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Effect of the preparation method on Au/Ce-Ti-O catalysts activity for VOCs oxidation

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Abstract

Studies concerning the preparation of gold phases dispersed on binary Ce-Ti oxide ($Ce_{0.3}Ti_{0.7}O_2$) were performed in order to elaborate catalysts for total oxidation of VOCs. Solids containing gold, cerium and titanium were synthesized by impregnation and deposition precipitation (DP) method using NaOH, Na_2CO_3 or urea as precipitant agent. These catalysts have been characterized by means of total surface area (BET), X-ray diffraction (XRD), diffuse reflectance ultra-violet–visible spectroscopy (DR/UV–vis) and temperature programmed reduction (TPR) and their reactivity towards the oxidation of propene was studied. Thus, it was revealed that the gold-based material prepared by DP method using urea as precipitant agent was the most efficient catalyst towards the total oxidation of propene. Based on the characterisation data, it has been shown that the preparation method has an effect on the catalytic activity.

Keywords: Ceria; Titania; Gold; TPR; XRD; DR/UV–vis; Propene oxidation

1. Introduction

The increasing environmental awareness in the last two decades has prompted the emergence of stricter regulations covering automobile and industrial activities. Among these, the reduction of volatile organic compounds (VOCs) is particularly important because VOCs represent a serious environmental problem. The deep catalytic oxidation of these pollutants to carbon dioxide and water has been identified as one of the most efficient ways to destroy VOCs at low concentrations and to meet the increasingly stringent environmental regulations. In practice, the catalytic oxidation process requires heating large amounts of gas containing low concentrations of VOCs to the oxidation temperature. Therefore, highly active catalysts which work at lower temperatures are required.

In the last decade, it has been widely proved that it is possible to prepare gold nanoparticles deposited on metal oxide supports [1,2], which exhibit high catalytic activity towards oxidation reactions [3–15]. Supported gold catalyst on titania is often studied since its efficiency for the CO oxidation at room temperature are evidenced [1–10]. This activity depends on different parameters related to their preparation method [7] and the nature of the support [8]. Moreover, gold supported on cerium oxide has been shown to possess high activity for VOCs oxidation [11–15]. Ceria has been widely used in catalysis to purify vehicle exhausts and becomes the most rare earth oxide for controlling pollutant emission. It is known that ceria CeO_2 increases the dispersion of active components and its most important property is to serve as an oxygen reservoir which stores and releases oxygen via the redox shift between Ce^{4+} and Ce^{3+} under oxidizing and reducing conditions. The Ce^{3+}/Ce^{4+} redox cycle leads to high catalytic activity of CeO_2 [16–18]. However, since single CeO_2 would be sintered after calcination at 750 °C, some mixed oxides are prepared by adding anti sintered oxides like titanium [19,20].

Thus, a previous work [21] has shown that it seems to be interesting to combine the physico-chemical properties of gold, cerium and titanium in order to obtain a suitable catalytic material for the total oxidation of VOCs.

Therefore, the aim of this work is to deposit gold particles on $Ce_{0.3}Ti_{0.7}O_2$ and to investigate the effect of the preparation method on the catalytic total oxidation of propene. Propene was chosen as probe molecule for the catalytic oxidation, because it is often found in industrial exhausts and presents high

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photochemical ozone creation potentials (POCP) [22,23]. The gold-based catalysts have been characterised by various techniques, such as BET, XRD, DR-UV–vis and H_2-TPR, and attempts have been made to correlate the catalytic activity with the physico-chemical properties of the catalysts.

2. Experimental techniques

2.1. Catalyst preparation

Ce-Ti oxide was synthesized using sol–gel method [24]. An aqueous solution of cerium nitrate $Ce(NO_3)_3 \cdot 6H_2O$ and ethanol CH_3CH_2OH were added under stirring to another solution of ethanol CH_3CH_2OH and titanium(IV) isopropoxide $Ti(OC_3H_7)_4$ with molar ratio $Ti(OC_3H_7)_4/CH_3CH_2OH = 1/2$. The molar ratio between H_2O and titanium(IV) precursor is $H_2O/Ti(OC_3H_7)_4 = 5$. The solution was gelled after finishing the reaction between titanium(IV) isopropoxide $Ti(OC_3H_7)_4$ and water. The gel was dried at 80 °C during 24 h and finally calcined under air for 4 h at 600 °C to obtain $Ce_{0.3}Ti_{0.7}O_2$ (the number in subscript represent atomic proportion of each element in the oxide).

In this study, the gold-based catalysts ($Au/Ce_{0.3}Ti_{0.7}O_2$) were prepared by several methods: the deposition–precipitation method (DP) using different precipitating agents (urea, sodium hydroxide and sodium carbonate) and the classical method of impregnation.

Firstly, the gold-based catalysts (with a gold content of 4 wt%) were prepared by the deposition precipitation (DP) method [2]. Aqueous solution of tetrachloroauric acid ($HAuCl_4$) was added under stirring to an aqueous suspension of oxide support $Ce_{0.3}Ti_{O.7}O_2$ calcined at 600 °C and aqueous solution of urea in excess. The solution was heated at 80 °C to decompose urea and obtain pH equal to 6.7. The pH of solution was maintained at the value of 6.7 during 4 h to obtain high dispersion of fine gold particles on the oxide supports. The mixture was filtered and washed with deionised water at 60 °C several times in order to eliminate the chloride ions, dried during 24 h at 80 °C and finally calcined under air for 4 h at 400 °C.

Catalysts were also prepared with the DP method using sodium hydroxide or sodium carbonate as precipitating agent. One gram of the support ($Ce_{0.3}Ti_{0.7}O_2$) was added to an aqueous solution at 80 °C containing the suitable amount of gold. The pH of $HAuCl_4$ solution was adjusted to 8 by addition of NaOH or Na_2CO_3 (0.1 M) drop by drop under stirring during 4 h. The suspension was filtered, washed several times with hot water in order to eliminate Na^+ and Cl^- ions. The catalyst was then dried in the oven at 80 °C followed by a thermal treatment under air at 400 °C (2 °C min^{-1}) during 4 h. The code names of these catalysts are respectively: $Au/Ce_{0.3}Ti_{0.7}O_2$ [DP urea], $Au/Ce_{0.3}Ti_{0.7}O_2$ [DP NaOH] and $Au/Ce_{0.3}Ti_{0.7}O_2$ [DP Na_2CO_3].

Finally wetness impregnation was also used to prepare catalyst. The code name of this solid is $Au/Ce_{0.3}Ti_{0.7}O_2$ [Impregnation]. The support ($Ce_{0.3}Ti_{0.7}O_2$) was dispersed in an aqueous solution of $HAuCl_4$ with a volume of 100 mL for 1 g of the support. The support was impregnated during solution evaporation using a rotary evaporator at atmospheric pressure and a temperature of 80 °C. The solid was dried and calcined under air at 400 °C during 4 h.

2.2. Catalyst characterisation

To determine the elemental composition of samples, chemical analysis of Ce, Ti and Au was performed by inductively coupled plasma atomic emission spectroscopy at the CNRS Centre of Chemical Analysis (Vernaison, France).

BET surface area was measured by nitrogen adsorption at −196 °C in a Thermo-Electron QSurf M1 apparatus. Before analysis, the samples were treated under vacuum for 30 min at 120 °C.

XRD analysis was performed on a BRUKER Advance D8 powder X-ray diffractometer using Cu Kα radiation ($\lambda = 0.15406$ nm). Diffraction patterns were recorded over a 2θ range of 15–80° and using a step size of 0.02° and a step time of 4 s. The mean crystallite sizes were estimated using the Scherrer equation.

DR-UV–vis spectroscopy experiments were carried out on a VARIAN CARY 5000. The measurements were performed on air exposed samples at ambient temperature between 200 and 800 nm.

The temperature programmed reduction experiments were carried out in an Altamira AMI-200 apparatus. The TPR profiles were obtained by passing a 5% H_2/Ar flow (30 mL min^{-1}) through 50 mg of samples heated at 5 °C min^{-1} from ambient temperature to 900 °C. The hydrogen concentration in the effluent was continuously monitored by a thermoconductivity detector (TCD).

2.3. Catalytic activity measurements

Catalytic tests were carried out at atmospheric pressure in a conventional fixed bed microreactor using 100 mg of fine powder catalyst. The reactive flow (100 mL min^{-1}) is composed of air and 6000 ppm of propene. The reactants and the reaction products were analysed by a VARIAN chromatograph equipped with FID and TCD detectors. The catalysts were first activated at 400 °C for 4 h under air (2 L h^{-1}) and the conversion measurement was studied on slowly heating ramp between 20 and 400 °C at 1 °C min^{-1}. The temperature ramp of 1 °C min^{-1} was considered to be sufficiently slow to reach a pseudo-steady state at every point. Each catalytic activity measurements consisted of at least two heating–cooling cycles, to monitor possible catalyst deactivation processes. In general, the activity of the catalyst decreases slightly during the second or third heating–cooling cycle, but the difference between the cycles did not exceed 20 °C. Therefore, to compare the catalytic performance of different catalysts tested in this study, the conversion achieved during the second heating cycle will be used.

3. Results and discussions

Fig. 1 represents the conversion of propene as a function of the temperature in the presence of the catalytic support