



Catalytic oxidation of toluene over Pd/Co₃AlO catalysts derived from hydrotalcite-like compounds: Effects of preparation methods

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ABSTRACT

A series of novel Pd/Co₃AlO catalysts derived from hydrotalcite-like compounds (HTLcs) have been prepared and investigated for total oxidation of toluene. The HTLcs phase Co–Al precursors were prepared by coprecipitation method and Pd active species were introduced by different approaches, *i.e.*, impregnation (IMP), wet ion exchange (WIE) or directly at coprecipitation stage (COP). It is found that all hydrotalcite-derived Pd/Co₃AlO catalysts are much more active than the Pd/Co₃AlO catalyst prepared via traditional thermal combustion method (TCB) in toluene elimination. The activities of all synthesized catalysts obey the following sequence: Pd/Co₃AlO (COP) > Pd/Co₃AlO (WIE) ≥ Pd/Co₃AlO (IMP) > Pd/Co₃AlO (TCB). Excellent catalytic activities of the novel hydrotalcite-derived Pd/Co₃AlO catalysts could be contributed to their high surface area, small mean crystallized size of support and highly dispersed PdO particles. Besides, they are well positively associated with catalyst reducibilities and the amounts of oxygen vacancies. According to the XPS, TEM and TPR results, it was found that the strong synergistic effect between Co₃O₄ and PdO, but not the amount of the surface palladium species which are generally believed to be the active sites, is the main factors determining the catalytic activity in this work. The stability tests indicate that all Pd/Co₃AlO catalysts have no obvious deactivation, and some catalysts even show improved activities during the reaction process due to the emergence of metal Pd.

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1. Introduction

The emission of volatile organic compounds (VOCs) to the environment is now strictly regulated due to the severe influence on health and ecological damage. Among many technologies available for VOCs control, the catalytic oxidation of these pollutants to carbon dioxide and water has been recognized as one of the most promising technologies [1,2]. In order to make the reaction economically competitive, it is necessary to explore higher active catalysts to perform at low temperatures. Currently, various kinds of catalysts, such as supported noble metals [3,4], and transition metal oxides [5,6], are being widely used for catalytic oxidation of VOCs. Among them, the supported noble metals have been generally regarded as the most desirable catalysts, in terms of their catalytic activity, selectivity and stability for catalytic oxidation [7]. They are usually prepared by wetness impregnation method [8]. However, this method is not fully reproduced and may give rise to some dishomogeneity of metal distribution on the surface and the interaction with the support is frequently weaker [9], which makes their catalytic activity and stability decreased. Recently, well dispersed and stable noble-supported catalysts produced by thermal

decomposition of noble metals-contained hydrotalcite compounds receive considerable attentions [10,11].

The hydrotalcite-like compounds (HTLcs) are known as anionic clays or layer double hydroxides and can be chemically expressed in a general chemical formula $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{II}, M^{III} represents divalent, trivalent metal cations, and Aⁿ⁻ is an anion (usually carbonate) [12]. The thermal decomposition through calcinations of HTLcs is a well known method for preparing homogeneous mixed oxides characterized by intimate mixing of components [13–15]. This method has recently been applied in the preparation of catalysts containing well dispersed noble metal atoms which, after calcination, form stabilized nanoparticles that have numerous applications (the liquid or gaseous phases) in many reactions [9–11,16,17]. It seems that synthesis from HTLcs precursors may overcome the problems of inhomogeneous distribution of the noble metals as the cations are uniformly distributed inside the brucite-type sheet of the HTLcs structure [18]. Basile et al. [19] have reported that the noble metals were uniformly distributed inside the Mg–Al-HTs precursor structure, and well-dispersed and stable noble metal particles could be obtained after further calcinations. Besides, as HTLcs can contain metal cations more than two types with various ratios, a limitless number of mixed oxides can be derived from the HTLcs precursor. For example, typical components required for a catalyst of VOCs catalytic oxidation could be all designed in a hydrotalcite-like compound. In our recent work [20], a

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series of Pd-containing hydrotalcite-like compounds ($M_3\text{Al-HTlcs}$) with different M^{2+} ($M = \text{Mg, Co, Ni, Cu, Zn}$) ions were prepared. Among them, the Pd-containing Co–Al-HTlcs catalysts show superior VOCs catalytic performance.

The aim of this work is to systematically investigate the catalytic properties and performance of hydrotalcite-derived Pd-containing Co–Al mixed oxides ($\text{Pd/Co}_3\text{AlO}$) in oxidizing VOCs, and emphatically examine the effect of different synthesis procedures on the catalytic activities. The physicochemical states of the catalysts varying with preparation methods were also examined by using the BET, XRD, XPS, TEM, TPR and TPD techniques.

2. Experimental

2.1. Catalyst preparation

2.1.1. Co-precipitation method

A solution containing adequate amounts of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and H_2PdCl_4 and a solution of NaOH (1 mol/L) and Na_2CO_3 (0.5 mol/L) were separately prepared with deionized water. At room temperature, both solutions were slowly and simultaneously added to a beaker containing deionized water under vigorous stirring, at a pH value around 10. The precipitate was aged in suspension at 60°C for 12 h and then filtered and thoroughly washed with deionized water. The resulting cake was dried at 70°C for 12 h and then at 120°C overnight. The solid was denoted as Pd/Co₃Al-HT (COP). As-prepared solid was calcined at 500°C for 4 h to obtain final mixed oxides, denoted as Pd/Co₃AlO (COP).

2.1.2. Impregnation method

Co₃Al-HT of hydrotalcite-like compounds (denoted as: Co₃Al-HT (COP)) was prepared according to the aforementioned Co-precipitation method. The as-synthesized hydrotalcite-like solid was dried at 120°C and calcined at 500°C for 2 h to obtain Co–Al mixed oxides powder. 1 M sodium hydroxide solution was added into the requisite amount of acidified (with HCl) aqueous PdCl₂ solution for adjusting the solution pH to 7; then the requisite amount Co–Al mixed oxides powder was added and aged at room temperature for 12 h. The precipitates were washed several times, dried at 120°C for 12 h. The dried solid was then crushed and calcined in air at 500°C for 2 h to get the final mixed oxide catalysts, denoted as Pd/Co₃AlO (IMP).

2.1.3. Wet-ion-exchange method

The precursor of Co₃Al-HT compound was also prepared by Co-precipitation method. For the incorporation of noble metal Pd, wet-ion exchange method was applied. Typically, stoichiometric H_2PdCl_4 was dissolved in deionized water, and then added to Co₃Al-HT precursor at once. The suspension was further diluted by adding additional deionized water up to a solid/liquid ratio of 30 (g/L). The anion exchange between PdCl_4^{2-} with the carbonate anions of HTlcs was carried out at 60°C for 24 h under vigorous mechanical stirring. Subsequently, the suspension was filtered and thoroughly washed with deionized water. The cake was dried at 70°C for 12 h and at 120°C overnight. The hydrotalcite-like solid was named Pd/Co₃Al-HT (WIE). As-prepared solid was calcined at 500°C for 4 h to obtain the final mixed oxides, denoted as Pd/Co₃AlO (WIE).

2.1.4. Thermal combustion method

The thermal combustion method was used for the synthesis of Pd/Co₃AlO (TCB) according to the description in Ref. [21]. In a typical preparation, cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), aluminum nitrate ($\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), urea ($\text{CO}(\text{NH}_2)_2$) and H_2PdCl_4 were mixed in the appropriate molar ratios in a minimum volume of distilled water to obtain a transparent solution. The initial urea/nitrate molar ratio

was adjusted to 4. The mixed solution was heated for a few minutes at 80°C and the resulting viscous gel was introduced into an open muffle furnace, preheated at 500°C . The gel started boiling and then burning, yielding a foamy, voluminous black powder sample. In order to burn-off carbon residues, the powders were further heated at 500°C for 3 h in air.

2.2. Material characterizations

X-ray diffraction measurement was carried out on a Rigaku powder diffractometer (D/MAX-RB) using Cu K α radiation ($\lambda = 0.15418 \text{ nm}$) in the 2θ range of $10\text{--}80^\circ$ with a scanning rate of $4^\circ/\text{min}$. The average crystallite size of spinal phase was calculated by using Scherrer equation from the width at half height of line profiles corresponding to crystal plane (3 1 1).

The thermal decomposition and stability of precursors was investigated with thermogravimetry (TG, Setaram, Labsys). Typically, around 30 mg of sample was heated in an Al₂O₃ crucible at a constant heating rate of $10^\circ\text{C}/\text{min}$ from 25 to 1000°C , with air purging at a flow rate of 30 ml/min.

The textural properties of the derived oxides ($\text{Pd/Co}_3\text{AlO}$) were determined by N₂ adsorption at liquid nitrogen temperature, using a gas absorption analyzer NOVA 1200. The specific surface area was calculated with the BET equation, and the pore volume and pore size distribution were obtained with the BJH method from the adsorption isotherm.

Chemical compositions of different Pd/Co₃AlO catalysts were analyzed by an inductively coupled plasma-optical emission spectroscopy (ICP-OES, OPTIMA 2000).

X-ray photoelectron spectra (XPS) were recorded with a Thermo Electron Escalab250 instrument using Al K α radiation. The base pressure was $5 \times 10^{-8} \text{ Pa}$. The binding energies were calibrated using C 1 s peak of contaminant carbon (BE = 285 eV) as standard, and quoted with a precision of $\pm 0.2 \text{ eV}$. The surface composition of the samples in terms of atomic ratios was calculated by correcting the intensity with theoretical sensitivity factors based on the Scofield cross-section.

Transmission electron microscopy (TEM) analysis was conducted using H-7500 microscope operating with an acceleration voltage of 80 kV. The specimens were prepared by ultrasonication in ethanol, evaporating a drop of the resultant suspension onto a carbon support grid.

The temperature programmed reduction of H₂ (H₂-TPR) was performed for all Pd/Co₃AlO catalysts on a Micromeritics chemisorb 2720. TPR profiles were obtained by passing a 5% H₂/He flow (50 ml/min) through the pretreated catalysts (about 50 mg). Temperature was increased from room temperature to 800°C at a rate of $10^\circ\text{C}/\text{min}$. Hydrogen concentration in the effluent was continuously monitored by a thermoconductivity detector. Prior to each TPR run, catalyst was pre-heated in 5% O₂/He flow from room temperature to 500°C and held for 30 min. After cooling to room temperature, the pure He was fed to the reactor at 50 ml/min for 1 h to purge away any residual oxygen.

The temperature programmed desorption of O₂ (O₂-TPD) was carried out on the same apparatus as that in H₂-TPR. Prior to each TPD test, 50 mg sample was pre-heated in 5% O₂/He flow from room temperature to 500°C and held for 30 min. After cooling to room temperature, the sample was heated from room temperature to 800°C at a rate of $10^\circ\text{C}/\text{min}$ in pure He. The oxygen concentration in the effluent was continuously monitored by a thermoconductivity detector.

2.3. Catalyst evaluation

Catalytic tests of all catalysts were carried out in a continuous-flow fixed-bed stainless steel reactor (i.d. 6 mm) under atmospheric

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