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Low temperature selective oxidation of methane to methanol using titania supported gold palladium copper catalysts.


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Abstract

The selective oxidation of methane to methanol has been studied using trimetallic AuPdCu/TiO$_2$ catalysts prepared by incipient wetness impregnation. They are able to catalyse the selective oxidation of methane to methanol under mild aqueous reaction conditions using H$_2$O$_2$ as the oxidant. When compared with bimetallic, Au-Pd/TiO$_2$ analogues, the new trimetallic catalysts present productivities which are up to 5 times greater under the same test conditions, and this is coupled with methanol selectivity of up to 83 %. Characterisation shows that whilst Au-Pd is present as Au-core Pd-shell nanoparticles, copper is present as either Cu or Cu$_2$O in < 5 nm particles.

Keywords

Methane, selective oxidation, methanol, AuPdCu, TiO$_2$, low temperature

1. Introduction

The direct oxidation of methane to methanol is a key challenge within the chemical sciences. Conventional natural gas reserves are estimated to exceed 200 trillion cubic meters $^1$, with further exploration ongoing. Owing to its high abundance, natural gas has been suggested as a fuel for society’s transition away from a petroleum-dependent economy $^2$. Direct conversion of the major components of natural gas (methane and ethane) to oxygenated products is a key challenge in achieving this. However, the direct catalytic upgrading of these short chain alkanes is yet to be achieved under mild/ green and industrially viable conditions. Processes for upgrading methane to value added products have been commercialised, however due to the relative inertness of the substrate ($\Delta H_{\text{CH}_4} = 439.57 \text{ kJ mol}^{-1}$), these utilise harsh conditions for its activation $^3$. Technologies for conversion of methane to methanol fall into two broad categories; indirect and direct. Indirect approaches utilise harsh conditions to convert methane to synthesis gas $^4$, which is then further converted to methanol, amongst other bulk chemicals. Although very selective, such processes have high energy and capital demands. Direct conversion of methane to methane-derivatives has also been reported. High temperature/ high pressure gas phase approaches have been reported $^5$, though these typically show low selectivity towards methanol. Methane oxidation in the liquid phase has also been
studied extensively. One approach involves oxidation of methane to yield methyl- esters, and often requires acidic media. The direct oxidation of methane to methanol is favourable, however, derivatization incurs additional workup and separation steps in the liquid phase. Several groups have used environmentally benign oxidants such as H$_2$O$_2$ in methane oxidation systems, though no system has as yet been deemed viable for commercialisation. Indeed, highly efficient H$_2$O$_2$ utilisation must be realised if H$_2$O$_2$ is to be used as the oxidant in the activation of methane. Circumventing the need to provide a premade H$_2$O$_2$ feed, liquid phase systems have been reported in which H$_2$O$_2$ is generated *in situ* from H$_2$ and O$_2$. However, these systems used acid promoters and yielded formic acid or methyl esters as major products.

It has previously been reported that supported AuPd catalysts catalyse the oxidation of methane with H$_2$O$_2$ at 50 °C in water. The reaction was shown to proceed through formation of methylhydroperoxide which underwent further conversion to yield methanol and CO$_2$. The reaction was also performed in the absence of added H$_2$O$_2$, with H$_2$O$_2$ instead generated *in situ* from H$_2$ and O$_2$. In this way AuPd/TiO$_2$ catalysed both H$_2$O$_2$ synthesis and methane oxidation reactions. We now extend these studies to show the effect of addition of copper to the previously reported catalyst systems. Catalysts are studied when H$_2$O$_2$ is both added and also generated *in situ*. We have assessed the effect of copper addition on the rate of H$_2$O$_2$ synthesis, methane activation, methanol selectivity and the efficiency with which H$_2$O$_2$ is utilised in products. Through catalyst characterisation studies, we aim to correlate catalyst structure and function.

2. Materials & Methods

2.1 Catalyst preparation

Supported catalysts were prepared by incipient wetness impregnation using chloride precursors. All loadings are given as wt%. The procedure for synthesis of a 2.5% Au 2.5% Pd 2.5% Cu/ TiO$_2$ catalyst is as follows;

Solutions of HAuCl$_4$·3H$_2$O (*Johnson Matthey*, 4.29 ml, 0.059 M) and CuCl$_2$·2H$_2$O (*Sigma Aldrich*, 5.3 ml, 0.149 M) were mixed, and then a solution of PdCl$_2$ (*Johnson Matthey*, 0.083 g) was added.
with vigorous stirring. Following dissolution of the PdCl$_2$, TiO$_2$ (P25, Degussa, 1.85 g) was added with vigorous stirring. Once a homogeneous slurry was formed, drying was carried out (16 h, 110 °C). The dry catalyst was then ground to a fine powder and calcined in static air (400 °C, 3 h, 20 °C min$^{-1}$).

2.2 Catalyst Testing

2.2.1 Oxidation of methane with added ex situ H$_2$O$_2$

Catalyst testing was carried out in a 50 ml Teflon-lined stainless steel Parr autoclave reactor. The reactor was charged with H$_2$O$_2$ (Sigma Aldrich, 5000 µmol, 0.5 M) and catalyst (1.0 x 10$^{-5}$ mol metal equivalent) was added. The reactor was sealed and purged 3 times with methane. The reactor was then charged with methane (BOC, 99.999 %, 30.5 bar) and the autoclave was heated to 50 °C. Once the setpoint temperature was reached, the system was vigorously stirred (1500 rpm) for 0.5 h. Following this the autoclave was cooled to ca. 12 °C to minimise loss of volatile products. Post reaction, the remaining H$_2$O$_2$ was quantified through titration versus acidified Ce(SO$_4$)$_2$ (8 x 10$^{-3}$ mol dm$^{-3}$) of known concentration, with a Ferroin indicator. Aqueous products were quantified with solvent suppressed $^1$H NMR at ambient temperature on a Bruker Ultrashield 500 MHz spectrometer using a TMS/CDCl$_3$ internal standard. Gaseous products were quantified using a Varian 450-GC fitted with a CP-Sil 5CB capillary column (50 m length, 0.32 mm diameter, carrier gas = He), a methaniser unit and both FID and TCD detectors.

2.2.2 Oxidation of methane with in situ generated H$_2$O$_2$

Methane oxidation experiments with in situ generated H$_2$O$_2$ followed the same procedure as outlined in 2.2.1 with the following exceptions. Once sealed, the reactor was purged with 5% H$_2$/N$_2$ (BOC) and then charged with 5% H$_2$/N$_2$ (BOC), 25% O$_2$/N$_2$ (BOC) and CH$_4$ (BOC, 99.999%) such that the total pressure equalled 32 bar. The gas phase composition was 0.86% H$_2$/1.72% O$_2$/75.86% CH$_4$/21.55% N$_2$ to ensure the mixture was outside of the explosive limits.

2.2.3 – H$_2$O$_2$ synthesis and decomposition

Hydrogen peroxide synthesis and hydrogenation was evaluated using a stainless steel Parr
 autoclave with a nominal volume of 100 ml. The autoclave was charged with catalyst 
(0.01g) and 8.5 g solvent (5.6 g MeOH and 2.9 g H₂O). The charged autoclave was then 
purged three times with 5% H₂/CO₂ before pressurising with 5% H₂/CO₂ (29 bar) and 25% 
O₂/CO₂ (11 bar) at 20 °C. The temperature was then allowed to decrease to 2 °C followed 
by stirring (at 1200 rpm) of the reaction mixture for 30 mins. H₂O₂ productivity was 
determined by titrating aliquots of the final solution after reaction with acidified Ce(SO₄)₂ 
(0.01 M) in the presence of two drops of ferroin indicator.

H₂O₂ degradation experiments were carried out in a similar manner as H₂O₂ synthesis 
experiments but without adding the 25%O₂/CO₂. Furthermore, 0.68 g of H₂O from the 8.5 g 
of solvent was replaced by a 50 % H₂O₂ solution to give a reaction solvent containing 4 wt% 
H₂O₂. The standard reaction conditions for H₂O₂ hydrogenation included: 0.01 g catalyst, 8.5 
g solvent (5.6 g MeOH, 2.22 g H₂O and 0.68 g H₂O₂ (50 %)), 29 bar 5%H₂/CO₂, 2 °C, 1200 
rpm, 30 mins.

2.3 Catalyst Characterisation

Powder X-ray diffraction (XRD) patterns were collected on a PANalytical MPD diffractometer fitted 
with a CuKα₁ radiation source (λ= 0.154098 nm) at ambient conditions. Samples were scanned in the 
range of 10- 70 ° at 40 kV and 40 mA.

HR-TEM was performed using a (LaB6) JEOL 2100 equipped with a high-resolution Gatan digital 
camera. In scanning transmission electron microscopy (STEM) mode, a dark field (HAADF/Z-
contrast) detector was used. An EDS system (Oxford Instruments) equipped with a 80 mm² SDD 
(Silicon Drift Detector) X-Max⁸ 80 T was employed to study the elemental composition in Point & 
ID, Line scans, layered and elemental mapping modes. EDS data was analysed using AZtecTEM 
software. For HR-TEM analysis, samples were suspended in DI water and ca.1 µL was added to a 
TEM grid and dried. EDS analysis of the samples containing Cu was carried out using Ni TEM grids 
and a Beryllium sample holder.
X-Ray photoelectron spectroscopy (XPS) was performed using a VG EscaLab 220i spectrometer, using a standard Al-Kα X-ray source (300 W) and analyzer pass energy of 20 eV. Samples were mounted using double-sided adhesive tape, and binding energies were referenced to the C 1s binding energy of adventitious carbon contamination at 284.7 eV.

Temperature programmed reduction (TPR) profiles were obtained using a ThermoElectron TPDRO 1100 instrument fitted with a TCD. Catalysts were pretreated at 90 °C under a flow of He (20 mL min⁻¹) for 0.5 h and then allowed to cool to ambient temperature. The flow was then switched to 10 % H₂/Ar (15 mL min⁻¹) and the temperature was raised to 700 °C using a linear ramp rate of 5 °C min⁻¹.

3. Results and Discussion

3.1 Liquid Phase oxidation of methane with preformed H₂O₂

Our previous studies have shown TiO₂ to be an effective support for methane activation over bimetallic AuPd catalysts. Whilst inactive in the reaction, the addition of TiO₂ to a homogeneous HAuCl₄·H₂O catalysed methane oxidation reaction resulted in an increase of methanol selectivity and decreased selectivity towards formic acid. In a similar way, studies into the oxidation of methane over ZSM-5 catalysts have reported that deposition of Cu²⁺ increases methanol selectivity dramatically by preventing further oxidation to formic acid. EPR studies showed that Cu²⁺ was either scavenging or preventing formation of hydroxyl radicals. Indeed, theoretical studies have reported Cu to be capable of oxidising methane to methanol. As copper has both been reported to increase selectivity to primary products and is able to oxidise methane to methanol, we investigated the possibility of adding Cu as a component to supported AuPd catalysts.

A series of mono, bi and tri-metallic catalysts comprising Au/Pd/Cu were prepared and tested for oxidation of methane with H₂O₂ added as the oxidant (Table 1). For comparison with previously published data, Table 1 Entry 1 presents previously published data for the optimal catalyst (2.5 % Au 2.5% Pd/ TiO₂ prepared by the incipient wetness impregnation method).

When deposited onto TiO₂ at 2.5 wt% loading, Cu is itself active (Table 1 Entry 2) which is consistent with the ability of Cu to catalyse Fenton’s type H₂O₂ conversion and generate oxygen based radical.
species\textsuperscript{29, 30}. Indeed, the methane oxidation products methylhydroperoxide, methanol and CO\textsubscript{2} were observed in the reaction mixture. The overall activity of this catalyst was higher than that of the previously reported bimetallic AuPd catalyst (Table 1 Entry 1) with a TOF of 1.0 compared to 0.70 mol\textsubscript{methane converted} mol\textsubscript{metal}^{-1} h\textsuperscript{-1}, and H\textsubscript{2}O\textsubscript{2} was more efficiently utilised with 4.9 \% of active oxygen retained in the products. This is compared with 2.1 \% for AuPd/TiO\textsubscript{2}. Moreover, monometallic Cu/TiO\textsubscript{2} displayed higher selectivity towards partially oxygenated products at 96 \%, which is compared with 90 \% for the 2.5\% Au 2.5\% Pd catalyst. The opposite trend was observed in methanol selectivity however, with 49\% for the AuPd catalyst and 14\% for monometallic Cu. This suggests that Cu does not catalyse the transformation of methylhydroperoxide to methanol at rates which are comparable to AuPd catalysts. Co-deposition of 2.5 wt\% Cu and 2.5 wt\% Au increased oxygenate productivity with no change in the product distribution. An added benefit of Au addition was an increase in efficiency of H\textsubscript{2}O\textsubscript{2} usage to 6.7 \%. Both Au- Cu and Pd- Cu catalysts showed lower methanol selectivity than the Au-Pd catalyst, with methylhydroperoxide the favoured reaction product (83 \% and 66 \% respectively).

Clearly both Au and Pd are required to effectively convert methylhydroperoxide to methanol. Hence, combining the high catalytic activity afforded by Cu and high methanol selectivity of AuPd nanoparticles would be desirable in a trimetallic catalyst. Addition of 2.5 wt\% Cu to a 2.5\% Au 2.5\% Pd catalyst led to a fivefold increase in catalyst productivity compared with the bimetallic AuPd (Table 1 Entry 1). This constituted a 135 \% increase in TOF from 0.7 to 1.65 mol\textsubscript{methane converted} mol\textsubscript{metal}^{-1} h\textsuperscript{-1}. Once more, addition of Cu led to increased efficiency of H\textsubscript{2}O\textsubscript{2} utilisation, reaching 12.2\% whilst H\textsubscript{2}O\textsubscript{2} conversion decreased from 93 \% to just 50 \%. This suggests that Cu is either altering the AuPd active sites by (i) changing the redox properties of active sites (ii) blocking active sites of non-desirable H\textsubscript{2}O\textsubscript{2} decomposition pathways, or (iii) that Cu is itself altering the rate of H\textsubscript{2}O\textsubscript{2} decomposition. This is explored later in this paper. As with Au- Cu and Pd- Cu catalysts, addition of Cu shifted the product distribution to favour the primary product methylhydroperoxide (69 \% selectivity). Indeed, methanol selectivity for the AuPdCu catalyst (7.5 wt\% metal loading, Table 1 Entry 5) was 27.8 \% which is compared with 49.3 \% for the Au-Pd catalyst (Table 1 Entry 1). This
effect of Cu is consistent with previous Cu/ZSM-5 studies, whereby Cu$^{2+}$ was shown to inhibit the hydroxyl radical-mediated oxidation of methanol to formic acid.$^{24,25}$ The wt% loading of Cu was therefore decreased, to determine whether higher methanol selectivity might be achieved whilst still minimising the unselective decomposition of H$_2$O$_2$. Comparable activity to 2.5% Au 2.5% Pd 2.5% Cu/TiO$_2$ was observed upon testing of a 2.5% Au 2.5% Pd 1% Cu/TiO$_2$ catalyst, with TOF (h$^{-1}$) of 1.65 and 1.40 respectively. Through lowering of the Cu loading, methanol selectivity increased from 27.8% to 82.7%, with H$_2$O$_2$ conversion also increasing to 83%. Catalyst performance for this trimetallic catalyst is superior to that of our previously reported AuPd catalyst (Table 1 Entry 1) under liquid phase conditions.$^{21}$ Furthermore, addition of Cu led to decreased CO$_2$ selectivity from 9.7% for Au-Pd/TiO$_2$ to 3.1 and 4.5% following deposition of 2.5 wt% and 1.0 wt% Cu respectively. Finally, a physical mixture of 2.5% Au 2.5% Pd/ TiO$_2$ and 2.5% Cu/TiO$_2$ was tested and showed a comparatively low TOF of 0.34 and high rate of H$_2$O$_2$ decomposition relative to its trimetallic analogue. This suggested a synergistic interaction when Au/Pd and Cu are in close proximity.

3.2 Liquid phase oxidation of methane with in situ generated H$_2$O$_2$

Addition of Cu to AuPd catalysts has been shown to enhance catalytic activity and selectivity for the oxidation of methane to methanol with added H$_2$O$_2$ as oxidant. A series of trimetallic AuPdCu/ TiO$_2$ catalysts of varying wt % Cu loading was therefore prepared and assessed for catalytic activity in the oxidation of methane with H$_2$O$_2$ generated in situ from H$_2$ and O$_2$. Catalytic data for the optimal bimetallic AuPd catalyst from our previous studies is shown in Table 2 Entry 1.

Co-deposition of Cu with AuPd (Table 2 Entries 2-5) led to a significant decrease in catalytic activity for methane oxidation when H$_2$O$_2$ was produced in situ. Deposition of Cu onto AuPd might alter or block the active sites responsible for generating H$_2$O$_2$ from dissolved H$_2$ and O$_2$ and thereby limit oxidant availability for the methane oxidation reaction. To explore this, catalysts were tested for activity in the synthesis and degradation of H$_2$O$_2$ under previously reported reaction conditions.$^{31}$ It is apparent (Table 3) that addition of Cu to 2.5% Au 2.5% Pd/ TiO$_2$ has a detrimental effect upon the net rate of H$_2$O$_2$ synthesis, with catalyst productivity falling from 83 mol kg$^{-1}$ h$^{-1}$ to 10 and 11 for Cu loadings of 1.0 wt% and 2.5 wt% respectively. The rate of H$_2$O$_2$ degradation is also lower for the
trimetallic catalysts (Table 3, Entries 2 and 3). This represents combined rates of \( \text{H}_2\text{O}_2 \) hydrogenation and decomposition pathways. Given that addition of Cu also led to decreased \( \text{H}_2\text{O}_2 \) synthesis rates, it can therefore be concluded that Cu blocks the sites needed for \( \text{H}_2 \) activation to \( \text{H}_2\text{O}_2 \). This indicates that the decomposition pathway would dominate the degradation rates in Table 3 Entries 2 and 3. The ability of Cu to decompose \( \text{H}_2\text{O}_2 \) at 50 °C was studied under an inert atmosphere of \( \text{N}_2 \) (\( P = 30 \text{ bar} \)) with all other test conditions set as in Table 1 (0.5 h, \( [\text{H}_2\text{O}_2] = 0.5 \text{ M}, 5000 \text{ µmol}, 50 \text{ °C}, 1500 \text{ rpm}, 1.0 \times 10^{-5} \text{ mol of metal} - 25.4 \text{ mg catalyst} \)). Upon testing, 2.5% Cu/TiO\(_2\) showed a high \( \text{H}_2\text{O}_2 \) decomposition rate of 384 mol \( \text{H}_2\text{O}_2 \text{ converted kg}^{-1} \text{cat h}^{-1} \). This is compared with a rate of 0.406 mol \( \text{methane converted kg}^{-1} \text{cat h}^{-1} \) when the same catalyst was tested for methane oxidation at 50 °C with added \( \text{H}_2\text{O}_2 \) (0.5 M, 5000 µmol, Table 1 Entry 2). The low oxygenate productivities shown for trimetallic catalysts in Table 2 can therefore be attributed to competition between a high rate of Cu- catalysed \( \text{H}_2\text{O}_2 \) decomposition and low rates of \( \text{H}_2\text{O}_2 \) synthesis/ methane oxidation reactions. This was confirmed through addition of 2.5% Cu/TiO\(_2\) to a reaction catalysed by 2.5% Au 2.5% Pd/TiO\(_2\). Physical mixing of these catalysts led oxygenate productivity to fall from 0.11 mol \( \text{methane converted kg}^{-1} \text{cat h}^{-1} \) to 0.074 mol \( \text{methane converted kg}^{-1} \text{cat h}^{-1} \) (Table 2, Entry 7). This is comparable to the productivity of 0.068 (same units) which was observed for 2.5% Au 2.5% Pd 2.5% Cu/TiO\(_2\) under the same reaction conditions (Table 2, Entry 2).

### 3.3 Catalyst characterisation

To correlate catalyst performance and structural/ electronic properties, catalysts were characterised using XRD, TEM, XPS and \( \text{H}_2\)-TPR.

X-ray diffraction patterns of the mono, bi and tri- metallic Au/Pd/Cu catalysts from studies in Table 1 were recorded and are shown in Figure 1. Comparison with reference patterns for Cu\(^0\) (JCPDS no: 01-085-1326), CuO (JCPDS no: 01-089-5986) (CuO) and Cu\(_2\)O (JCPDS no: 01-071-3645) showed no peaks corresponding to copper species for mono bi or tri- metallic Cu- containing catalysts. This suggests that the crystallite size of supported copper species is below the detection limit of the instrument. Characteristic signals for metallic Au were observed at \( 2\theta = 38.2^\circ, 44.3^\circ \) and \( 64.5^\circ \) in Au-containing samples. These are assigned to the (111), (200) and (311) planes respectively (JCPDS no.
No Pd phases were observed in the monometallic Pd catalyst (Figure 1 d). In all samples the characteristic peaks of the TiO$_2$ (P25) support were clearly observed (Figure 1 a). Based upon the diffraction peak at 44.3°, the mean Au crystallite size for 2.5% Au 2.5% Pd 2.5% Cu/TiO$_2$ was calculated to be 18.5 nm, using the Scherrer equation. This increased to 23.5 nm for 2.5% Au 2.5% Pd 1.0% Cu/TiO$_2$. Au- catalysts contained Au in a cubic phase with comparable unit cell parameters to monometallic Au (ICSD no. 53764) as shown in Table 4. No apparent alloying of Au/Pd and Cu was observed in XRD diffractograms. Although no reflections indicative of bulk alloyed nanoparticles were observed, a portion of nanoparticles which are beneath the detection limit of the XRD method could be present. To determine whether this was indeed the case, catalysts were studied using HRTEM. Micrographs and corresponding particle size distributions are shown in Figure 2. Based upon a sample of 530 nanoparticles the catalysts; 2.5% Au 2.5% Pd/TiO$_2$, 2.5% Au 2.5% Pd 1.0% Cu/TiO$_2$ and 2.5% Au 2.5% Pd 2.5% Cu/TiO$_2$ showed average nanoparticle sizes of 1.32, 1.20 and 1.37 nm respectively. Due to restrictive particle dimensions, visualisation of core shell features was not possible. However, previous studies of AuPd/ TiO$_2$ catalysts prepared via the same impregnation method described in Section 2.1 have shown Au- core Pd- rich shell nanoparticles to form upon calcination at 400 °C in air. We rationalised the disparity between average particle sizes as determined by XRD (Scherrer, Figure 1) and HRTEM (Figure 2) methods using STEM-EDX. This showed the presence of ~ µm sized gold- rich particles (Supporting Information Figure S1). Formation of large (200 nm – 2 µm) Au- rich particles, and Au- core/ Pd-rich shell nanoparticles during impregnation of TiO$_2$ with HAuCl$_4$.6H$_2$O and PdCl$_2$ is consistent with previous work by Meenakshisundaram et al.

XPS spectra were collected to evaluate the oxidation state and surface composition of Cu, Pd and Au species present in 2.5% Au 2.5% Pd 1% Cu/TiO$_2$ following calcination (Figure 3). Copper species of differing oxidation state show characteristic binding energies and satellite structures with Cu$^{2+}$ (934 eV) species exhibiting a shakeup peak at ca. 10 eV above the Cu (2p 3/2) signal. These peaks are not observed for Cu$^+$ or Cu$^0$ and can therefore be used to differentiate between Cu$^{2+}$ and reduced species. The Cu (2p) spectra for 2.5% Au 2.5% Pd 2.5% Cu/TiO$_2$, both before and after
calcination, are shown in Figure 3 (a) and (b) respectively. The main peak is observed at a binding energy of 932.8 eV and attributed to reduced Cu species (Cu$^+$/Cu$^{+}$) suggesting either Cu$_2$O or metallic Cu. A minor Cu$^{2+}$ contribution is also observed as a weak shoulder at 934 eV and a weak satellite peak at 944 eV.

The corresponding Au (4d)/Pd (3d) spectra for the same catalysts are shown in Figure 4 (a) and (b). It is evident that prior to calcination the spectrum is composed of Pd (3d) peaks superimposed on the Au (4d$_{5/2}$) peak (ca 335 eV). Pd is present as Pd$^{2+}$, as evidenced by the binding energy of 337.6 eV, whilst the presence of any Pd (0) in this uncalcined sample could not be ascertained due to a strong overlap with the Au signal.

Following calcination Pd is present as both Pd$^{2+}$ (337.8 eV) and Pd (0) (335.3 eV) in an atomic ratio of 6.14:1 (Figure 3 b). After heat treatment no signal corresponding to Au (4d) is observed (Figure 3 b) whereas a significant attenuation of the Au (4f) signal at 83.8 eV is apparent (Figure 3 c and d). The Au(4f) signal is observable over the Au(4d) signal due to the difference in the mean free path of the photoelectron at the different kinetic energies.

A summary of quantified surface metal composition of the uncalcined and calcined catalysts is given in Table 5. Following heat treatment a significant decrease in Au surface concentration is observed, with the Pd/Au atomic ratio increasing from 0.54 to 15.17. A similar increase in the Cu/Au ratio also occurred. This indicates that Au core – Pd shell alloyed nanoparticles are formed upon calcination, and the increase in Pd/Au ratio is consistent with aforementioned attenuation of the Au signal, which is analogous to the observed attenuation by Pd overlayers as previously reported by Edwards et al. for AuPd/ TiO$_2$ catalysts prepared under comparable conditions. Furthermore, quantitative analysis in Table 5 suggests that following heat treatment the TiO$_2$ surface is enriched with both Pd and Cu. Cu enrichment could arise from; formation of Au- core PdCu-shell nanoparticles or Cu being more highly dispersed across the TiO$_2$ surface than Au. XRD data shown in Figure 1 and the low Cu loadings used support the latter. Little change in the Pd/Cu ratio is apparent in Table 5, indicating that core shell Pd- Cu species are not forming. XPS surface analysis of 2.5% Pd 2.5% Cu/TiO$_2$ (Table 5 Entry 3) shows a Pd: Cu ratio of ca. 1, which further supports this. Therefore, whereas Pd-Cu alloying
has been reported for supported TiO\(_2\) catalysts following heat treatment in hydrogen\(^{37}\), calcination in static air appears to favour surface segregation between Pd and Cu. Future EDX mapping studies at a higher resolution are required to determine whether Pd and Cu are indeed phase-segregated.

H\(_2\)-TPR was carried out on Au/Pd/Cu/TiO\(_2\) catalysts to probe the reducibility of metal sites and determine the nature of supported metal species. No reduction was observed in the TPR of unmodified TiO\(_2\) (P25) shown in Figure 5 a. Deposition of 2.5\% Cu (Figure 5 b) gave rise to a single major reduction peak centred at 180 °C. This was assigned to a 2 electron Cu\(^{II}\) – Cu\(^0\) reduction in highly dispersed CuO species\(^{38}\). The monometallic Cu catalyst also presented a second, less intense reduction centred at 300 °C, which was assigned to reduction of larger particles of bulk CuO on the surface of TiO\(_2\)\(^{39}\). TPR data suggested that no Au-Cu alloys are present in bimetallic catalysts (Figure 5 b and c). If Au-Cu alloys were formed in bimetallic (c) or trimetallic (d) catalysts, an additional reduction peak would be expected at \(ca.\) 260 – 280 °C\(^{38,40}\). Given that the catalysts in this study were calcined in air (3 h at 400 °C), alloy formation would not be expected. Indeed, Bracey et al. have previously reported minimal interaction between Au and Cu under such heat treatment conditions\(^{41}\). Disappearance of the Cu\(^{II}\)-Cu\(^0\) reduction event at 180°C in the trimetallic catalyst (c) is in agreement with XPS data from Figure 3, which suggests that Cu presents as reduced species following calcination. Figure 5 (e) shows the reduction profile for 2.5\% Au 2.5\% Pd/TiO\(_2\). This catalyst is known to contain alloyed AuPd nanoparticles\(^{21}\). Comparison with the reduction profile of 2.5\% Au 2.5\% Pd 1.0\% Cu/TiO\(_2\) (Figure 5 d) suggests that the trimetallic catalyst also contains alloyed AuPd nanoparticles. Meanwhile, the negative peak observed at \(ca.\) 95 °C in Figures 4 (d) and (e) is assigned to the low temperature decomposition of palladium hydride species\(^{42,43}\).

Catalyst characterisation showed that in trimetallic AuPdCu/TiO\(_2\) catalysts, Au-core Pd-shell nanoparticles form upon calcination at 400°C in static air. This was found to be consistent with previous studies\(^{21,32}\). Though no alloying of Au/Pd and Cu is observed, copper speciation was affected by the presence of Pd, with Cu\(^{II}\) favoured in Cu / AuCu catalysts and Cu\(^0\) / Cu\(^1\) species in trimetallic AuPdCu catalysts. Trimetallic catalysts showed increased productivity and TOF for the oxidation of methane with added H\(_2\)O\(_2\) when compared with either bimetallic AuPd catalysts or a
physical mixture of AuPd/TiO₂ and Cu/TiO₂. As Cu⁺ can catalyse the conversion of H₂O₂ to oxygen based radicals in a Cu⁺/Cu²⁺ redox couple, an increase in rate is expected. However the decrease in the rate of H₂O₂ conversion and simultaneous increase in rate of methane oxidation observed following impregnation of Cu onto 2.5% Au 2.5% Pd/TiO₂ (Table 1 Entries 5 and 6) suggest an additional role of Cu in blocking Au/Pd sites, which would otherwise catalyse H₂O₂ decomposition in a non-selective way. Future studies should therefore further characterise these trimetallic catalysts to probe for Cu – Au/Pd interactions and map the atomic composition/distribution of constituent nanoparticles.

4. Conclusions

Trimetallic AuPdCu catalysts are active for the oxidation of methane under mild reaction conditions using the green oxidant H₂O₂. We have shown that by depositing copper together with Au/Pd on the surface of TiO₂ the rate of methane oxidation with added H₂O₂ is significantly enhanced. In particular 2.5% Au 2.5% Pd 1.0% Cu/TiO₂ showed ca. 83% selectivity to methanol, a significant improvement on the 49.3% selectivity previously reported for a bimetallic 2.5% Au 2.5% Pd/ TiO₂ analogue. At the same time deposition of 2.5 wt% Cu increased catalyst productivity by a factor of 5. Furthermore, through control of the Cu/ AuPd ratio catalysts might be tailored to effect either high methanol selectivity or increased efficiency in H₂O₂ utilisation. These catalysts were tested for the oxidation of methane with H₂O₂ generated in situ from H₂ and O₂. In this instance the addition of Cu was disadvantageous, leading to a decrease in the rate of methane oxidation. This trend was attributed to low rates of H₂O₂ synthesis coupled with competing Cu- catalysed H₂O₂ conversion reactions, which proceed at far higher rates than the oxidation reaction. Characterisation studies of these trimetallic catalysts using XRD, XPS and H₂-TPR indicate that Au and Pd alloy in an Au- core Pd- shell structure, whilst Cu is highly dispersed as reduced species, probably as Cu₂O or Cu. The beneficial effect of Cu is ascribed to its ability to direct the selective catalytic conversion of H₂O₂. The mechanism by which specific Cu sites effect selective conversion of H₂O₂, and its impact upon reaction rates in partial alkane oxidation will be explored in a future paper.

Acknowledgements
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References


Table 1 Methane oxidation activity of mono, bi or trimetallic Cu/Au/Pd/ TiO$_2$ catalysts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Product amount / µmol</th>
<th>Oxygenate Selectivity / %</th>
<th>Methanol Selectivity / %</th>
<th>Oxygenate Productivity</th>
<th>TOF</th>
<th>H$_2$O$_2$ Remain / µmol</th>
<th>H$_2$O$_2$ efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CH$_3$OH</td>
<td>HCOOH</td>
<td>CH$_3$OOH</td>
<td>CO$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>2.5 % Au 2.5 % Pd/TiO$_2$</td>
<td>1.89</td>
<td>0</td>
<td>1.57</td>
<td>0.37</td>
<td>90</td>
<td>49.3</td>
<td>0.250</td>
</tr>
<tr>
<td>2</td>
<td>2.5 % Cu/TiO$_2$</td>
<td>0.76</td>
<td>0</td>
<td>4.40</td>
<td>0.19</td>
<td>96</td>
<td>14.2</td>
<td>0.406</td>
</tr>
<tr>
<td>3</td>
<td>2.5 % Au 2.5 % Cu/TiO$_2$</td>
<td>0.91</td>
<td>0</td>
<td>6.18</td>
<td>0.39</td>
<td>95</td>
<td>12.2</td>
<td>0.739</td>
</tr>
<tr>
<td>4</td>
<td>2.5 % Pd 2.5 % Cu/TiO$_2$</td>
<td>0.64</td>
<td>0</td>
<td>2.30</td>
<td>0.56</td>
<td>84</td>
<td>18.3</td>
<td>0.369</td>
</tr>
<tr>
<td>5</td>
<td>2.5 % Au 2.5 % Pd/2.5 % Cu/TiO$_2$</td>
<td>2.36</td>
<td>0</td>
<td>5.87</td>
<td>0.26</td>
<td>97</td>
<td>27.8</td>
<td>1.243</td>
</tr>
<tr>
<td>6</td>
<td>2.5 % Au 2.5 % Pd/1.0 % Cu/TiO$_2$</td>
<td>6.08</td>
<td>0</td>
<td>0.94</td>
<td>0.33</td>
<td>96</td>
<td>82.7</td>
<td>0.729</td>
</tr>
<tr>
<td>7</td>
<td>2.5 % Au 2.5 % Pd/TiO$_2$ and 2.5 % Cu/TiO$_2$*</td>
<td>0.49</td>
<td>0</td>
<td>1.23</td>
<td>0.34</td>
<td>83</td>
<td>23.8</td>
<td>0.128</td>
</tr>
</tbody>
</table>

Test conditions: 0.5 h, 50 °C, P(CH$_4$) = 30 bar, Catalyst: 1.0 x $10^{-5}$ mol of metal., [H$_2$O$_2$] = 0.5 M (5000 µmol), 1500 rpm

[a] Oxygenate selectivity = (mol of oxygenate/ total mol of products) * 100, [b] Oxygenates productivity = mol oxygenates kg$_{cat}$^{-1} h^{-1}, [c] Turn over frequency (TOF) = mol$_{oxygenates}$ mol$_{metal}$^{-1} h^{-1}, [d] Assayed by Ce$^{4+}$ (aq) titration. [e] (mol O$_2$ in products/ mol H$_2$O$_2$ converted) *100 [f] Pre-treated in a flow of 5 % H$_2$/Ar (400 °C, 3h, 20°C min$^{-1}$).

*Reaction of physical mixture comprising 2.5 % Au 2.5% Pd/TiO$_2$ and 2.5 % Cu/TiO$_2$
Table 2 Liquid phase oxidation of methane using heterogeneous Au/Pd/Cu/TiO$_2$ catalysts with in-situ generated H$_2$O$_2$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Product amount (µmol)</th>
<th>Oxygenate Selectivity / %$^a$</th>
<th>Methanol Selectivity / %</th>
<th>Oxygenate Productivity$^b$</th>
<th>TOF [c]</th>
<th>H$_2$O$_2$ Remaining / µmol$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5 % Au 2.5 % Pd /TiO$_2$</td>
<td>1.31</td>
<td>83</td>
<td>68.2</td>
<td>0.11</td>
<td>0.320</td>
<td>56</td>
</tr>
<tr>
<td>2</td>
<td>2.5% Au 2.5 % Pd 2.5 % Cu/TiO$_2$</td>
<td>0.45</td>
<td>98</td>
<td>81.8</td>
<td>0.068</td>
<td>0.090</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>2.5% Au 2.5 % Pd 1.0 % Cu/TiO$_2$</td>
<td>0.39</td>
<td>75</td>
<td>75.0</td>
<td>0.040</td>
<td>0.078</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>2.5 % Au 2.5 % Pd 0.5 % Cu/TiO$_2$</td>
<td>0.31</td>
<td>61</td>
<td>60.8</td>
<td>0.027</td>
<td>0.062</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>2.5 % Au 2.5 % Pd 0.25 % Cu/TiO$_2$</td>
<td>0.25</td>
<td>22</td>
<td>21.6</td>
<td>0.020</td>
<td>0.050</td>
<td>14</td>
</tr>
<tr>
<td>6</td>
<td>2.5 % Cu/TiO$_2$</td>
<td>0</td>
<td>n/a</td>
<td>0</td>
<td>0</td>
<td>n/a</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>2.5 % Au 2.5 % Pd /TiO$_2$ and 2.5 % Cu/TiO$_2$*</td>
<td>0.49</td>
<td>98</td>
<td>83.1</td>
<td>0.074</td>
<td>0.098</td>
<td>9</td>
</tr>
</tbody>
</table>

Test conditions: 0.5 h, 50 °C, Catalyst: 1.0 x 10$^{-3}$ mol of metal, 1500 rpm, Gases: 0.86 % H$_2$/ 1.72 % O$_2$/ 75.86 % CH$_4$/ 21.55 % N$_2$, P(Total pressure) = 32 bar

$^a$ Oxygenate selectivity = (mol of oxygenate/ total mol of products) * 100,

$^b$ Oxygenates productivity = mol oxygenates kg$_{cat}^{-1}$ h$^{-1}$,

$^c$ Turn over frequency (TOF) = mol$_{oxygenates}$ mol$_{metal}^{-1}$ h$^{-1}$,

$^d$ Assayed by Ce$^{4+}$ (aq) titration,

*Reaction of physical mixture comprising 2.5 wt% Au 2.5 % Pd /TiO$_2$ and 2.5 % Cu/TiO$_2$
Table 3. H$_2$O$_2$ synthesis and degradation rates for Titania-supported AuPd and AuPdCu catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Productivity mol / kg$_{cat}$/ h$^{[a]}$</th>
<th>Degradation mol / kg$_{cat}$/ h$^{[b]}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5% Au 2.5% Pd / TiO$_2$</td>
<td>83</td>
<td>215</td>
</tr>
<tr>
<td>2</td>
<td>2.5% Au 2.5% Pd 2.5% Cu / TiO$_2$</td>
<td>11</td>
<td>143</td>
</tr>
<tr>
<td>3</td>
<td>2.5% Au 2.5% Pd 1% Cu / TiO$_2$</td>
<td>10</td>
<td>184</td>
</tr>
</tbody>
</table>

$^{[a]}$ Test conditions: 5% H$_2$/CO$_2$ (29 bar) and 25% O$_2$/CO$_2$ (11 bar), 8.5 g solvent (2.9 g HPLC water, 5.6 g MeOH) 0.01 g catalyst, $2^\circ$C, 1200 rpm, 30 mins.

$^{[b]}$ Test conditions: 5% H$_2$/CO$_2$ (29 bar), 8.5 g solvent (5.6 g MeOH, 2.22 g H$_2$O and 0.68 g 50%H$_2$O$_2$), 0.01 g catalyst, $2^\circ$C, 1200 rpm, 30 mins.
Figure 1 XRD diffractograms of TiO$_2$ deposited with (a) Support only, (b) 2.5 % Cu, (c) 2.5 % Au, (d) 2.5 % Pd, (e) 2.5% Au 2.5% Pd, (f) 2.5 % Au 2.5 % Pd 1.0 % Cu, (g) 2.5 % Au 2.5 % Pd 2.5 % Cu

- TiO$_2$ phase, ○ Au/Au-Pd phase.
Table 4 Calculated Au particle properties from XRD

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal Phase</th>
<th>Unit Cell Volume / Å³</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5% Au/TiO$_2$</td>
<td>Au</td>
<td>67.79</td>
</tr>
<tr>
<td>2.5% Au 2.5% Pd/TiO$_2$</td>
<td>Au</td>
<td>67.84</td>
</tr>
<tr>
<td>2.5% Au 2.5% Pd 1.0% Cu/TiO$_2$</td>
<td>Au</td>
<td>67.73</td>
</tr>
<tr>
<td>2.5% Au 2.5% Pd 2.5% Cu/TiO$_2$</td>
<td>Au</td>
<td>67.51</td>
</tr>
<tr>
<td>Reference $^a$</td>
<td>Au</td>
<td>67.85</td>
</tr>
</tbody>
</table>

$^a$ Reference no. ICSD no. 611624
Figure 2  Representative electron micrographs and associated particle size distributions for: (a, i, ii, iii) 2.5% Au 2.5% Pd/TiO$_2$, (b, iv, v, vi) 2.5 % Au 2.5 % Pd 1% Cu/ TiO$_2$ and (c, vii, viii, ix) 2.5% Au 2.5% Pd 2.5% Cu/ TiO$_2$. 
Figure 3 XPS spectra in the Cu (2p) region for 2.5% Au 2.5% Pd 1.0% Cu/ TiO$_2$ before (a) and after (b) calcination at 400 °C.
Figure 4 XPS spectra of 2.5% Au 2.5% Pd 1.0% Cu/ TiO$_2$ before (a, c) and after (b, d) calcination at 400 °C. Spectra show (a, b) the Au (4d) / Pd (3d) region and (c, d) the Au (4f) region.
<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Treatment</th>
<th>Composition / atom %</th>
<th>Atom ratio Pd/Au</th>
<th>Atom ratio Cu/Au</th>
<th>Atom ratio Pd/Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.5% Au 2.5% Pd</td>
<td>Uncalcined</td>
<td>0.040 0.022 0.022</td>
<td>0.54</td>
<td>0.54</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>2.5% Cu/TiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>Calcined</td>
<td>0.003 0.046 0.043</td>
<td>15.17</td>
<td>14.17</td>
<td>1.07</td>
</tr>
<tr>
<td>3</td>
<td>2.5% Pd 2.5% Cu/TiO₂</td>
<td>Calcined</td>
<td>- 0.056 0.054</td>
<td>-</td>
<td>-</td>
<td>1.04</td>
</tr>
</tbody>
</table>
Figure 5 TPR profiles of (a) TiO$_2$, (b) 2.5% Cu/TiO$_2$, (c) 2.5% Au 2.5% Cu/ TiO$_2$, (d) 2.5% Au 2.5 wt% Pd 1.0% Cu/ TiO$_2$, (e) 2.5% Au 2.5% Pd/ TiO$_2$. 
Chemical reaction:

\[ \text{CH}_4 + \text{H}_2\text{O}_2 \rightarrow \text{CH}_3\text{OH} \]

Catalyst: \( \text{TiO}_2 \) (P25)

Rate: \( \times 5 \)

Catalyst components: AuPd and Cu (63.55 amu)