

Promotional effect of gold added to palladium supported on a new mesoporous TiO₂ for total oxidation of volatile organic compounds

M. Hosseini^a, S. Siffert^{a,*}, H.L. Tidahy^a, R. Cousin^a, J.-F. Lamonier^a,
A. Aboukais^a, A. Vantomme^b, M. Roussel^b, B.-L. Su^b

^a *Laboratoire de Catalyse et Environnement, E.A. 2598, Université du Littoral-Côte d'Opale,
145 avenue Maurice Schumann, 59140 Dunkerque, France*

^b *Laboratoire de Chimie des Matériaux Inorganiques, FUNDP Namur, Belgium*

Available online 20 April 2007

Abstract

Gold and palladium were supported on a mesoporous TiO₂ for total oxidation of volatile organic compounds (VOCs). Mesoporous high surface area titania support was synthesised using of Ti(OC₂H₅)₂ in the presence of CTMABr surfactant. After removing the surfactant molecules, 0.5 or 1.5 wt% of palladium and 1 wt% of gold were precipitated on the support by, respectively, wet impregnation and deposition–precipitation methods. The activity for toluene and propene total oxidation of the pre-reduced samples follows the same order: 0.5%Pd-1%Au/TiO₂ > 1.5%Pd/TiO₂ > 0.5%Pd/TiO₂ > 1%Au-0.5%Pd/TiO₂ > 1%Au/TiO₂ > TiO₂. Moreover, a catalytic comparison with samples based on a conventional TiO₂, shows the catalytic advantage of the mesoporous TiO₂ support. The promotional effect of gold added to palladium could be partly explained by small metallic particles (TEM), but mainly by metallic particles made up of Au-rich core with a Pd-rich shell. Moreover, the hydrogen TPR profile of 0.5%Pd-1%Au/TiO₂ shows only the signal attributed to small PdO particles. Gold also implies a protecting effect of the support under reduction atmosphere. Operando diffuse reflectance infrared fourier transform (DRIFT) spectroscopy was carried on and allowed to follow the VOCs oxidation and the formation of coke molecules, but also a metallic electrodonor effect to the adsorbed molecule which increases in the same order as the activity for oxidation reaction. The presence of coke after test was also shown by DTA–TGA by exothermic signals between 300 and 500 °C and by EPR (*g* = 2.003).

© 2007 Elsevier B.V. All rights reserved.

Keywords: VOC oxidation; Palladium; Gold; Mesoporous titania

1. Introduction

The development of active catalysts for total combustion of volatile organic compounds (VOCs) is desired from the viewpoint of environmental protection. Noble metals which possess high activity for total oxidation are widely applied to the low temperature complete oxidation [1,2]. Bimetallic catalysts have attracted extensive attention because of their markedly different properties from either of the constituent metals, and often enhanced catalytic stabilities, activities and/or selectivities [3]. Moreover, palladium catalysts are well known for high activity in oxidation reactions [4] and modification of palladium with gold can result in improvement

of the catalytic activity of palladium. The addition of a second metal can favour the reduction of the first, increase the dispersion of a metal which has a tendency to form large particles or decrease its sintering [5]. Thus, Pd–Au metals based catalysts were found to be more active for several reactions as trichloroethene hydrodechloration [6], acetoxylation of ethylene [7] and direct synthesis of hydrogen peroxide from H₂ and O₂ [8] than Pd based catalysts.

Moreover, it was found that the support plays an important role in the improvement of the efficiency of the catalyst, particularly in oxidation reaction. Various metal oxides, including TiO₂, have been investigated as gold and/or palladium supports, with the aim of high catalytic activity [9]. Moreover, TiO₂ was used to support Pd–Au leading to a good catalyst for H₂ oxidation to H₂O₂ [8] and TiO₂ was shown to have a unique chemistry in stabilizing Au particles and/or participating in the oxidation reaction [9]. Indeed, recently

* Corresponding author. Tel.: +33 3 28 65 82 56; fax: +33 3 28 65 82 39.

E-mail address: Siffert@univ-littoral.fr (S. Siffert).

many nanostructured mesoporous oxides with high surface areas and uniform pore size distributions are used as support for multiple catalyst applications [10–12]. Thus, their high surface areas and porous volumes are real assets to improve plenty of catalytic reactions and adsorption/separation performance. For example, nanostructured mesoporous zirconia and titania supports for vanadia and gold catalysts have provided excellent catalytic properties for complete benzene oxidation [10] and the mesoporous TiO₂ used in this work, impregnated by Pd, was found to be a very active catalyst for VOC total oxidation [13].

In this work, we studied the promotional effect of gold added to palladium by the use of gold and/or palladium mono and bimetallic phase supported on mesoporous TiO₂ for total oxidation of volatile organic compounds.

Propene and toluene were used as probe molecule because alkenes and aromatics are present in the industrial and automotive emissions and they present important photochemical ozone creativity potential (POCP) [14]. As VOCs are precursor of ozone through a modification of the Chapman's cycle, a POCP scale relative to POCP of ethylene (=100) was established by Derwent et al. [14] allowing to attribute a value for each VOC.

2. Experimental

Mesoporous high surface area titania support was synthesised by the use of Ti(OC₂H₅)₂, as titanium oxide precursors in the presence of surfactant CTMABr [15] and was calcined at 400 °C under air. The solid was characterised by XRD, TEM, SEM and BET [13].

After removing the surfactant molecules, the new support is precipitated by 0.5 or 1.5 wt% of palladium and 1 wt% of gold. Gold was deposited using deposition–precipitation method [16]. The amount of TiO₂ required was dispersed into a solution containing HAuCl₄ heated to 80 °C. The pH of the solution was adjusted to 8 with NaOH. The suspension of TiO₂ in the solution was stirred for 4 h at 80 °C. After the deposition–precipitation, the sample was washed with water (60 °C) six times, and dried 24 h at 80 °C. Palladium supported samples were prepared by aqueous impregnated method using palladium nitrate and all the samples were calcined in air at 400 °C for 4 h. The solids obtained, 1%Au/TiO₂, 1%Au-0.5%Pd/TiO₂, 0.5%Pd-1%Au/TiO₂, 0.5%Pd/TiO₂ and 1.5%Pd/TiO₂, were all characterised by elementary analysis, thermal analysis, specific area analysis, X-ray diffraction and H₂ temperature programmed reduction (TPR), electron paramagnetic resonance (EPR) and transmission electron microscopy (TEM). Moreover, for a comparison purpose, samples prepared from palladium and gold supported on a conventional titania oxide (called 0.5%Pd/conventional TiO₂ and 0.5%Pd-1%Au/conventional TiO₂) were also synthesised by the same procedure. This support coming from Huntsman Tioxide (sulphate method) and calcined at 400 °C possesses a high specific surface of 134 m² g⁻¹.

The palladium and gold content was determined by the Analytical Center of French CNRS (Vernaison) by inductive coupled plasma optical emission spectroscopy and mass

spectroscopy (ICP/OES/MS) after dissolution of sample on a mixture of HF and HNO₃ solution.

Thermal analysis measurements were performed using a Netzsch STA 409 equipped with a microbalance differential analysis (DTA) and a flow gas system. The dried catalyst was treated under air; the temperature was raised at a rate of 5 °C min⁻¹ from room temperature to 1000 °C.

N₂ adsorption–desorption isotherms and BET specific surface areas were measured at -196 °C with a volumetric adsorption analyser Sorptomatic 1990 manufactured by Thermo Finnigan.

The structures of solids were analyzed by powder X-ray diffraction (XRD) technique at room temperature with a Bruker diffractometer using Cu K α radiation scanning 2 θ angles ranging from 10° to 80°.

Temperature programmed reduction experiments were carried out in an Altamira AMI-200 apparatus. The TPR profiles were obtained by passing a 5% H₂/Ar flow (30 mL min⁻¹) through the calcined sample (about 100 mg). The temperature was increased from -40 to 500 °C at a rate of 5 °C min⁻¹. The hydrogen concentration in the effluent was continuously monitored by a thermoconductivity detector (TCD).

Electron paramagnetic resonance measurements were performed at -196 and 25 °C on an EMX Bruker spectrometer. A cavity operating with a frequency of 9.5 GHz (X band) was used. Precise *g* values were determined from simultaneous precise measuring of frequency and magnetic field values. All EPR spectra were treated with the Bruker WINEPR program.

TEM was performed on a Philips Tecnai-10 microscope at 100 kV. The specimens for TEM observation were prepared by embedding the samples in epoxy resin and ultramicrotoming and mounting on a copper grid.

The mono and bimetallic catalysts were tested in the oxidation of propene and toluene. Toluene and propene oxidation were carried out in a conventional fixed bed microreactor and studied between 25 and 400 °C (1 °C min⁻¹) and with operando diffuse reflectance infrared fourier transform (DRIFT) spectroscopy. The reactive flow (100 N mL min⁻¹) was composed of air and 1000 ppm of gaseous toluene or propene. Before the catalytic test, the solid (100 mg) was calcined under a flow of air (2 L h⁻¹) at 400 °C (1 °C min⁻¹) and reduced under hydrogen flow (2 L h⁻¹) at 200 °C (1 °C min⁻¹).

3. Results and discussion

Elemental analysis of the samples was determined to especially verify the gold and palladium content. The results given in Table 1 are close to those expected.

XRD experiment of the calcined samples shows that the mesoporous TiO₂ support and the conventional TiO₂ present both the anatase phase with a low part of brookite phase for the mesoporous TiO₂ [13]. However, it was not possible to observe metallic gold and/or palladium or any of their oxides. The particle sizes are too small and/or there is not enough metal to observe these phases.

Download English Version:

<https://daneshyari.com/en/article/58418>

Download Persian Version:

<https://daneshyari.com/article/58418>

[Daneshyari.com](https://daneshyari.com)