Catalysis Today xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

# $Au/TiO_2$ catalysts promoted with Fe and Mg for *n*-octanol oxidation under mild conditions

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ARTICLE INFO

*Article history:*
Received 2 January 2016
Received in revised form 4 May 2016
Accepted 4 May 2016
Available online xxx

*Keywords:*
*n*-Octanol oxidation
Gold catalysts
Modification with Mg and Fe oxides
Gold electronic state

ABSTRACT

This work aims to further the understanding of gold-based catalytic oxidation of *n*-octanol in liquid phase. Modification of catalysts with metal oxides additives (Fe or Mg) was used as a tool for transforming and stabilizing gold species. Structural, electronic and catalytic properties of gold catalysts were systematically investigated by means of DRS, $H_2$, CO FTIR, $S_{BET}$, EDS and SEM, HRTEM, SR-XRD, XANES, XPS and liquid phase *n*-octanol oxidation. Addition of modifiers affects Au electronic properties, but not the structural ones. Characterization results allow excluding $Au^{3+}$ ions as candidates for active sites in *n*-octanol oxidation. In $Au/Mg/TiO_2$, gold exhibited more reduced states while in $Au/Fe/TiO_2$ gold was more oxidized; $Au/TiO_2$ for intermediate oxidized states was found. The proper balance of oxidation states in the gold surface of $Au/Mg/TiO_2$ can be responsible for its higher activity compared with $Au/Fe/TiO_2$ and $Au/TiO_2$ towards *n*-octanol oxidation. Finally our approach shed light on the nature of active sites for *n*-octanol oxidation on gold and furthers the development of green base-free catalytic oxidation of alcohols.


## 1. Introduction

To address the upcoming petroleum shortage, two main approaches have been developed to ensure fuel supply for energy purposes. For instance, hydrate gas and shale gas exploitation have become increasingly popular in this matter; while on the other hand, by shifting to renewable sources, it is expected that the use of petroleum undergoes a drastic reduction. Meanwhile, processing and production of number of commodities in our daily life that are based on petroleum-derived feedstock might also face paucity, thus the search for alternative feedstock useful for fine-chemical industry is a continuing and challenging task.

Biomass offers not only a sustainable alternative to petrochemical feedstock, but the industrial application of feedstock from renewable resources could also be convenient in valorizing waste from a variety of economic sectors such as food, agriculture and paper industries. Biomass accounts for more than half of the renewable energy potential [1]; but also huge amounts of new raw materials for chemicals production, including a vast source of alcohols due to fermentation, among others process. In this regard, selective oxidation of fatty alcohols to the corresponding aldehydes, acids and ester, holds potential to open the path for the synthesis of products with high added value for fine-chemicals. From the sustainability viewpoint, the use of biomass fits well with the principles of green chemistry, which include atom economy, chemicals with low toxicity, avoidance of volatile organic solvents and derivatization, use of renewable resources, production of biodegradable materials and use of catalysis.

Focusing on the latter, catalysts comprising supported gold nanoparticles (Au NPs) are among the most investigated systems

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http://dx.doi.org/10.1016/j.cattod.2016.05.002
0920-5861/

for the catalytic aerobic oxidation of alcohols in liquid phase, which circumvent the use of bases [2]. Catalytic oxidation of fatty alcohols is a complex reaction that involves several intermediates. In fact, current data available in the literature fail identifying a clear general trend and forecasts that permit to direct the catalyst selectivity or that allows an overall optimization of the reaction conditions. Although Au NP-based catalyst have proved to be efficient in catalyzing oxidation of alcohols, a number of parameters such as gold content, Au NPs size, electronic state of gold, influence of additives, redox pretreatment, *etc*., have not been investigated in detail.

It is worth mentioning that oxidation of *n*-octanol is being used as a convenient model for comparative studies between catalysts activity towards oxidation of alcohols, specifically for primary alcohols of long chain (so called fatty alcohols). As oxidation of *n*-octanol is more difficult than most alcohols of industrial importance, it is expected that catalysts active for *n*-octanol oxidation will be also effective in similar processes involving biomass transformation.

Normally, base-mediated oxidation of alcohols in liquid phase requires neutralizing the carboxylates formed during oxidation with strong acids, which generates large amounts of inorganic salts as waste. This justifies the need for base-free catalytic oxidation of alcohols in order to obtain aldehydes, acid or esters in a more sustainable way. Villa et al. first reported a base-free oxidation of *n*-octanol by Au NPs with the aid of $O_2$, which were supported on nanometer-sized NiO [3]; while Ishida et al. [4] reported an extensive and specific study concerning a base-free oxidation of *n*-octanol (in water) by Au NPs under $O_2$ atmosphere at moderate pressure. By screening the Au NPs supported on a variety of metal oxides ($Al_2O_3$, $TiO_2$, $MnO_2$, $Fe_2O_3$, $Co_3O_4$, NiO, ZnO, $ZrO_2$ and $CeO_2$), it was evidenced that their activity strongly depends upon both the supportís nature and the solvent used, while selectivity varied broadly. All these results were obtained under moderate pressure of oxygen (5 bar), but recent studies have shown that, by using heptane as solvent, *n*-octanol can be oxidized even with oxygen flowing at normal pressure and in the absence of bases [5].

Catalytic oxidation of *n*-octanol under mild conditions, *i.e.* base-free, at low temperature and under atmospheric pressure, has been the focus of recent investigations conducted by our group [6,7]. We have demonstrated that a catalyst consisting in Au NPs supported on alumina $CeO_2$-modified ($Au/CeO_2/Al_2O_3$) is able to promote the oxidation of *n*-octanol rendering a mixture of equal parts of the corresponding aldehyde and ester, *n*-octanal and octyl octanoate respectively [5]. On the other hand, selectivity towards aldehyde, acid or ester formation can be tuned in by addition of metal oxides as modifiers, even at low conversions [6]. In the present study $TiO_2$ was chosen as support since $Au/TiO_2$ catalysts are among the most active gold catalysts in oxidation reactions [8–16]. Modification of $Au/TiO_2$ catalyst was carried out through introduction of electron-donor (Mg) and electron-acceptor (Fe) oxides. Finally, this work aims to shed light on the nature of gold active sites origin of the catalytic activity of nanometric gold, which is an unexplored topic for base-free catalytic oxidation of *n*-octanol.

## 2. Experimental

### 2.1. Catalysts preparation

Titania Degussa P25 (45 $m^2\,g^{-1}$, nonporous, 70% anatase and 30% rutile, purity >99.5%) was used as starting support. Before use, $TiO_2$ was dried in air at 100 °C for at least 24 h. Modification of titania with molar ratio Ti/M = 40 (M = Mg, Fe) was made by impregnation (2.5 $cm^3/g$) of initial $TiO_2$ with aqueous solutions of modifier precursors $Fe(NO_3)_3 \times 9H_2O$ or $Mg(NO_3)_2$ from Aldrich. Then, impregnation products were dried at room temperature for 48 h and at 110 °C for 4 h, and calcined at 550 °C for 4 h. Commercial $HAuCl_4 \times 3H_2O$ (Aldrich) was used as gold precursor. $Au/TiO_2$ and $Au/M/TiO_2$ catalysts (nominal loading 4 wt.% Au) were prepared by deposition-precipitation with urea in the absence of light, following the previously reported procedure [17–19].

### 2.2. Samples characterization

Catalyst samples, either as-prepared or pretreated in hydrogen at 300 °C for 1 h, were studied by diffuse reflectance UV–vis spectroscopy (DRS) with a CARY 300 SCAN (Varian) spectrophotometer. Optical spectra of $Au/TiO_2$ or $Au/M/TiO_2$ samples presented in this work were obtained by subtracting the spectra of pure supports from those of catalyst samples.

$H_2$-TPR measurements of as-prepared samples were performed in a fixed-bed quartz reactor with an AutoChem 2950 analyzer, M̈icromeritics.. Temperature-programmed experiments were performed by heating at a rate of 10 °C $min^{-1}$ from 25 up to 900 °C under the reducing feed (10 vol.% of $H_2$/Ar, 20 $cm^3\,min^{-1}$). Hydrogen consumption was measured by the thermal conductivity detector.

Fourier transformed infrared spectra (FTIR) of CO adsorbed on the catalysts were recorded by using a Bruker Tensor 27 FTIR spectrometer in transmittance mode with 4 $cm^{-1}$ resolution. *In situ* experiments were carried out in a quartz cell with NaCl windows capable of working at temperatures from −100 to 300 °C and pressures from $10^{-2}$ to 760 Torr. The sample powder was pressed into disks of 13 mm diameter and weight ~20 mg. The sample was pretreated in $H_2$ or $O_2$ (100 Torr) at 300 °C for 1 h and then cool down for room temperature. After that, $H_2$ or $O_2$ was evacuated and CO adsorption (Matheson Research grade, $P^0$ = 30 Torr) were carried out. CO spectra presented in the work were obtained by subtracting the CO gas phase spectrum.

Due to conditions of equipment exploitation, prior any other characterization the samples were pretreated in hydrogen at 300 °C for 1 h.

Textural properties of samples were determined from nitrogen adsorption-desorption isotherms (−196 °C) recorded with a Micromeritics TriStar 3000 apparatus. Prior to experiments, samples were degassed at 300 °C in vacuum for 5 h. The N2 adsorbed volume was normalized to a standard temperature and pressure. The specific areas of the samples were calculated by applying the BET method to the nitrogen adsorption data within the P/P0 range 0.05–0.25.

A JEOL-5300 scanning electronic microscope (SEM) was utilized for a general sample morphology observation. Gold contents were measured by energy dispersive spectroscopy (EDS) in the same system equipped with a Kevex Superdry detector.

High resolution transmission electronic microscopy (HRTEM) studies were carried out using a JEM 2100F microscope operating with a 200 kV accelerating voltage. The samples were ground into a fine powder and dispersed ultrasonically in hexane at room temperature. Then, a drop of the suspension was put on a lacey carbon-coated Cu grid. At least ten representative images were taken for each sample. Particle size distribution was obtained by counting *ca.* 100 particles for each sample.

X-ray powder diffraction was conducted by the step-scanning procedure (step size 0.02°; 0.5 s) with a Philips XPert PRO diffractometer, using Ni-filtered CuKα (λ = 0.15406 nm) radiation. Assignment of crystalline phases was based on the ICDD- 2013 powder diffraction database. Synchrotron radiation X-ray diffraction (SR-XRD) experiments were carried out at the Structural Materials Science beamline of the Kurchatov Synchrotron Radiation Source as described in [20]. Diffraction patterns of powdered materials were taken in transmission mode at λ = 0.68886 Å, using an Imaging Plate 2D detector (exposure time 30 min). EXAFS exper-

Please cite this article in press as: Y. Kotolevich, et al., $Au/TiO_2$ catalysts promoted with Fe and Mg for *n*-octanol oxidation under mild conditions, Catal. Today (2016), http://dx.doi.org/10.1016/j.cattod.2016.05.002