Journal of Catalysis 364 (2018) 80-88

Contents lists available at ScienceDirect

Journal of Catalysis

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

# *Operando* Raman-online FTIR investigation of ceria, vanadia/ceria and gold/ceria catalysts for toluene elimination



<sup>a</sup> Department of Chemical and Biological Engineering, Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong Special Administrative Region <sup>b</sup> Spectroscopy and Industrial Catalysis Group, Instituto de Catálisis y Petroleoquímica, ICP-CSIC, Marie Curie 2, E-28049 Madrid, Spain

## ARTICLE INFO

Article history: Received 19 January 2018 Revised 4 April 2018 Accepted 1 May 2018

Keywords: Ceria catalyst VOCs oxidation reaction Operando reactor Vanadium oxides Gold

# ABSTRACT

Toluene oxidation on three ceria catalysts, CeO<sub>2</sub>, VO<sub>x</sub>/CeO<sub>2</sub> and Au/CeO<sub>2</sub>, was investigated by an *operando* Raman-online FTIR reactor cell. The reactive surface oxygen sites were preferred sites for vanadium and gold deposition. The deposited vanadium existed as V<sup>5+</sup>, while most of the gold was in Au<sup>+</sup> state and roughly a third of ceria was in the reduced Ce<sup>3+</sup> state. The Au/CeO<sub>2</sub> and CeO<sub>2</sub> catalysts (T<sup>\*</sup><sub>50</sub> = 260 and 290 °C) were more active and selective toward the complete oxidation of toluene than VO<sub>x</sub>/CeO<sub>2</sub> catalysts (T<sup>\*</sup><sub>50</sub> = 370 °C), where T<sup>\*</sup><sub>50</sub> refers to the temperature for 50% of CO<sub>2</sub> yield. The  $\eta^2$ -peroxide O<sub>2</sub><sup>2-</sup><sub>ads</sub> was detected on Au/CeO<sub>2</sub> and CeO<sub>2</sub> catalysts, where toluene molecules preferentially adsorbed parallel to the surface via  $\pi$ -bonding. Au/CeO<sub>2</sub> gave complete combustion producing mainly CO<sub>2</sub>. On the other hand,  $\eta^1$ -superoxide O<sub>2</sub><sup>2-</sup><sub>ads</sub> was found on VO<sub>x</sub>/CeO<sub>2</sub> catalyst and the toluene molecule adsorbed via  $\sigma$ -bonding forming carbenium ions on the vanadia Brønsted acid sites. This catalyst produced significant amount of benzaldehyde as partial oxidation byproduct and CO (<25%). The nature of the active sites, configurational adsorption of toluene and the reactive oxygen species play important roles in the catalyst activity and selectivity leading to a large contrast in the catalytic behavior of the CeO<sub>2</sub>, VO<sub>x</sub>/CeO<sub>2</sub> and Au/CeO<sub>2</sub> catalysts.

© 2018 Elsevier Inc. All rights reserved.

# 1. Introduction

Volatile organic compounds (VOCs) are important indoor air pollutants. Most VOCs are irritants that cause discomfort and psychological stresses to the occupants. Many VOCs can trigger autoimmune response (e.g. asthma, eczema) and airway inflammation causing respiratory distress [1,2], while others such as formaldehyde, benzene and toluene are known or suspected carcinogens [3,4]. Studies have shown that catalytic oxidation is effective in removing airborne VOCs [5] and ceria is one of the most promising catalysts [6]. Ceria has a large capacity for oxygen storage and displays good redox property [7]. Ceria itself is active enough to catalyze the oxidation of hydrocarbons including toluene. The numerous defects in ceria in form of oxygen vacancies or polarons are believed to be responsible for its unique catalytic properties [7–10].

Noble metals supported on ceria are reported to be more active and selective for catalytic oxidation of VOCs [11]. Ousmane and coworkers [12] reported Au/CeO<sub>2</sub> catalyst is more active than gold supported on TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. Ceria could stabilize gold at high

\* Corresponding authors.

dispersion (<2.5 nm) to yield catalysts of high activity and selectivity. Transition metal oxide catalysts including CuO,  $V_2O_5$ , MnO<sub>x</sub>, ZrO<sub>2</sub>, Co<sub>3</sub>O<sub>4</sub> and related mixed oxides have been shown to be active for VOCs abatement [5,13]. Vanadia in particular is an attractive catalyst for VOC oxidation not only because of its high turnover frequency, but also its tolerance to SO<sub>2</sub>, H<sub>2</sub>S, NO<sub>x</sub>, organosulfur compounds as well as organochloride compounds that are ubiquitous in the environment [14,15]. Dai's group [16] reported that  $VO_x/CeO_2$  can deliver complete conversion of 1,2-dichloroethane oxidation at 250 °C with no observable deactivation over 360 h.

There are still considerable debates as to the exact reaction mechanism for VOCs oxidation on ceria catalysts [17,18]. The present work employed an *operando* Raman reactor cell with an online FTIR to investigate toluene oxidation on ceria catalysts (CeO<sub>2</sub>, VO<sub>x</sub>/ CeO<sub>2</sub>, Au/CeO<sub>2</sub>) to gain a better understanding of the "working" catalyst and identify the surface species during reaction, in order to establish the structure-activity relationship at a molecular level.

## 2. Experimental

# 2.1. Preparation of ceria catalysts

Ceria (CeO<sub>2</sub>) was prepared from 0.01 M Ce(NO<sub>3</sub>)<sub>3</sub> solution obtained by dissolving Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O salt (99%, Sigma-Aldrich)





JOURNAL OF CATALYSIS

*E-mail addresses:* kekyeung@ust.hk (K.L. Yeung), miguel.banares@csic.es (M.A. Bañares).

in warm deionized distilled (DDI) water. The pH of the solution was adjusted gradually from pH 4.5 to pH 9 with the addition of 0.5 M NH<sub>4</sub>OH (BDH) solution. The original clear solution changed to light pink and then to light yellow following vigorous stirring (ca. 1000 rpm). The yellow slurry obtained overnight, was washed repeatedly with warm, distilled water (60 °C) and centrifuged in JA-14 rotor (14,000 rpm) until the supernatant's pH was neutral. The solids were vacuum dried at 65 °C for 4 h, followed by calcination in flowing air (1000 sccm) at 300 °C for 2 h to produce the CeO<sub>2</sub> catalyst (Ce1).

The 2.5 wt% vanadia on ceria catalyst (2.5VCe) was obtained by an impregnation method. Briefly, 0.5 g ceria (Ce1) powder was first dispersed in 250 ml DDI by ultrasound for 30 min to obtain a suspension. The vanadia precursor,  $(NH_4)_3[VO_2(C_2O_4)_2]\cdot 2H_2O$ , was obtained by boiling an equal volume mixture of 0.02 M NH<sub>4</sub>VO<sub>3</sub> (98%, Nacalai Tesque) and 0.04 M  $(NH_4)_2C_2O_4$  (99%, Sigma-Aldrich) solutions. Afterward, a 0.024 g  $(NH_4)_3[VO_2(C_2O_4)_2]\cdot 2H_2O$ crystal was dissolved in 50 ml DDI water and added to the Ce1 suspension and the mixture was placed in a rotary evaporator kept at 65 °C under a rotation speed of 120 rpm. The resulting paste was then dried in vacuum at 65 °C for 2 h, before calcining in 1000 sccm flowing air at 300 °C for 2 h to produce a bright yellow 2.5VCe catalyst.

The 2.5 wt% gold on ceria catalyst (2.5AuCe) was prepared by the following procedure. 0.5 g Ce1 was dispersed by ultrasound in 250 ml DDI water before the drop-wise addition of a 0.001 M gold solution. The solution was prepared from HAuCl<sub>4</sub>·xH<sub>2</sub>O (99.999%, Sigma-Aldrich) after adjusting the pH to 8.5 by adding 0.05 M NH<sub>4</sub>OH solution. After vigorous mixing at 1200 rpm at 80 °C for 2 h, the mixture was cooled to room temperature and stirred overnight. The resulting slurry was washed repeatedly with warm, distilled water (60 °C) and centrifuged (14,000 rpm) to remove ammonium and chloride ions. The paste was then vacuum dried at 65 °C for 4 h, and calcined in 1000 sccm flowing air at 300 °C for 2 h. The Ce1, 2.5VCe and 2.5AuCe catalysts were stored in sealed containers under dry atmosphere before use.

## 2.2. Characterization of ceria catalysts

The Ce1, 2.5VCe, 2.5AuCe catalysts were examined by JEOL 2100 high resolution transmission electron microscopy (HRTEM)

operated at 200 kV with a resolution of 0.29 nm. A selected area electron diffraction (SAED) and interplanar d-spacing measurement were carried out by Gatan Digital Micrograph program. The catalyst powder was dispersed in ethanol (Absolute, Merck) and deposited on a holey carbon TEM grid. The catalysts were also analyzed by the PANalytical X'pert model X-ray diffractometer (XRD) and Physical Electronics 5600 X-ray photoelectron spectroscopy (XPS). The XRD patterns was obtained from powder X-ray diffractometer with X-ray source of Cu anode, wavelength of 1.5406 Å and graphite monochromator. The samples were grounded into fine powder and then placed in a glass sample holder. The XPS was equipped with a 150 W monochromatic Al K $\alpha$  X-ray source (hv = 1486.6 eV) and Kratos Axis Ultra DLD spectrometer. The spectra were calibrated with the C1s peak at 285.0 eV. The catalyst was placed on an indium foil (99.99%) and outgassed under ultrahigh vacuum. Nitrogen physisorption was carried out in a Beckman Coulter SA 3100 surface area analyzer. The 0.1 g catalyst was outgassed in vacuum at 200 °C before nitrogen adsorption at -196 °C. The adsorption and desorption isotherm data were used to calculate the Brunauer-Emmett-Teller (BET) surface area, pore volume and the Barrett-Joyner-Halenda (BJH) pore size distribution.

## 2.3. Operando reaction study

The toluene oxidation reaction was carried out in an operando fixed bed reactor cell made of optical-grade quartz. The reactor fitted snuggly into an insulated heating block as shown in Fig. 1 [19]. The reaction temperature was monitored by a type 2 thermocouple (thermocoax) inserted into the catalyst bed and controlled by a temperature programmer unit (PID Eng&Tech). The catalyst was observed in situ by a Renishaw micro-Raman System 1000 using a LEICA DMILM microscope with a  $20 \times$  long-distance objective lens and the spectra were obtained under Argon laser (514 nm) excitation at 4 scans and 30 s acquisition time. The composition of the reaction gases were analyzed by an on-line ThermoNicolet 6700 Fourier transformed infrared (FTIR) spectrometer fitted with a thermostated (120 °C) gas cell. The spectra were collected from 650 to  $4000 \text{ cm}^{-1}$  with a resolution of  $4 \text{ cm}^{-1}$  and sampling interval of 9.85 s. FTIR calibrations were made and the details are discussed in the Supplementary Information Part 1 (SI. Part 1).



Fig. 1. Schematic diagram of the operando reactor setup equipped with in situ Raman and online FTIR spectrometers.



Fig. 2. High-resolution transmission electron microscopy (HRTEM) images of (a) 2.5VCe and (b) 2.5AuCe with the selected area electron diffraction (SAED) in the figure insets.



Fig. 3. Powder X-ray diffraction patterns of 2.5VCe, Ce1 and 2.5AuCe catalysts.

#### Table 1

Particle sizes of  $CeO_2$  particles in 2.5VCe, Ce1 and 2.5AuCe catalysts as determined from TEM and XRD measurements.

Catalyst	CeO <sub>2</sub> Particle size (nm)		
	TEM	XRD	
2.5VCe	11 ± 4	12.6	
Ce1	$12 \pm 4$	12.8	
2.5AuCe	11 ± 4	10.6	

The catalyst was ground in an agate mortar and sieved to produce 0.25–0.50 mm powder (i.e. 32–60 mesh). A 0.150 g catalyst was packed into the *operando* reactor cell. The catalyst bed was sandwiched between two inert SiC (Aldrich) beds to facilitate heat transfer and minimize the void volume. The ensemble was held in place by quartz wool. The catalyst was pretreated at 300 °C in flowing 200 sccm synthetic air (20%  $O_2/80\%$   $N_2$ , Air Liquide) for 2 h before reaction. The toluene vapor was generated in argon (UHP, Air Liquide) by bubbler kept at 10 °C in a circulating oil bath



**Fig. 4.** Nitrogen physisorption isotherms of 2.5VCe, Ce1 and 2.5AuCe catalysts with their corresponding pore size distributions shown in the figure inset.

Table 2Textural properties of 2.5VCe, Ce1 and 2.5AuCe catalysts.

Sample	BET surface area $(m^2 \cdot g^{-1})$	Pore volume $(cm^3 \cdot g^{-1})$	Pore size (nm)
2.5VCe	123.8	0.17	5.1
Ce1	121.9	0.17	5.1
2.5AuCe	133.9	0.20	5.1

(PolyScience 9106A12E), then concentrated toluene vapor was blended downstream with synthetic air (UHP, Air Liquide) using a pair of mass flow controllers (PID Eng&Tech) to obtain 1000 ppm toluene in 18.8%  $O_2$ , 5.8% Ar and 75.4%  $N_2$ , and a gas hourly speed volume (GHSV) of 34,500 h<sup>-1</sup>. The reaction was carried out at temperatures between 25 and 450 °C.

Detailed study of the catalyst stability under humid conditions (SI. Part 2) was carried out at 26,000 ppm  $H_2O$  (19.8 Torr) with catalyst subjected to temperature from 100 to 350 °C. Another mode with 692,000 ppm  $H_2O$  (634.0 Torr) representing extreme humid conditions with a relative humidity level of 5.44% at 200 °C was



Fig. 5. X-ray photoelectron spectra of (a) Ce3d (b) O1s (c) V2p (d) Au4f from Ce1, 2.5VCe and 2.5AuCe catalysts.

also tested. A typical catalytic stability on-stream experiment was run for 48 h under continuous catalytic process.

## 3. Results and discussion

## 3.1. Characterizations

The transmission electron micrographs of 2.5VCe and 2.5AuCe catalysts are shown in Fig. 2a and b respectively with highresolution transmission electron microscopy (HRTEM) images and selected area electron diffraction (SAED) patterns. For reference, the micrograph for their support Ce1 is included in SI. Part 3. The powder X-ray diffraction patterns (XRD) are presented in Fig. 3. Ceria displays predominantly  $CeO_2$  (1 1 1), (2 0 0), (2 2 0), (331) and (222) crystallographic planes, which is observed on both HRTEM/SAED and XRD analysis. Particle sizes estimated from the TEM micrographs are consistent with the values determined from X-ray diffraction patterns (Table 1). The detailed calculations based on Debye-Scherrer equation are given in SI. Part 4. The vanadia species are highly dispersed and crystalline V<sub>2</sub>O<sub>5</sub> could not be detected by SAED (Fig. 2a) and XRD (Fig. 3). Gold is not evident in the XRD of 2.5AuCe (Fig. 3), but it can be clearly observed in the micrographs (Fig. 2b). The Au (111) was detected by SAED and can be identified in the HRTEM images from its characteristic d-spacing of 0.23 nm. The gold nanoparticles on ceria was also confirmed by energy dispersive X-ray spectroscopy (EDX) analysis, shown as SI. Part. 3. The gold has a mean particle size of  $4 \pm 1$  n m. It appears to be supported mainly on  $CeO_2$  (1 1 1), which agrees with the literature report [20].

The nitrogen physisorption isotherms of Ce1, 2.5VCe and 2.5AuCe catalysts are plotted in Fig. 4 and the textural properties

of the catalysts are summarized in Table 2. In general, all three catalysts display similar type IV mesoporous adsorption-desorption isotherms with a type H2 hysteresis loop [21]. The three catalysts have comparable surface area of  $128 \pm 8 \text{ m}^2 \text{ g}^{-1}$ . The pore size distribution was calculated from adsorption branch of the isotherm using BJH model [22] and plotted as an inset in Fig. 4. All catalysts have the same average pore size of 5.1 nm and pore volume of 0.17–0.20 cm<sup>3</sup>·g<sup>-1</sup>.

The XPS spectra of Ce3d, O1s, V2p and Au4f are plotted in Fig. 5 for Ce1, 2.5VCe and 2.5AuCe catalysts. Fig. 5a presents five peaks belonging to  $Ce3d_{3/2}$  with two main bands (u<sub>0</sub>, u) and three satellite bands (u', u'', u'''), and another five peaks belonging to Ce3d<sub>5/2</sub> with two main bands ( $v_0$ , v) and three satellite bands (v', v'', v'''). The Ce<sup>3+</sup> shows Ce3d<sub>3/2</sub> bands,  $u_0$  (900.3 eV) and u' (902.2 eV), and Ce 3d<sub>5/2</sub> bands v<sub>0</sub> (880.2 eV) and v' (884.3 eV), while Ce<sup>4+</sup> displays Ce3d<sub>3/2</sub> bands, u (901.2 eV), u'' (907.9 eV), u''' (917.0 eV), and Ce3d<sub>5/2</sub> bands, v (882.5 eV), v'' (889.3 eV), v''' (898.6 eV) [23,24]. The plots of O1s spectra in Fig. 5b indicates that in addition to the lattice oxygen  $O_{\alpha}$  (529.5 eV), there is a separate band  $O_{\beta}$ (531.6 eV) belonging to the oxygen near vacancy sites [8,25,26]. The summary data in Table 3 shows that oxygen vacancies and reduced Ce<sup>3+</sup> are abundant in all three catalysts. The deposition of vanadium and gold leads to 0.4 eV upward binding energy shift of  $O_{\alpha}$  and  $O_{\beta}$  (Fig. 5b) and a decrease of  $O_{\beta}/(O_{\alpha} + O_{\beta})$ . This is particularly evident for 2.5VCe, suggesting that vanadium bonds on the oxygen sites near vacancies  $(O_{\beta})$ . Gold adatom appears to nucleate on the oxygen vacancy site of ceria [27]. Table 3 also shows catalyst deposition caused a significant increase (ca. 10%) in the fraction of  $Ce^{3+}$  from around 0.3 to 0.33.

Fig. 5c shows vanadia in 2.5VCe exists mainly as  $V^{5+}$  (517.4 eV). The characteristic  $V^{4+}$  (516.4 eV) and  $V^{3+}$  (515.5 eV) were not

 Table 3

 XPS analysis of surface species concentrations. (calculated based on peak area).

Sample	$Ce^{3+}/(Ce^{4+}+Ce^{3+})$	$O_{\beta}/(O_{\alpha} + O_{\beta})$	V <sup>5+</sup> , V <sup>4+</sup> , V <sup>3+</sup> & Au <sup>3+</sup> , Au <sup>+</sup> , Au <sup>0</sup>		
2.5VCe	32.4%	21.7%	V <sup>5+</sup> 99.0%	V <sup>4+</sup> 1.0%	V <sup>3+</sup> 0%
Ce1 2.5AuCe	29.8% 33.7%	45.7% 36.8%	Au <sup>3+</sup> 10.0%	Au <sup>+</sup> 73.2%	Au <sup>0</sup> 16.7%

detected [28]. Nearly all the vanadium formed V<sup>5+</sup>—O—Ce<sup>3+</sup> with the sacrificial reduction of ceria at the interface [29]. Bañares and coworkers [19,29] provided experimental evidence that a strong interaction between vanadia and ceria would reduce ceria sites at the interface. Discussion with Sauer's group delivered a DFT calculation that provided insight on the nature of the strong interaction between vanadia and ceria responsible for the partial reduction of Ce [30], of which the experimental evidence has been reported recently [31]. The gold in 2.5AuCe catalyst exists mainly

as Au<sup>+</sup> (88.6 eV and 85.0 eV) followed by Au<sup>0</sup> (88.4 eV and 84.4 eV), and Au<sup>3+</sup> (90.2 eV and 86.3 eV) as shown by Fig. 5d [32]. The Au<sup>+</sup> (73.2%) is reported to promote the reducibility of ceria and enhance its catalytic activity [33,34].

# 3.2. Operando study of toluene oxidation reaction

The toluene oxidation was carried out in an *operando* fixed-bed reactor cell. The reaction over the ceria catalyst was observed



Fig. 6. Operando Raman spectra of (a) 2.5VCe, (b) Ce1, (c) 2.5AuCe catalysts and Raman contour projection of (d) 2.5VCe, (e) Ce1, (f) 2.5AuCe. [Notes: The color on Raman contour maps is qualitative relative intensity.]



**Fig. 7.** Operando Raman bands intensity of ring breathing mode  $v_1$  of  $\pi$ -bonding (at 646 cm<sup>-1</sup>) and  $\sigma$ -bonding (at 786 cm<sup>-1</sup>) for (a) 2.5VCe, (b) Ce1, (c) 2.5AuCe, and intensity of carbenium ion  $[C_7H_9^+]$  (at 1346 cm<sup>-1</sup>) for (d) 2.5VCe, (e) Ce1, (f) 2.5AuCe. [Notes:  $\triangleleft$ - $\sigma$ -bonding,  $\blacklozenge$ - $\pi$ -bonding,  $\blacktriangle$ - $\pi$ -bonding,  $\blacktriangle$ - $\pi$ -bonding,  $\blacklozenge$ - $\mu$ -bonding,



**Fig. 8.** Relative intensity ratio  $I_D/I_{F2g}$  Raman bands of CeO<sub>2</sub> for (a) 2.5VCe (b) Ce1 (c) 2.5AuCe; *Operando* Raman peak intensity of superoxide  $O_{2 ads}^-$  (at 1121 cm<sup>-1</sup>) for (d) 2.5VCe and peroxide  $O_{2 ads}^-$  (at 838 cm<sup>-1</sup>) for (e) Ce1 and (f) 2.5AuCe. [Notes:  $\Box$ -I<sub>D</sub>/I<sub>F2g</sub>,  $\bullet$ -O<sub>2 ads</sub>-superoxide,  $\bigcirc$ -O<sub>2 ads</sub>-peroxide.]

in situ by micro-Raman spectroscopy, while the gas composition at the reactor outlet was monitored in real-time by an online FTIR. Fig. 6a-c plot the operando Raman spectra of the catalysts at representative reaction temperatures ranging from 25 to 450 °C with the corresponding contour maps shown in Fig. 6d-f. The Raman bands intensity are normalized to the intensity of the ceria  $F_{2g}$  mode at  $457 \text{ cm}^{-1}$ . The other Raman peaks of CeO<sub>2</sub> include 590 and 1179 cm<sup>-1</sup> have been respectively assigned to defect-related (D) band and the second longitudinal optical (2LO) modes [35,36]. The Raman bands for vanadia at 1019 and 1033 cm<sup>-1</sup> belong to the vanadyl mode of ceria-supported vanadia species in 2.5VCe catalyst [30,37]. These bands are obscured by toluene during reaction, but reappear following complete conversion of toluene at temperatures above 350 °C. Gold usually does not display any characteristic Raman signals itself, but its presence causes broadening of the  $CeO_2$  peak at 457 cm<sup>-1</sup>, implying smaller particle size following gold deposition [38] which is consistent with the XRD results (Table 1).

The adsorbed toluene displays red shifted  $v_{8a}$  (1590 cm<sup>-1</sup>),  $v_{19a}$  $(1495 \text{ cm}^{-1})$  and  $v_{12}$   $(1001 \text{ cm}^{-1})$  modes from the aromatic ring and the  $v_{9a}$  (1161 cm<sup>-1</sup>) and  $v_{18a}$  (1027 cm<sup>-1</sup>) from the in plane C-H bending modes [39-42]. There is a noticeable suppression of v<sub>2</sub> C–H stretching vibration at 3068 cm<sup>-1</sup> in 2.5AuCe and Ce1 compared to 2.5VCe. The phenyl ring adsorbed in flat orientation is reported to cause weaker v<sub>2</sub> C-H stretching vibration and an observable frequency downshift and broadening of v1 ringbreathing vibration compared to adsorption of toluene perpendicular to the surface [41,42]. The  $v_1$  ring-breathing mode indicates  $\sigma$ -bonding (786 cm<sup>-1</sup>) on 2.5VCe catalyst (Fig. 6a) and  $\pi$ -bonding (646 cm<sup>-1</sup>, belongs to benzoate intermedia) on Ce1 and 2.5AuCe catalysts (Fig. 6b and c) [41,42]. Plotting these characteristic Raman bands in Fig. 7 shows that toluene is adsorbed via the  $\pi$ bonding on all three ceria catalysts at low temperatures (<100 °C). Above 100 °C, the adsorbed toluene forms  $\sigma$ -bonding on 2.5VCe catalyst (Fig. 7a) with a concomitant appearance of Raman band at  $1346 \text{ cm}^{-1}$  (along with  $1239 \text{ cm}^{-1}$ ) that belong to carbenium ion (Fig. 7d) [43,44]. Studies suggest that the carbenium

ion is formed at the Brønsted acid sites of vanadia [44,45]. Furthermore, the absence of  $C_6H_5$ -CH<sub>3</sub> stretching vibration mode  $v_{13}$  $(1209 \text{ cm}^{-1})$  and CH<sub>3</sub> bending mode  $(1380 \text{ cm}^{-1})$  suggests a distortion of methyl group following adsorption [40]. Both 786 cm<sup>-1</sup> and 1346 cm<sup>-1</sup> Raman bands disappear at high temperatures with the conversion of toluene over 2.5VCe catalyst. In contrast, the toluene is adsorbed by  $\pi$ -bonding on both Ce1 and 2.5AuCe catalysts as shown in Fig. 7b and c, respectively. The Raman signals for carbenium are absent in these two catalysts (Fig. 7e and f). The contour maps in Fig. 6d-f provide an overview of the effects of reaction temperature on the catalyst and surface adsorbates. It can be seen from the data that carbonaceous species build-up is most severe on 2.5VCe followed by Ce1 and 2.5AuCe, and their disappearance occurs at temperatures in order of 2.5VCe > Ce1 > 2.5AuCe. The carbon balance of 2.5VCe, Ce1, and 2.5AuCe is shown in Fig. S10, and thermogravimetric analysis confirms 2.5VCe has the most severe carbonaceous deposits among the three catalysts. (Fig. S11).

Besides the adsorbed toluene molecules, reactive oxygen species were detected on the catalysts. Observation of reactive oxygen species on ceria surface is rare under reaction conditions particularly at high temperatures [36,46]. The Raman signals for  $\eta^{1}$ -superoxide  $O_{2 ads}^{-}$  (1121 cm<sup>-1</sup>) on 2.5VCe (Fig. 8d) and  $\eta^{2}$ peroxide O<sub>2 ads</sub><sup>2-</sup> (838 cm<sup>-1</sup>) on Ce1 and 2.5AuCe catalysts (Fig. 8e and f) [36,46] were detected due to the reducing effects of toluene. Superoxide species was observed by Long et al. [47] during alkane oxidations (i.e. methane and ethane) up to temperatures of 750 °C. The spectral assignments for these reactive oxygen species have been confirmed in a recent study on polycrystalline ceria [48]. The  $O_{2 ads}^{-}$  and  $O_{2 ads}^{2-}$  species not only participate in the oxidation of toluene, they also play an important role in the re-oxidation of CeO<sub>2</sub> via  $O_{2 ads}^{-} \rightarrow O_{2 ads}^{2-} \rightarrow 2O_{ads}^{-} \rightarrow 2O_{lattice}^{2-}$  [7,36]. The presence of  $O_{2 ads}^{-}$  on 2.5VCe is consistent with the reducing effects of vanadia on ceria and an indication of the degree of reduction of the ceria support [46].

Oxygen vacancies account for most of the defects found in  $CeO_2$ and the ceria Raman intensity ratio  $I_D/I_{F2g}$  shows there are less oxygen vacancies in 2.5VCe and 2.5AuCe than in Ce1(Fig. 8a–c). This is



**Fig. 9.** Representative online FTIR spectra of toluene oxidation outgas released over (a) 2.5VCe (b) Ce1 (c) 2.5AuCe catalysts in the operando reactor.

consistent with the XPS results in Table 3. Along with increasing temperature, the defects sites in CeO<sub>2</sub> lattice (indicated by I<sub>D</sub>/I<sub>F2g</sub>) decrease with increasing adsorbed oxygen species (Fig. 8d–f). The plot of  $\eta^1$ -superoxide O<sub>2 ads</sub> on 2.5VCe (Fig. 8d) suggests that the strong interactions between ceria and vanadia was hindering the re-oxidation of the reduced ceria [29,30]. On the other hand,  $\eta^2$ -peroxide O<sub>2 ads</sub> on 2.5AuCe (Fig. 8f) increases with temperature up to 300 °C, before a rapid decline with a concomitant increase

in CeO<sub>2</sub> 2LO Raman signal  $(1179 \text{ cm}^{-1})$  (Fig. 8f. inset), which indicates that gold species facilitates the re-oxidation of CeO<sub>2</sub>. In short, the Raman spectra suggest that vanadia hinders re-oxidation of reduced ceria, while gold promotes its re-oxidation.

The composition of the reaction gas was monitored by an online FTIR, representative spectra are plotted in Fig. 9 for Ce1, 2.5VCe and 2.5AuCe catalysts. The online concentrations of toluene, CO<sub>2</sub> and H<sub>2</sub>O are determined from gas calibration and plotted in Fig. 10a–c for the three catalysts. There is a significant toluene conversion over 2.5VCe at low temperatures, but the main products are benzalde-hyde and CO (Fig. 10a). The selectivity for benzaldehyde is up to 40%. (SI. Part. 7). Ignition occurs at 300 °C with a substantial CO<sub>2</sub> generation, but CO concentration remains considerable. In contrast, Ce1 and 2.5AuCe catalysts produce less byproducts (Fig. 10b and c). Also, both catalysts have significantly lower ignition temperatures of 200 °C. 2.5AuCe performs better than Ce1, delivering nearly complete toluene oxidation to CO<sub>2</sub> and H<sub>2</sub>O at 300 °C.

Fig. 11 plots the conversion, yields of CO<sub>2</sub> and byproducts (CO &  $C_6H_5$ CHO) at different reaction temperatures. Fig. 11a shows that 2.5AuCe is most active catalyst with conversion at 300 °C ( $C_{300}$ ) of 96%, followed by Ce1 (70%) and 2.5VCe (23%). It is also the best catalyst for deep oxidation of toluene according to CO<sub>2</sub> yield with only a trace amount of CO produced (Fig. 11b). Ce1 has similar  $T_{50}^*$  of 290 °C, but toluene conversion never exceeded 90% with partial oxidation products (ca. 25%). On these two catalysts, toluene is adsorbed parallel to the surface *via*  $\pi$ -bonding (Fig. 7b and c). A strong  $\pi$ -interaction destabilizes the aromatic ring resulting in ring decomposition and oxidation. Toluene oxidation over Ce1 catalyst is believed to proceed Mars-van Krevelen reaction mechanism [11,13]. The role of gold on the redox cycle ( $Ce^{3+}$  to  $Ce^{4+}$ ) of ceria has been proposed by S. Scirè's group [49] and they suggested that gold on ceria weaken the Ce-O bond and further increase the mobility of the surface lattice oxygen, thus promoting toluene oxidation.

Low temperature toluene conversion over 2.5VCe produces mostly partial oxidation products, like benzaldehyde and CO. Significant toluene conversion to CO<sub>2</sub> does not occur until 370 °C ( $T_{50}^*$ ), and yield of byproducts remains high even at 450 °C. Toluene is adsorbed on 2.5VCe catalyst *via* the methyl group forming  $\sigma$ bonding with the surface. The clear observation of carbenium ion on *operando* Raman spectra suggests that adsorption is forming by adsorption on Brønsted acid site of V<sup>5+</sup>–O–Ce<sup>3+</sup> in 2.5VCe. This leads to partial oxidation and production of benzaldehyde. Vanadium also titrates the re-oxidation of ceria *via* surface oxygen vacancies and hinders access to active Ce<sup>4+</sup> sites for complete oxidation of toluene.

Dispersion of gold and vanadium on ceria improves the stability of the catalyst to water vapor (SI. Part 2). Toluene oxidation reaction in the presence of 26,000 ppm H<sub>2</sub>O has led to a significant decrease in Ce1 activity particularly in terms of CO<sub>2</sub> yield (Fig. S5



Fig. 10. Integration of characteristic online FTIR peaks for (a) 2.5VCe, (b) Ce1 and (c) 2.5AuCe catalysts. [Notes: ■-C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, ●-CO<sub>2</sub>, ◆-H<sub>2</sub>O, ×-CO, ▶-C<sub>6</sub>H<sub>5</sub>CHO.]



Fig. 11. (a) Conversion and (b) CO<sub>2</sub> yield and byproduct yield of 2.5VCe, Ce1 and 2.5AuCe catalysts in the operando reactor.

and Table S2). The effect is reversible and the catalyst regained its original activity once the water was turned off, as observed from a 48 h experiment. (Fig. S6). Water adsorption particularly on the defect sites of Ce1 is believed to play a role in decrease of catalytic performance under humid condition. 2.5AuCe and 2.5VCe with Au and V occupying the defect sites were less affected by the water vapor. This is particularly true for 2.5AuCe which maintained its activity even under 692,000 ppm  $H_2O$  (Table S3).

The Raman spectra in Fig. 6 indicate that toluene adsorption on 2.5VCe catalyst is via  $\sigma$ -bonding of methyl group on the catalyst surface. Similar toluene adsorption configuration on V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalysts was observed by van Hengstum and coworkers during toluene selective oxidation to benzaldehyde/benzoic [50]. On 2.5VCe catalyst, benzyl carbenium ion is formed when toluene adsorbed on the Brønsted acid sites of vanadia (Fig. 7), which further leads to formation of carbonaceous deposits on surface (Fig. S11) and high concentrations of partial oxidation products (Figs. 10 and 11). On ceria surface, toluene adsorbs parallel to the surface via  $\pi$ -bonding, destabilizing the aromatic ring and resulting in higher oxidation rates on Ce1 and 2.5AuCe catalysts. In the latter catalyst, gold is reported to enhance the oxidation reaction by increasing the reducibility of the lattice oxygen of ceria and possibly their mobility [11]. López et al. [8] suggested that the prevalence of surface oxygen vacancies play an important role in toluene oxidation over ceria catalysts. They found that catalysts with a high surface oxygen-to-bulk oxygen ratio is more active for toluene oxidations, as measured by temperature programmed reduction (TPR) experiments [8]. Similar positive correlation was observed in this work between the surface oxygen species  $O_{2 ads}^{2-}$  (or  $O_{2 ads}^{-}$ ) in Fig. 8 and the catalytic activity in Fig. 11. The strong adsorption of benzyl alcohol and styrene on Au(1 1 1) with phenyl-ring parallel to surface was indicated by C.M. Friend's group [51,52], in line with the presence of benzoate intermediates [53], which would be readily burnt without intermediate oxidation products [49]. Furthermore, small size gold nanoparticles (ca. 2-4 nm) is said to have influence on the surface peroxide species  $(O_{2ads}^{2-})$  [54], as also observed in this study (Fig. 8). The experimental results of this study indicate that gold is responsible for 2.5AuCe catalyst's high selectivity for toluene oxidation to carbon dioxide, either directly as a catalyst or indirectly by facilitating the re-oxidation of ceria (Fig. 8). The 2.5AuCe catalyst has the added advantage of being stable even at high humidity conditions (SI. Part. 2).

# 4. Conclusions

The CeO<sub>2</sub>,  $VO_x/CeO_2$  and Au/CeO<sub>2</sub> catalysts present different active sites for toluene adsorption and reaction, resulting in very

different reaction behavior. Vanadium and gold nucleate on oxygen vacancy sites of CeO<sub>2</sub> and have a reducing effect on the ceria with concomitant increase in Ce<sup>3+</sup>. Vanadium and gold mainly exist in the oxidized states of  $V^{5+}$  (99.0%) and Au<sup>+</sup> (73.2%). Toluene molecule is adsorbed with its aromatic ring parallel to the surface of Ce1 and 2.5AuCe catalysts *via*  $\pi$ -bonding that appears to destabilize the aromatic ring resulting in a more rapid and complete oxidation to CO<sub>2</sub> and H<sub>2</sub>O. For both catalysts,  $\eta^2$ -peroxide O<sub>2 ads</sub> shows up on operando Raman spectra, but gold appears to catalyze the transformation of  $\eta^2$ -peroxide  $O_{2ads}^{2-}$  in the re-oxidation of CeO<sub>2</sub>. This could explain the better performance of 2.5AuCe for complete oxidation of toluene. Toluene is adsorbed as carbenium ion on Brønsted acid sites of 2.5VCe and produces benzaldehyde as the main partial oxidation byproduct. 2.5VCe appears to stabilize  $\eta^{1}$ superoxide  $O_{2 ads}^{-}$  preventing the re-oxidation of CeO<sub>2</sub>, which explained its poorer oxidation performance with significant CO production.

## Acknowledgments

This work was financial supported by the Spanish Ministry [CTQ2014-57578-R] and [CTM2017-82335-R]; NSFC/RGC Joint Research Scheme [N-HKUST626/13]; European Commission Grant 760928 BIORIMA and Guangzhou Collaborative Innovation Key Program [201704030074]. The authors express their gratitude to Dr. Laura Pascual, Dr. Wei Han, Ms. Mei Leng Liu, Mr. Hoi Yau Cheng and Mr. Nick K C Ho for technical supports. Also, thanks to the Oversea Research Award from School of Engineering, HKUST for supporting the exchange program at the ICP-CSIC, in Spain.

## **Appendix A. Supplementary material**

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcat.2018.05.001.

## References

- U. Nurmatov, N. Tagiyeva, S. Semple, G. Devereux, A. Sheikh, Eur. Respir. Rev. 24 (2015) 92–101.
- [2] M. Hulin, M. Simoni, G. Viegi, I. Annesi-Maesano, Eur. Respir. J. 40 (2012) 239– 254.
- [3] S. Burgaz, O. Erdem, G. Çakmak, N. Erdem, A. Karakaya, A.E. Karakaya, Biomarkers 7 (2002) 151–161.
- [4] J.E. Huff, J.K. Haseman, D.M. DeMarini, S. Eustis, R.R. Maronpot, A.C. Peters, R.L. Persing, C.E. Chrisp, A.C. Jacobs, Environ. Health Perspect. 82 (1989) 125–163.
- [5] M.S. Kamal, S.A. Razzak, M.M. Hossain, Atmos. Environ. 140 (2016) 117-134.
- [6] L. Vivier, D. Duprez, ChemSusChem 3 (2010) 654-678.
- [7] A. Trovarelli, Catal. Rev. Sci. Eng. 38 (1996) 439-520.
- [8] J.M. López, A.L. Gilbank, T. García, B. Solsona, S. Agouram, L. Torrente-Murciano, Appl. Catal. B 174–175 (2015) 403–412.

- [9] Y.M. Chiang, E.B. Lavik, I. Kosacki, H.L. Tuller, J.Y. Ying, Appl. Phys. Lett. 69 (1996) 185–187.
- [10] A. Trovarelli, Catalysis by Ceria and Related Materials, Imperial College Press, London, 2002, pp. 15–50.
- [11] S. Scirè, P.M. Riccobene, C. Crisafulli, Appl. Catal. B 101 (2010) 109–117.
- [12] M. Ousmane, L.F. Liotta, G. Di Carlo, G. Pantaleo, A.M. Venezia, G. Deganello, L.
- Retailleau, A. Boreave, A. Giroir-Fendler, Appl. Catal. B 101 (2011) 629–637. [13] W.B. Li, J.X. Wang, H. Gong, Catal. Today 148 (2009) 81–87.
- [14] C. Cho, S. Ihm, Environ. Sci. Technol. 36 (2002) 1600-1606.
- [15] J.J. Spivey, J.B. Butt, Catal. Today 11 (1992) 464–500.
- [16] Q. Dai, S. Bai, H. Li, W. Liu, X. Wang, G. Lu, Appl. Catal. B 168–169 (2015) 141– 155.
- [17] D.M. Gómez, V.V. Galvita, J.M. Gatica, H. Vidal, G.B. Marin, Phys. Chem. Chem. Phys. 16 (2014) 11447–11455.
- [18] N. Burgos, M. Paulis, M. Antxustegi, M. Montes, Appl. Catal. B 38 (2002) 251– 1158.
- [19] M.V. Martínez-Huerta, G. Deo, J.L.G. Fierro, M.A. Bañares, J. Phys. Chem. C 112 (2008) 11441–11447.
- [20] T. Akita, M. Okumura, K. Tanaka, M. Kohyama, M. Haruta, J. Mater. Sci. 40 (2005) 3101–3106.
- [21] G. Leofanti, M. Padovan, G. Tozzola, B. Venturelli, Catal. Today 41 (1998) 207-219.
- [22] K.S.W. Sing, Pure Appl. Chem. 57 (1985) 603-619.
- [23] A. Pfau, K. Schierbaum, Surf. Sci. 321 (1994) 71–80.
- [24] M.M. Natile, A. Glisenti, Surf. Sci. Spectra 13 (2006) 17–30.
- [25] H. Huang, Y. Gu, J. Zhao, X. Wang, J. Catal. 326 (2015) 54–68.
- [26] X. Wang, B. Chen, G. Chen, X. Sun, RSC Adv. 6 (2016) 87978–87987.
- [27] Z. Liu, S.J. Jenkins, D.A. King, Phys. Rev. Lett. 94 (2005) 196102.
- [28] A. Shi, X. Wang, T. Yu, M. Shen, Appl. Catal. B 106 (2011) 359–369.
   [29] M.V. Martínez-Huerta, J.M. Coronado, M. Fernández-García, A. Iglesias-Juez, G.
- Deo, J.L.G. Fierro, M.A. Bañares, J. Catal. 225 (2004) 240–248. [30] M. Baron, H. Abbott, O. Bondarchuk, D. Stacchiola, A. Uhl, S. Shaikhutdinov, H.
- Freund, C. Popa, M.V. Ganduglia-Pirovano, Angew. Chem. Int. Ed. 48 (2009) 8006–8009.
- [31] A. Iglesias-Juez, M.V. Martínez-Huerta, E. Rojas-García, J.-M. Jehng, M.A. Bañares, J. Phys. Chem. C 122 (2018) 1197–1205.
- [32] A. Karpenko, R. Leppelt, V. Plzak, R.J. Behm, J. Catal. 252 (2007) 231-242.

- [33] H. Bake, S.F. Zaman, Y.A. Alhamed, A.A. Al-Zahrani, M.A. Daous, S.U. Rather, H. Driss, L.A. Petrov, RSC Adv. 6 (2016) 22555–22562.
- [34] R. Si, M. Flytzani-Stephanopoulos, Angew. Chem. Int. Ed. 47 (2008) 2884– 2887.
- [35] Z. Wu, A.J. Rondinone, I.N. Ivanov, S.H. Overbury, J. Phys. Chem C. 115 (2011) 25368–25378.
- [36] Z. Wu, M. Li, J. Howe, H.M. Meyer, S.H. Overbury, Langmuir 26 (2010) 16595– 16606.
- [37] M.V. Bosco, M.A. Bañares, M.V. Martínez-Huerta, A.L. Bonivardi, S.E. Collins, J. Mol. Catal. A 408 (2015) 75–84.
- [38] J.E. Spainer, R.D. Robinso, F. Zhang, S. Chan, I.P. Herman, Phys. Rev. B 64 (2001) 245407.
- [39] D. Lin-Vien, N.B. Colthup, W.G. Fateley, J.G. Grasselli, The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules, Academic Press, San Diego, 1991, p. 412.
- [40] M. Tasumi, T. Urano, M. Nakata, J. Mol. Struct. 146 (1986) 383-396.
- [41] Y.J. Kwon, D.H. Son, S.J. Ahn, M.S. Kim, K. Kim, J. Phys. Chem. 98 (1994) 8481– 8487.
- [42] X. Gao, J.P. Davies, M.J. Weaver, J. Phys. Chem. 94 (1990) 6858-6864.
- [43] A.A. Davydov, Mater. Chem. Phys. 19 (1988) 97-112.
- [44] A.A. Davydov, A.A. Budneva, E.A. Paukshtis, React. Kinet. Catal. Lett. 39 (1989) 419-424.
- [45] M. Badlani, I.E. Wachs, Catal. Lett. 75 (2001) 137-149.
- [46] V.V. Pushkarev, V.I. Kovalchuk, J.L. D'Itri, J. Phys. Chem. B 108 (2004) 5341– 5348.
- [47] R. Long, Y. Huang, H. Wan, J. Raman Spectrosc. 28 (1997) 29-32.
- [48] C. Schilling, A. Hofmann, C. Hess, M.V. Ganduglia-Pirovano, J. Phys. Chem. C 121 (2017) 20834–20849.
- [49] S. Scirè, S. Minicò, C. Crisafulli, C. Satriano, A. Pistone, Appl. Catal. B 40 (2003) 43-49.
- [50] A.J. Hengstum, J. Pranger, S.M. Hengstum-Nijhuis, J.G. Ommen, P.J. Gellings, J. Catal. 101 (1986) 323–330.
- [51] J.C.F. Rodríguez-Reyes, C.M. Friend, R.J. Madix, Surf. Sci. 506 (2012) 1129– 1134.
- [52] R.G. Quiller, X. Liu, C.M. Friend, Chem. Asian J. 5 (2010) 78-86.
- [53] X.E. Verykios, F.P. Stein, R.W. Coughlin, Catal. Rev. Sci. Eng. 22 (1980) 197-234.
- [54] B.K. Min, C.M. Friend, Chem. Rev. 107 (2007) 2709–2724.