Journal of Catalysis 352 (2017) 638–648

Contents lists available at ScienceDirect

Journal of Catalysis

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

Plasmon enhanced selective electronic pathways in TiO_2 supported atomically ordered bimetallic Au-Cu alloys

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ARTICLE INFO

Article history:
Received 1 May 2017
Revised 27 June 2017
Accepted 28 June 2017
Available online 19 July 2017

Keywords:
Bimetallic
Gold
Copper
Titanium dioxide
Plasmonic
Selective electron transfer

ABSTRACT

Herein, we investigate the mechanisms involved in the selective oxidation of ethanol to acetaldehyde by localised surface plasmon resonance (LSPR) enhanced Au-Cu alloys. Temperature programmed oxidation results in tandem with quantitative in-situ DRIFTS of the surface species under different illumination conditions revealed that the cleaving of C—C bonds at the Au-TiO_2 interface were inhibited in the presence of Cu at temperatures <175 °C. HAADF-STEM and XPS analysis of the spent catalysts demonstrated that the suppression of C—C cleavage was due to selective electron transfer between the atomically ordered Cu and Au arrays. Thus, the selectivity of Au-Cu/TiO_2 towards the formation of acetaldehyde could be enhanced by over 800% at 100 °C under visible light illumination compared to standard thermal catalysis. Nonetheless, the selective electron charge transfer was disrupted at temperature >175 °C, lowering acetaldehyde selectivity. The work suggests that LSPR photo-enhancement is defined by the inherent electronic interactions within the bimetallic alloy and is facilitated by atomically ordering of the Au-Cu arrays. As such, in addition to performance enhancement, LSPR photo-enhancement can be used in combination with other characterisation techniques to ascertain the selective electronic pathways in bimetallic catalysts.

1. Introduction

Research into catalysis has historically focussed independently on either thermal-catalysis or photocatalysis although selected recent studies are beginning to investigate materials and methods which bridge the two fields. For instance, Scott et al. [1,2] observed a thermal catalytic contribution of Pt in Pt/TiO_2 during the photocatalytic degradation of selected organics and that pre-treating Pt/TiO_2 with UV light improved the catalytic oxidation of formic acid by a factor of 7. Zhu et al. [3,4] has demonstrated the enhancement of selective catalytic oxidation under visible light irradiation in the presence of gold- or silver-based plasmonic catalysts. Dumesic et al. [5] found that the high temperature reverse water-gas shift reaction over Au/TiO_2 was enhanced by 30–1300% under visible light illumination. A key application for these new photo-thermal catalysts is solar energy harvesting, whereby the aim is to utilize the whole solar spectrum at its highest thermodynamic potential. One class of materials exhibiting promise is plasmonic-semiconductors which, if well-understood, can be designed to deliver catalytic selectivity via photo-enhancement under: (i) UV illumination through congruent roles of the photo- and thermal-catalysis; and (ii) visible light illumination through plasmonic-mediated electron charge transfer from the metal (e.g. Au) deposits to the TiO_2 support [6,7].

Although Au can impart valuable plasmonic effects, it is restricted by its inertness as a thermal catalyst. To overcome this, researchers have proposed to improve the functionality of Au by coupling it with other active metal species, such as Cu, Ni, Pt, and Pd [8–12]. Alloyed bimetallic catalysts enable control of the electronic and/or structural properties at a nanoscale level [13]. Alloying Au with Cu, in particular, is intriguing because Cu nanoparticles also exhibit localised surface plasmon resonance (LSPR) at 700 nm, potentially yielding an alloy with broader plasmonic activity [8,14]. Thermal catalytic enhancement by supported bimetallic Au-Cu alloys have been reported for applications such as CO oxidation and the selective oxidation of alcohol by Liu et al. [15–18]. Recently, Du et al. synthesised Au/$CuSiO_3$ nanotubes for the selective conversion of ethanol to acetaldehyde. A similar system was examined by Dai et al. for silica-supported AuCu and

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http://dx.doi.org/10.1016/j.jcat.2017.06.034
0021-9517/

$AuCuO_x$ nanoparticles [19,20]. Using electron spin resonance (ESR) spectroscopy and supporting characterisation, Sugano et al. demonstrated visible light illumination-based regeneration of the catalytic activity of a TiO_2 supported Au-Cu alloy by reducing surface oxidised Cu species in the presence of alcohol [8]. The literature has shown that Au-Cu/TiO_2 can be a highly active heterogeneous catalyst, although understanding of Au-Cu interactions within the bimetallic alloy and the metal-support interface, especially under light illumination to selectively promote certain pathways, is still lacking.

As was suggested in earlier works, probing surface intermediate species using in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is key to understanding the mechanism of LSPR enhanced photo-thermal-catalysis [6,7]. Herein, we investigate the selective oxidation of ethanol to acetaldehyde over TiO_2-supported Au-Cu bimetallic alloys by probing the effects of catalyst composition, temperature, and illumination conditions. In conjunction with high resolution electron micrograph and X-ray photoelectron spectroscopy (XPS), electronic metal-metal and metal-support interactions within the TiO_2-supported Au-Cu bimetallic alloys will be elucidated.

2. Experimental methods

2.1. Materials

Aeroxide® TiO_2 P25 (primary particle size >25 nm, surface area ~50 m^2/g, anatase to rutile ratio of around 4:1) was used as the catalyst support in all experiments. Chemicals and gases were used as supplied: gold (III) chloride trihydrate (Sigma-Aldrich), copper (II) nitrate trihydrate (Ajax-Finechem), sodium hydroxide (Chem-Supply), absolute ethanol (Ajax-Finechem), compressed ethanol (500 ppm, synthetic air balance, Coregas®), compressed ethanol (1000 ppm, nitrogen balance, Coregas®), and zero air (20% oxygen, nitrogen balance, Coregas®).

2.2. Synthesis and characterisations of bimetallic Au-Cu/TiO_2

The 1 atm% TiO_2 supported bimetallic Au-Cu alloys were synthesised in this study by co-depositing Au and Cu precursors onto the surface of Aeroxide® TiO_2 P25 nanoparticles via a modified deposition-precipitation (DP) method [8,21]. The TiO_2 support was stirred in the presence of the mixed Au and Cu precursor solution (pH 7.5 at 80 °C) for 3 h, washed with deionised water, air dried, ground and spread onto 3 × 3 cm films via the doctor blading method, to give a film loading of 30 ± 4 mg. For characterisation purposes, the catalysts in powder form were reduced ex-situ at 400 °C in a 20% H_2/Ar mixture.

HAADF-STEM of the Au/TiO_2 particles was taken on a JEOL JEM-ARM200F operating at 200 kV. Metal deposit sizing was performed using a Phillips CM200 High Resolution Transmission Electron Microscope (HR-TEM) operated at 200 kV. Prior to the measurements, the samples were dispersed in ethanol and sonicated for 5 min with the resulting suspension loaded on a Cu grid. During Energy Dispersive Spectroscopy (EDS) mapping, Cu, Au and Al TEM grids were used for Au/TiO_2, Cu/TiO_2, Au-Cu/TiO_2, respectively, to minimise signal interference with the samples. The total metal content in the catalysts was analysed by a Perkin Elmer OPTIMA 7300 Inductively Coupled Plasma – Atomic Emission Spectrometer (ICP-AES) using aqua regia as the digestive agent. Brunauer-Emmett-Teller (BET) surface area was assessed by a Micrometritics TriStar 3000 Analyser. UV–Vis spectra were measured with a Shimadzu UV-3600 UV–Vis-NIR Spectrophotometer using $BaSO_4$ as the reference. H_2-temperature programmed reduction (H_2-TPR) was carried out using a Micromeritics Autochem I chemisorption analyser under 20 mL min^{-1} of 10% H_2/Ar at 10 °C min^{-1}. X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific ESCALAB250i using a mono-chromated aluminium K-alpha radiation source (energy ~ 1.5 keV).

2.3. Catalytic performance

Gas phase ethanol oxidation experiments were performed using an in-house designed plug flow reactor system at atmospheric pressure (Scheme S1). Prior to reaction, the catalyst film (including the neat TiO_2 control) was reduced in-situ at 400 °C (ramp rate 5 °C/min) for 2 h under a 50 mL/min 20% hydrogen/argon gas mix. The catalyst film was then cooled and held at a temperature of 100 °C. A 500 ppm ethanol-air gas mixture was introduced to the reactor at 100 mL/min and the system purged for 2 h. Catalyst performance under thermal, visible-light/thermal and UV light/thermal conditions was assessed by measuring activity (ethanol consumption, acetaldehyde and CO_2 production) at 25 °C intervals over the range 100–250 °C. Reactor effluent gas products were injected into a gas chromatograph (Shimadzu GC2010) equipped with a methanizer and flame ionization detector. Product separation was achieved using an Agilent J&W HP-PLOT Q capillary column. Sample bed illumination were performed with a LX300F Xe illuminator (Perkin Elmer/ILC Technologies) equipped with a Schott UG-11 band pass glass filter (UV light illumination, <400 nm) or Schott GG-420 long pass glass filter (visible light illumination, >420 nm).

2.4. In-situ DRIFTS

In-situ DRIFTS was performed using a Brüker VERTEX 70v FTIR spectrometer, equipped with a liquid N_2 cooled MIR source, KBr optics, and a RockSolid interferometer (Scheme S2). In-situ DRIFTS analysis of Au/TiO_2 and neat TiO_2 were studied in three consecutive steps: (i) in-situ pre-treatment of the catalysts at 400 °C to both remove surface organics and reduce the catalysts; (ii) ethanol adsorption at 50 °C; and (iii) photo-thermal-catalytic oxidation at 100 °C under dark, UV and visible light illumination. Due to space constraints in the optical chamber, sample illumination was conducted using LED light sources with a narrow bandgap corresponding to the TiO_2 bandgap and Au plasmon excitation wavelengths, 365 nm and 530 nm, respectively. Quantification of the DRIFTS results involved an initial normalising of all the measured DRIFTS spectra to the characteristic infrared absorbance spectra of TiO_2. The normalised spectra were then smoothened and adjusted according to Kubelka-Munk theory to improve the linearity of the peak intensities in relation to the adsorbed organic concentration. Subsequently, a background correction was applied to remove the broad O—H peaks spanning the range 2400–3800 cm^{-1} which corresponds to adsorbed water and the characteristic absorbance spectra of TiO_2 [22–24].

Further information regarding the methodology used can be found in the Supporting Information.

3. Results

3.1. Synthesis and characterisation of bimetallic Au-Cu/TiO_2

The 1 atm% TiO_2 supported bimetallic Au-Cu alloys were synthesised in this study by co-depositing Au and Cu precursors onto the surface of Aeroxide® TiO_2 P25 nanoparticles via a modified DP method [8,21]. The specific surface area of all synthesised catalysts (Table 1) was determined to be approximately 52 m^2/g, based on the BET surface area analysis, indicating there was a negligible impact by the DP method on the surface area of the TiO_2 support