also prepared by impregnating CeO_2 powder into aqueous solution of $Pd(NO_3)_2$. The support CeO_2 was prepared by thermal decomposition of $Ce(NO_3)_3\cdot6H_2O$ at 600 °C for 4 h ($S_{BET} = 50.4\ m^2\,g^{-1}$). After drying at 120 °C overnight, the solid was calcined in air at 500 °C for 4 h.

In addition, a series of Co_3O_4–CeO_2 catalysts with Co/(Co + Ce) ratio of 0.2 were also prepared by co-precipitation, impregnation and combustion. The co-precipitated sample, denoted as CeCo20-CP, was synthesized by dropwise addition of NaOH (2 M) to a mixed solution of $CoCl_2\cdot6H_2O$ and $CeCl_3\cdot7H_2O$ at room temperature under vigorous stirring until pH arrived at ca. 11. After stirring for 2 h, the obtained precipitate was filtered and washed with distilled water until no Cl^- ions in the filtrate could be detected by $AgNO_3$. The sample synthesized by combustion, denoted as CeCo20-CB, was prepared by introducing a minimum volume of mixed solution of $Co(NO_3)_2\cdot6H_2O$, $Ce(NO_3)_3\cdot6H_2O$ and urea (molar ratio: urea/nitrate = 4) into an open muffle furnace, preheated at 400 °C. The solution was boiling and then burning, yielding a foamy, voluminous black powder catalyst. For the impregnation sample, denoted as CeCo20-IM, it was prepared by immersing CeO_2 powder ($S_{BET} = 50.4\ m^2\,g^{-1}$) into aqueous solution of $Co(NO_3)_2\cdot6H_2O$. All the precursors of above catalysts were dried at 120 °C and calcined in air at 500 °C for 4 h to obtain the final catalysts.

2.2. Evaluation of catalytic activity

The evaluation of catalytic activity of the catalysts was carried out in a continuous fixed-bed quartz tubular reactor (i.d. 8 mm) mounted in a tube furnace. The reaction temperature was measured by putting a thermo-couple in the middle of catalyst bed. The feed and product mixtures were analyzed by a gas chromatograph (BFS SP-3430) equipped with thermal conductivity and flame ionization detectors. The feed gas mixture consisting of 1 vol% CO, 5 vol% O_2 and balance N_2 was led over the catalyst (600 mg) at a flow rate of 100 $ml\,min^{-1}$, equivalent to a weight hourly space velocity (WHSV) of 10 000 $ml\,g^{-1}\,h^{-1}$.

2.3. Catalyst characterization

Surface area, pore volume and pore size distribution were measured by nitrogen adsorption/desorption at 77 K using a