Cu supported on mesoporous ceria: water gas shift activity at low Cu loadings through metal–support interactions†

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We have synthesized and tested a highly active Cu doped mesoporous CeO₂ catalyst system for the low temperature water–gas shift (WGS) reaction. While typical oxide-supported copper WGS catalysts are characterized by high copper loadings (30–40%), the morphological properties of the mesoporous CeO₂ material enable high catalytic activity at copper loadings as low as 1%. *Operando* X-ray diffraction, *in situ* X-ray absorption near-edge structure spectroscopy (XANES), and *operando* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) methods were used to probe the interactions between the metal and mesoporous oxide components under reaction conditions. Copper was observed to undergo reduction from oxide to metal under WGS conditions at 150 °C, while the CeO₂ lattice was observed to expand upon heating, indicating Ce³⁺ formation correlated with CO₂ production. The active state of the catalysts was confirmed by *in situ* XANES to contain Cu⁰ and partially reduced CeO₂. DRIFTS analysis revealed carboxyl species bound to copper during reduction, as well as formate and carbonate surface species on ceria. Lower concentrations of copper were observed to foster enhanced metal–support interactions.

Introduction

Hydrogen remains an expensive and essential chemical fuel of paramount importance to numerous existing industrial processes (*i.e.* Haber–Bosch) and newer renewable energy processes (*i.e.* fuel cells). Large scale, energy efficient hydrogen production with minimal carbon emissions has been the object of significant research effort over the last several decades. Much of this research has been focused on identifying and expanding various

avenues of hydrogen production using heterogeneous catalysts.^{1–4} In the present day, reforming of coal, oil, and natural gas accounts for the production of over 95% of the world's hydrogen supply.⁵ These reforming processes yield the production of reformat gas (syngas),⁶ chiefly consisting of hydrogen, carbon monoxide, and carbon dioxide components.

The water–gas shift (WGS: CO + H₂O → CO₂ + H₂) reaction is typically utilized as part of a purification process that enables the isolation of pure hydrogen from reformat gas through conversion of the carbon monoxide content.⁷ This purification step is necessary for the application of hydrogen for ammonia synthesis or as fuel for polymer electrolytic membrane fuel cells (PEMFCs), which contain catalysts easily poisoned by carbon monoxide.^{7,8} The WGS process in industry is enacted using a two-step process, consisting of high temperature (HT-WGS) and low temperature (LT-WGS) reactions enabled through the use of heterogeneous catalysts.^{9,10} HT-WGS is carried out under temperatures up to 600 °C using ferrochrome catalyst materials, while LT-WGS is usually carried out between 200 °C and 300 °C using CuO/ZnO/Al₂O₃ catalysts. The complexity and high energy requirements of this process have prompted research efforts aimed at the development of new single-step, low-temperature WGS catalysts.

Metals in conjunction with cerium oxide in various configurations and have been studied as promising catalysts for reactions such as the water–gas shift, with their activity often

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† Electronic supplementary information (ESI) available: Includes CuO particle size distribution (Fig. S1), surface area normalized activity (Fig. S2), *operando* X-ray diffraction data on 10%, 3%, and 1% mesoporous Cu/CeO₂ catalysts, along with Rietveld refinement results (Fig. S3–S11). Additionally, DRIFTS data is available for 10% mesoporous Cu/CeO₂ (Fig. S12). See DOI: 10.1039/c7cp02378b

attributed not only to the affinity of the metal component to carbon monoxide conversion, but also to the reducibility and oxygen transport properties of cerium oxide, which acts as an active support material.^{11,12} Typical supported catalysts contain well dispersed metals anchored as nanoscale particles to oxygen vacancies on the oxide surface, which are activated for selective conversion through metal-support interactions. Metal-support interactions have been discussed in detail for several decades with consensus that there are strong effects from the support that can influence chemistry of the metal.¹³

In the WGS reaction, metal sites may adsorb CO or dissociate H₂O, while the reduction of cerium from Ce⁴⁺ to Ce³⁺ leads to the formation of oxygen vacancies. Ceria has been identified as a unique support that can be used to tune chemistry of metal particles through interaction between the metal particles and oxygen vacancies.¹⁴ These vacancies have also been identified as water dissociation sites in the reaction mechanism for the WGS reaction.¹⁵ In addition, metal-ceria oxide catalysts has been shown to facilitate the formation of carbonaceous intermediates through the reaction of surface adsorbate CO and OH, enabling an associative mechanism for the WGS through H₂CO₂ intermediate species such as formates, carbonates, or carboxyls.¹⁶

The development of the Cu/CeO₂ mesoporous catalysts presented in this study originates from the advent of a novel CeO₂ sol-gel synthesis technique developed at the University of Connecticut.¹⁷ This synthetic approach yielded highly crystalline CeO₂ nanoparticle aggregates that exhibit inter-particle pores of controllable size. In a previous study, we have reported this CeO₂ material as an active, stand-alone, metal-free catalyst for the WGS reaction.¹⁸ The ceria mesoporous material exhibits a much higher catalytic activity than traditional ceria systems.¹⁶ Building upon the promising activity of this material, a modified sol-gel synthesis technique was again used to produce mesoporous Cu/CeO₂. The choice to introduce a copper phase into this catalyst system is based on copper's widely known properties as an active phase in water-gas shift catalysis.^{19–21} In this manuscript, we have examined *in situ* the structural, electronic, and catalytic properties of the mesoporous Cu/CeO₂ catalysts. We particularly focused on the nature of metal-support interactions between the two phases of the catalyst system, and the role of these interactions in WGS catalytic activity. We have concluded that metal-support interactions could be used to tune WGS chemistry.

In this study, the mesoporous Cu/CeO₂ catalysts of various loadings will be referred to as 1CuCe, 3CuCe, 5CuCe, and 10CuCe. The mesoporous 5% Cu/CeO₂ sample, or 5CuCe, was chosen as the representative sample for discussion of most *in situ* experiments. The reason for this choice is the fact that lower concentrations of Cu are much harder to observe and study using techniques such as XPS and XRD.

Experimental

Catalyst synthesis

The catalysts were synthesized by an inverse-micelle templated sol-gel method.¹⁷ Briefly, 8.5 g of Ce(III)(NO₃)·3H₂O, a quantity

of Cu(II)(NO₃)₂·6H₂O, 3 g of poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (average M.W. 5800 kDa), 15 mL of 1-butanol, and 2 mL of concentrated nitric acid were mixed to homogeneity in a 250 mL beaker under gentle heating (~60 °C). The solution was placed in a ventilated oven at 120 °C for five hours. The products were washed with ethanol three times and dried *in vacuo* overnight. The solid powder was then ground and aliquots were placed in a ceramic crucible and calcined in a ventilated tube furnace to 450 °C for four hours (5 °C min⁻¹ ramp rate). 1, 3, 5, and 10% mesoporous Cu/CeO₂ materials were produced. These materials are denoted in this study as 1CuCe, 3CuCe, 5CuCe, and 10CuCe, respectively.

High resolution transmission electron microscopy (HRTEM)

Microstructural characterization by HRTEM was performed at the Technical University of Catalonia using JEOL 2010F microscope at 200 kV equipped with a field emission source. The point-to-point resolution of the electron microscope was 0.19 nm, and the resolution between lines was 0.14 nm. STEM-HAADF-EDX characterization was carried out using a Tecnai G2 F20 S-TWIN microscope equipped with a field emission electron source and operated at 200 kV.

Textural studies

N₂ sorption experiments on the Mesoporous ceria were performed with a Quantachrome Autosorb-1-1C automated sorption system. All the samples were degassed at 150 °C for 6 hours under vacuum prior to measurement. The surface areas were calculated using the Brunauer-Emmett-Teller (BET) method, and pore sizes and volumes were calculated from the desorption branch of the isotherm using the Barrett-Joyner-Halenda (BJH) method.

Catalytic activity

The catalytic activity was evaluated in a home-built horizontal fixed-bed reactor equipped with a gas manifold and a standardized process gas chromatograph (GC, SRI International Multi-gas #2) for sampling the outlet gas. About 50 mg of catalyst were packed into a quartz reactor and supported by quartz wool. The catalyst was cleaned under flowing helium at 200 °C for an hour, cooled to room temperature, and then was exposed to the WGS conditions (5% CO/3% H₂O/He) at a 9500 h⁻¹ GHSV. The catalyst was then ramped to 150 °C and temperatures taken in 50 degree increments up to 500 °C with a ramp rate of 5 °C min⁻¹ between temperatures. At each temperature, 3 data points were taken after a 30 minute equilibration period.

X-ray photoelectron spectroscopy (XPS)

XPS measurements were carried out at the Center for Functional Nanomaterials at Brookhaven National Laboratory. Powder samples were adhered to carbon tape mounting material, and introduced into ultra-high vacuum environment, where a conventional Mg X-ray source was used to probe the materials. Ce 3d, Cu 2p, and O 1s regions were probed, data plotted and analyzed using CasaXPS software.²²

Synchrotron techniques (XRD and XANES)

The *operando* X-ray Diffraction (XRD) and *in situ* Cu K-edge and Ce L₃-edge XANES experiments detailed in this study were performed at the Advanced Photon Source (APS) in Argonne National Laboratory at beamlines 17BM-B and 20BM-B, respectively. The experiments were carried out using the Clausen²³ capillary flow reactor. A quartz capillary with an inner diameter of 0.9 mm and outer diameter of 1.1 mm is loaded with approximately 5 mg of sample between two segments of quartz wool. Reactant gas consists of 5% CO (in Helium) flown through a room temperature water bubbler to achieve 3% H₂O concentration. The reactant gas mixture is flown continuously through the capillary at a rate of 10 cc min⁻¹ for XRD experiments and 20 cc min⁻¹ for XANES experiments. The temperature of the reactor cell is controlled using a heating coil and a Eurotherm or similar temperature controller. The temperature profile for the experiments consists of stepwise heating up to 450 °C (XANES) and stepwise heating and cooling up to 400 °C (XRD). X-ray diffraction patterns are collected continuously during the experiment. XANES spectra were collected only during constant temperature steps. Outflow gas during XRD experiments was analyzed using a Residue Gas Analyzer (RGA) quadrupole mass spectrometry unit in order to provide a qualitative WGS activity analysis by monitoring the production of H₂ and CO₂ gas.

Soft X-ray absorption spectra (O K-edge and Ce M_{4,5}-edge) were collected in total electron yield (TEY) mode at beamline 23-ID-2 (CSX-2) at the National Synchrotron Light Source II (NSLS II). All X-ray absorption spectra were processed using the Athena software,²⁴ which includes plotting, normalization, and basic principal component analysis.

The X-ray wavelength utilized for XRD at beamline 17-BM-B at APS was 0.72768 Å. X-ray diffraction patterns were plotted in origin and processed using the GSAS II software²⁵ to obtain structural and composition information *via* Rietveld refinement.²⁶

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)

DRIFTS experiments were performed at Brookhaven National Laboratory. The Harrick reactor cell was loaded with sample material and heated to 100 °C, followed by stepwise heating in 50 °C up to 400 °C under helium. Infrared spectra (4000 to 750 cm⁻¹) were recorded every 85 seconds. The sample is then cooled to room temperature and WGS reactants (5% CO in He, 3% H₂O *via* bubbler, balance He) are introduced into the cell. The cell is then heated in the same stepwise manner up to 400 °C while collecting infrared spectra. KBr background was subtracted from all spectra.

Results and discussion

Local morphology

A representative HRTEM image of the 5% mesoporous Cu/CeO₂ catalyst, 5CuCe, is reported in Fig. 1. Fourier transform analysis

Fig. 1 HRTEM of 5CuCe catalyst. Fourier transform inset with CuO spots labelled.

of the image revealed multiple ceria crystallites exhibiting lattice fringes at 3.12 Å, which corresponds to the {111}-family crystallographic planes. The ceria particles were found to be highly monodisperse and measured to be 4–6 nm in diameter. In addition to the lattice fringes of CeO₂, another set of planes were identified in some particles. The spots at 2.75 and 1.87 Å (inset) correspond to the {110} and {202} planes of CuO. The identification of CuO lattice fringes and the absence of lattice fringe modification of the ceria lattice indicate that the copper present in this material exists initially as CuO. These CuO particles were measured to be approximately 3–5 nm in diameter. See Fig. S1 (ESI†) for CuO particle size distribution.

Textural studies

The textural properties of the copper-doped samples were analyzed and the isotherms are shown in Fig. 2, while the derived metrics are given in Table 1. All four samples showed type IV isotherms, indicating mesoporosity. The surface area ranged from 117 to 203 m² g⁻¹, while the pore diameter was relatively constant at 1.43 nm in size. The 1CuCe and 3CuCe samples had relatively similar surface areas (~120 m² g⁻¹) while the 5CuCe and 10CuCe samples demonstrated a significantly increased surface area. The pore volume increased with the addition of the copper dopant from 0.089 up to 0.200 cc g⁻¹.

Spectroscopic characterization

X-ray photoelectron spectroscopy was utilized to study the surface chemical state of the mesoporous Cu/CeO₂ materials. Ce 3d_{3/2,5/2} XPS spectra of fresh 5CuCe and 10CuCe catalysts are reported in Fig. 3a. Individual peaks were fit to the spectra and labeled according to Burroughs formalism.²⁷ Each Ce 3d spectrum is observed to consist of five spin-orbit split doublet 3d_{3/2} and 3d_{5/2} features, indicated as *u* and *v*, respectively. Each 3d_{3/2}/

Fig. 2 Adsorption isotherms for mesoporous Cu/CeO₂ catalysts.

Table 1 Textual properties of mesoporous Cu/CeO₂ catalysts

	Surface area (m ² g ⁻¹)	Pore volume (cc g ⁻¹)	Pore diameter (nm)
1CuCe	117	0.089	1.43
3CuCe	127	0.101	1.42
5CuCe	181	0.123	1.42
10CuCe	203	0.200	1.42

3d_{5/2} doublet is split by approximately 18.6 eV, and the intensity ratio $I_{(3d_{5/2})}/I_{(3d_{3/2})}$ was fixed to 1.5 for fitting of each doublet.^{28,29}

The features observed on the XPS spectra of the catalysts indicate a majority Ce⁴⁺ species composition, with significant

minority presence of Ce³⁺. The areas of the features fit to the Ce 3d XPS spectrum were used to calculate an approximate concentration of Ce³⁺ ions (eqn (1)).

$$\% \text{Ce}^{3+} = \frac{A(u') + A(u0)}{A(u) + A(u') + A(u'') + A(u''') + A(u0)} \quad (1)$$

This treatment yielded an approximate surface Ce³⁺ concentrations of 22% and 15% for 5% and 10% Cu/CeO₂ samples, respectively. However, Ce³⁺/Ce⁴⁺ concentration estimates from XPS analysis can be overestimated due to problems related to X-ray irradiation, local heating, and other quantification difficulties.^{30,31}

Cu 2p XPS spectra for the 5CuCe and 10CuCe catalysts are reported in Fig. 3b. The position and broadening of the primary Cu 2p features around 933 and 953 eV, as well as the strong shake-up features present in the 10CuCe spectrum strongly indicate the presence of a CuO state,³² although the presence of a minority Cu₂O phase may not be ruled out. This observation is further corroborated with TEM, XRD, and Cu K-edge XANES measurements. Although decreased Cu 2p XPS intensity was observed for the 5CuCe sample, the primary features as well as one strong satellite feature associated with CuO were nevertheless present.

Cerium M_{4,5}-edge soft X-ray spectra measured for 5CuCe and 10CuCe are reported in Fig. 3c. The spectra consist of two sharp features at 883.4 eV (Ce M₅) and 901.0 eV (Ce M₄), separated by 17.6 eV. Broader, lower intensity features were observed at 888.5 eV (Y) and 906.1 eV (Y') Ce⁴⁺ component. This profile is largely consistent with Ce⁴⁺ present in unreduced cerium oxide.³³ This observation contrasts with the XPS data which indicates up to 22% of cerium content as Ce³⁺. This difference may be explained by the fact that XPS functions as a surface sensitive probe, whereas XAS measurements yield information regarding the bulk of the material. An inference may therefore be made that the catalyst support material consists of CeO₂ nanoparticle aggregates that are partially reduced at the surface as a consequence of interactions with Cu/CuO.

The oxygen K-edge XAS data for these materials is reported in Fig. 3d. The first three features correspond to electronic transition from the O 1s orbital to the 4f, 5d-e_g, and 5d-t_{2g} orbitals, which are characteristically dominated by cerium.^{34,35} The O K-edge XAS profile observed in this experiment is strongly indicative of an unreduced CeO₂ material, as it is well differentiated from spectra recorded for reduced cerium species.³⁶ This further underlines the unreduced bulk state of the CeO₂ nanoparticle aggregates.

WGS catalytic activity

Activity measurements for the mesoporous Cu/CeO₂ catalysts under WGS conditions were carried out at temperatures ranging from 200 °C to 350 °C. The resulting measurements were normalized by weight, catalyst surface area, and nominal copper content. 33% Cu impregnated commercial CeO₂ is included for comparison to typical copper loadings in Cu/

Fig. 3 (a) Ce 3d XPS, (b) Cu 2p XPS, (c) Ce M_{4,5}-edge XAS, and (d) O K-edge XAS of fresh 10CuCe and 5CuCe.

Fig. 4 (a) Reaction rate at 300 °C and (b) Arrhenius plot for mesoporous Cu/CeO₂ catalysts and 33% Cu impregnated commercial CeO₂. Both figures normalized by weight, surface area, and nominal copper loading.

ZnO/Al₂O₃ catalysts for the WGS reaction. Copper doped mesoporous CeO₂ catalysts display substantially improved WGS catalytic activity over the bare mesoporous CeO₂ material by 3 orders of magnitude.¹⁸ This effect is demonstrated in Fig. S2 (ESI†), which reports the WGS activity of these materials normalized to surface area (but not copper content). These catalysts were also observed to outperform the 33% bulk impregnated Cu/CeO₂ material. When accounting for the surface area and copper content of the catalysts, the most active specimen was observed to be 1% mesoporous Cu/CeO₂.

The measurements in Fig. 4 may be interpreted as WGS activity per unit copper, adjusted for surface area. Individual activity data at 300 °C are presented for direct comparison in Fig. 4a, while overall Arrhenius trends for all the copper-containing samples are plotted in Fig. 4b. The inverse relationship between activity and copper concentration suggests an abundance of active sites available at lower copper concentrations, likely due to close contact between the highly-dispersed copper and mesoporous ceria support. The diminishing effect with increased copper loadings may be attributed to an increase in copper particle size, leading to fewer copper atoms in close contact with CeO₂ material per unit copper present in the catalyst. Notably, the 10CuCe catalyst displayed comparable activity to the 33% Cu impregnated commercial ceria material when corrected for the substantially increased surface area of the mesoporous support. This observation underlines the utility of mesoporous CeO₂ beyond a simple surface area effect.

Active bulk structure

Operando XRD allowed for an examination of the properties of the crystalline components in the mesoporous Cu/CeO₂ catalytic system under WGS reaction conditions as a function of temperature. Refinement of Rietveld models based on this diffraction data yielded a time resolved view of the CeO₂ and Cu lattice parameters, as well as the crystalline phase composition of each catalyst. An examination of these properties has elucidated the nature of the catalytic activity of these samples for the WGS reaction.

Fig. 5 shows the *operando* XRD patterns (1/10 of all collected patterns shown) for the representative mesoporous Cu/CeO₂ catalyst in the study, 5CuCe. The most prominent phase visible

Fig. 5 *Operando* X-ray diffraction plot for 5CuCe.

in these patterns is the fluorite structure of CeO₂, which is evident from defining features such as the characteristic (111) face at $2\theta = 13.4$. Fluorite CeO₂ accounts for all other unlabeled features in the figure. Immediately apparent in the room temperature and 100 °C patterns are two features at around $2\theta = 16.6$ and 18.0 , which correspond to the (11 $\bar{1}$) and (111) faces of CuO.³⁷ This phase is also observed at room temperature and 100 °C patterns in 10CuCe and 3CuCe (Fig. S3 and S4, ESI† respectively). The presence of CuO at room temperature is in agreement with the TEM observations of dispersed CuO on the as-prepared 5CuCe sample at room temperature. A sharp reduction in the oxidation state of copper from Cu²⁺ to Cu⁰ is observed at 150 °C. This transition is made evident by the rapid disappearance of the characteristic CuO features and the appearance of metallic Cu features,³⁷ the most prominent of which is the (111) face at $2\theta = 20.1$. This reduction at 150 °C occurs in each of the three samples where the copper phase is visible (5CuCe, 10CuCe, and 3CuCe), and it is highlighted by the black spectra in Fig. 5 and Fig. S3, S4 (ESI†). A plot was also prepared for 1CuCe (Fig. S5, ESI†), however no visible crystalline copper phase was observed due to the low metal content of the catalyst.

Rietveld refinements of structural models to fit X-ray diffraction data were carried out for a closer look at the crystalline phase composition of the catalysts. The change in observed crystalline phase composition of 5CuCe as it is heated under WGS conditions is documented in Fig. 6. At room temperature, the calculated composition is approximately 98% CeO₂ and 2% CuO. The sharp reduction from CuO to Cu is evident at 150 °C, as the CuO composition decreases to 0% and Cu composition increases to approximately 5%. The observed increase in Cu content over initial CuO content may be explained by initial presence of amorphous copper species, or copper incorporated within the CeO₂ lattice.³⁸ The copper remains metallic upon cooling of the catalyst to room temperature under WGS conditions (Fig. S6, ESI†).

The phase composition of 10CuCe as it is heated under WGS conditions is documented in Fig. S7 (ESI†). A similar pattern to 5CuCe is observed, featuring a sharp reduction to metallic Cu at 150 °C. The difference between CuO and Cu content is

Fig. 6 Phase composition of 5CuCe on heating. From Rietveld model of XRD data.

somewhat larger for the 5CuCe material, indicating a greater percentage of amorphous or incorporated Cu. As with 5CuCe, the reduction of Cu was not reversed.

Phase composition analysis was also carried out for 3CuCe, where the appearance of a metallic Cu phase was recorded at 150 °C (Fig. S8, ESI†). As with the higher loading percentages, this phase persisted upon cooling under WGS conditions. Refinement of the minority CuO phase was not carried out, as the CuO diffraction features were indistinguishable from the background.

In all cases where crystalline copper phases are visible in the diffraction data, no CuO is present at temperatures of WGS activity. Consequently, oxidized copper may be ruled out as an active species in the WGS reaction. The presence of metallic copper is likely a source of the increased catalytic activity observed on the mesoporous Cu/CeO₂ samples. This is further supported by the increase of catalytic activity with increased loadings of copper.

Rietveld refinement of structural models to fit *operando* XRD data additionally allows for monitoring of changes in the lattice

structure of identified crystalline phases over the course of the experiment. Fig. 7 documents the refined CeO₂ and Cu lattice parameters for the 5CuCe sample as it is heated and cooled under WGS reaction conditions. Additionally, Fig. 7a reports the simultaneous production of H₂, as measured by the RGA.

CeO₂ lattice expansion from 5.409 Å to a maximum of 5.456 Å was observed as the catalyst was heated. A portion of this expansion, particularly the step-wise components at higher temperatures, may be attributed to thermally induced expansion (estimated $6.3 \times 10^{-5} \text{ Å K}^{-1}$),³⁹ as this expansion is observed to have an approximately linear relationship with increasing temperature (Fig. 7b). This relationship is not present, however, at 100–150 °C, where the lattice is observed to expand even under constant temperature. This sort of expansion may be attributed to the reduction of a small amount of Ce⁴⁺ to Ce³⁺, and the subsequent formation of oxygen vacancies in the lattice.^{40,41} After 150 °C, the CeO₂ lattice appears to remain relatively stable with respect to oxidation state, with the exception of a slight contraction of the lattice after reaching 400 °C. Upon cooling, non-thermal contraction is observed below 100 °C, which may correspond to the re-oxidation of ceria. The original room temperature lattice parameter is not recovered while the sample remains under the reducing WGS reaction environment. WGS activity was not observed until the full transition of the CeO₂ lattice into its stable state after heating past 150 °C. Additionally, activity is seen to increase in tandem with the CeO₂ lattice parameter. These observations suggest that the reduced cerium and oxygen vacancies may play a role in the activity of the catalyst for the WGS reaction, in tandem with the presence of metallic copper at these temperatures. Comparable behavior of the CeO₂ lattice is observed for all copper loaded samples (Fig. S9–S11, ESI†), although differences in the stability of the lattice at 400 °C, as well as differences in initial Ce reduction temperature and rate were observed.

The metallic Cu lattice parameter was also monitored over the course of the experiment (blue lines in Fig. 7). In contrast to the CeO₂ lattice, copper was observed to solely exhibit thermal

Fig. 7 (a) Cu and CeO₂ lattice parameters from 5CuCe with H₂ production. (b) Cu and CeO₂ lattice parameters over temperature.

Fig. 8 *In situ* (a) Ce L₃-edge and (b) Cu K-edge XANES: 5CuCe under WGS conditions.

expansion properties in the mesoporous Cu/CeO₂ catalysts.^{42,43} This observation is made evident by the linear relationship between the Cu lattice parameter and temperature of the sample throughout the entirety of the experiment (Fig. 7b). Fig. S9 and S10 (ESI†) document similar behavior of the metallic Cu lattice parameter for the 10CuCe and 3CuCe samples, respectively. The Cu lattice parameter was not measured for 1CuCe (Fig. S11, ESI†), as the phase is not observed.

Active chemical state

In situ X-ray absorption near-edge structure (XANES) experiments were performed in order to closely probe the active states present in the mesoporous Cu/CeO₂ catalysts under WGS reaction conditions. Ce L₃ XANES spectra for the representative 5CuCe are reported in Fig. 8a. The room temperature measurement indicates the presence of Ce⁴⁺ as in the plain CeO₂ standard material. Starting at 150 °C, a shoulder on the lower energy side of the cerium feature (approximately 6727 eV) indicates an additional presence of Ce³⁺. This appearance of reduced cerium is in agreement with the observation of CeO₂ lattice expansion in the XRD experiments from 100 °C to 150 °C, and is correlated with the onset of WGS catalytic activity. The Cu K edge absorption spectra for the same material (Fig. 8b) indicates that the reduction of copper from a nearly uniform Cu²⁺ state at room temperature, to a fully reduced Cu⁰ state at 150 °C, with trace presence of Cu¹⁺, particularly at 100 °C. This observation further corroborates the findings from the XRD experiments, where a room temperature CuO phase is seen to reduce completely to metallic Cu at 150 °C, prior to the onset of catalytic activity.

In situ surface chemistry

Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) allows for the probe of chemical species existing on the surface of the catalysts under reaction conditions. DRIFTS spectra of Cu doped mesoporous CeO₂ were recorded under Helium flow as well as WGS reaction conditions up to 400 °C. When heating the catalysts under pure Helium flow, the development of features associated with the presence of monodentate⁴⁴ and bidentate formate^{44,45} species may be seen starting at or below 100 °C. These features are subsequently removed by 400 °C, and this removal is irreversible. The origin

Fig. 9 *In situ* DRIFTS: 5CuCe under WGS conditions.

of these features likely stems from carbonaceous remnants of synthesis precursors on the catalyst surface, or from the prolonged exposure of the materials to air.

The DRIFTS spectra recorded for 5CuCe are reported in Fig. 9. Production of CO₂ through WGS reaction activity is made evident by the evolution of the gas phase CO₂ feature near 2350 cm⁻¹, as well as the decrease in integrated intensity of the gas phase CO feature at 2143 cm⁻¹. A broad feature indicating the presence of water around 3300 cm⁻¹ is observed at room temperature up to 100 °C, along with a feature at 1635 cm⁻¹, which corresponds to molecularly adsorbed water.⁴⁴ Hydroxyl features around 3600 cm⁻¹ are observed to demonstrate a significantly diminished intensity compared to those observed for the metal-free mesoporous CeO₂ catalyst under WGS conditions.⁴⁶ This may indicate a highly labile, short-lived hydroxyl species participating in the reaction.

The peak at around 856 cm⁻¹ is assigned to surface carbonate species on CeO₂.^{47,48} A general increase in intensity of this feature with temperature has been observed. This behavior of carbonate on mesoporous CeO₂ has also been documented in the DRIFTS study of the metal-free mesoporous CeO₂ material under WGS conditions,⁴⁶ and may be attributed to the strong binding tendency of tridentate carbonate to the CeO₂(100) surface.⁴⁹ The general trending of carbonate presence with temperature and activity suggests that this species may serve as a spectator or intermediate in the WGS reaction.

A sharp feature at 2094 cm⁻¹ was observed at temperatures under 150 °C for all mesoporous Cu/CeO₂ catalysts. This sharp feature is assigned to CO bound to the Cu¹⁺ cation.⁵⁰ The presence of this species further corroborates the copper reduction phenomenon observed in XANES. Data obtained from the XANES experiments shows the presence of Cu₂O as a transient minority species most prevalent around 100 °C, when the CuO phase begins undergoing its reduction to metallic Cu⁰ (Fig. 7b). A more detailed examination of this feature is presented in Fig. 10, where the integrated intensity of

Fig. 10 Integrated intensity of 2094 cm^{-1} DRIFTS feature over time. Top inset: Maximum integrated intensity of 2094 cm^{-1} peak vs. nominal copper loading percentage. Bottom inset: Normalized for copper content.

the CO/Cu^{1+} peak is plotted against time and temperature. This intensity reflects the quantity of interfacial Cu^{1+} sites present on the catalyst surface.^{51,52} The feature initially appears at room temperature (not shown) upon the introduction of WGS reactants (particularly CO) following pretreatment, and decays to baseline over 25 minutes. Upon heating from room temperature under WGS conditions, the CO/Cu^{1+} feature evolves as shown in Fig. 10, reaching a maximum around 100°C . This maximum is plotted against nominal copper loading in the top inset of Fig. 10. With respect to Cu loading, the maximum intensity of the CO/Cu^{1+} trends $1\text{CuCe} < 5\text{CuCe} < 10\text{CuCe}$. This measurement of relative surface concentration of Cu^{1+} at lower temperatures does not correlate strongly with activity ($1\text{CuCe} < 5\text{CuCe} < 10\text{CuCe}$). However, if the peak Cu^{1+} feature intensity is normalized to the nominal copper content (Fig. 10 bottom inset), the opposite trend emerges. Per unit copper, the CO/Cu^{1+} feature intensity trends $10\text{CuCe} < 5\text{CuCe} < 1\text{CuCe}$, which correlates closely with catalytic activity normalized by surface area and copper content (Fig. 8b).

The behavior of the CO/Cu^{1+} feature with respect to copper loading serves to corroborate the notion that lower copper concentration mesoporous CeO_2 catalysts exhibit enhanced metal-support interactions, yielding an abundance of CO-binding surface sites that may serve as active sites in the WGS reaction. Although the higher copper loadings ultimately exhibit greater net activity, it is nevertheless desirable to promote the type of catalytic surface environment observed on the 1CuCe sample. A more optimized mesoporous Cu/CeO_2 catalyst system would preserve these catalytically favorable metal-support interactions while taking advantage of the significant catalytic activity boost provided by increasing copper concentrations.

The trends in the CO/Cu^{1+} DRIFTS feature may also be partially attributed to two-electron reduction of copper directly

Fig. 11 In situ DRIFTS: 1CuCe under WGS conditions.

from Cu^{2+} to the active phase, Cu^0 , since this process would be invisible to this DRIFTS analysis. DRIFTS experiments on 1CuCe (Fig. 11) and 10CuCe (Fig. S12, ESI†) yielded similar carbonate trends to those observed for 5CuCe (Fig. 9). Another type of carbonaceous surface species, however, was observed most prominently on the 1CuCe catalyst (Fig. 11). This feature at 2831 cm^{-1} is attributed to bidentate formate on CeO_2 .⁴⁴ This species first appeared at 150°C , and increased in intensity until 300°C , followed by a decrease in intensity at 400°C . Bidentate formate was observed by DRIFTS to exhibit this same behavior on the metal-free mesoporous CeO_2 under WGS conditions.⁴⁶ This observation suggests the presence of additional reaction pathways available on the surface of the 1CuCe catalyst, which could account for a portion of the catalyst's enhanced activity when normalized to surface area and copper loading. These additional pathways may be mechanistically similar to those observed for metal-free mesoporous Cu/CeO_2 material.⁴⁶

Conclusions

Mesoporous Cu/CeO_2 materials were synthesized using a sol-gel method based on a novel technique developed at the University of Connecticut.¹⁷ Initial characterization of these materials under *ex situ* conditions was carried out using XPS, XAS, TEM, and textural techniques. These methods informed of a highly crystalline material consisting of 4–6 nm CeO_2 particles and 4–5 nm CuO particles, with approximately 1.4 nm diameter inter-particle pores. XPS analysis suggested partially reduced cerium surface states.

These materials were found to exhibit high catalytic activity for the WGS reaction. Specifically, our 1% mesoporous Cu/CeO_2 catalyst proved to be a superior specimen for WGS catalytic application in terms of WGS activity adjusted for surface area and copper content. An examination into the nature of this activity elucidated the active state of the catalyst, consisting of

metallic copper nanoparticles and partially reduced, oxygen vacancy rich cerium oxide. This configuration manifests at just 150 °C under WGS conditions, immediately yielding hydrogen production as measured by mass spectrometry during *operando* XRD and DRIFTS experiments. These findings are in accordance with previous determinations of metallic copper and CeO₂ lattice oxygen vacancies as active sites in non-porous Cu/CeO₂ catalysts for the WGS reaction.⁴¹

The mesoporous Cu/CeO₂ catalysts were observed to benefit from metal-support interaction effects that promote catalytic activity beyond the surface area and copper loading effects. DRIFTS experiments elucidated that this effect is most pronounced at lower copper concentrations, as the presence of CO-binding copper sites per unit copper increases with the decrease in overall copper loading. This metal-support interaction effect is central to the promising results reported for these materials.

The development of improved catalysts for reactions such as the water-gas shift is an area of significant research interest. Understanding and exploiting the structural and chemical properties of catalytic materials is of importance in the search for cheap, reliable, and highly active materials. The mesoporous Cu/CeO₂ system examined in this study is an example of intelligent material design and synthesis culminating in demonstrated utility, the nature of which was thoroughly examined in order to inform the development of future catalytic systems.

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Notes and references

- 1 J. A. Turner, *Science*, 2004, **305**, 972–974.

- 2 A. Haryanto, S. Fernando, N. Murali and S. Adhikari, *Energy Fuels*, 2005, **19**, 2098–2106.
- 3 I. K. Kapdan and F. Kargi, *Enzyme Microb. Technol.*, 2006, **38**, 569–582.
- 4 M. Ni, M. K. H. Leung, D. Y. C. Leung and K. Sumathy, *Renewable Sustainable Energy Rev.*, 2007, **11**, 401–425.
- 5 I. Dincer and C. Acar, *Int. J. Hydrogen Energy*, 2015, **40**, 11094–11111.
- 6 D. A. Hickman and L. D. Schmidt, *Science*, 1993, **259**, 343–346.
- 7 M. S. Batista, E. I. Santiago, E. M. Assaf and E. A. Ticianelli, *J. Power Sources*, 2005, **145**, 50–54.
- 8 Q. Li, R. He, J.-A. Gao, J. O. Jensen and N. J. Bjerrum, *J. Electrochem. Soc.*, 2003, **150**, A1599–A1605.
- 9 G. Kolb, J. Schürer, D. Tiemann, M. Wichert, R. Zapf, V. Hessel and H. Löwe, *J. Power Sources*, 2007, **171**, 198–204.
- 10 J. J. Spivey, *Catal. Today*, 2005, **100**, 171–180.
- 11 R. Si and M. Flytzani-Stephanopoulos, *Angew. Chem., Int. Ed.*, 2008, **47**, 2884–2887.
- 12 W. C. Chueh, C. Falter, M. Abbott, D. Scipio, P. Furler, S. M. Haile and A. Steinfeld, *Science*, 2010, **330**, 1797–1801.
- 13 S. J. Tauster, S. C. Fung and R. L. Garten, *J. Am. Chem. Soc.*, 1978, **100**, 170–175.
- 14 J. A. Farmer and C. T. Campbell, *Science*, 2010, **329**, 933–936.
- 15 E. S. Putna, J. M. Vohs and R. J. Gorte, *J. Phys. Chem.*, 1996, **100**, 17862–17865.
- 16 J. A. Rodriguez, P. Liu, J. Hrbek, J. Evans and M. Pérez, *Angew. Chem., Int. Ed.*, 2007, **46**, 1329–1332.
- 17 A. S. Poyraz, C.-H. Kuo, S. Biswas, C. K. King'andu and S. L. Suib, *Nat. Commun.*, 2013, **4**.
- 18 C. Guild, D. Vovchok, D. Kriz, A. Bruix, B. Hammer, J. Llorca, W. Xu, A. El-Sawy, S. Biswas, J. Rodriguez, S. Senanayake and S. L. Suib, *ChemCatChem*, 2017, DOI: 10.1002/cctc.201700081.
- 19 A. A. Gokhale, J. A. Dumesic and M. Mavrikakis, *J. Am. Chem. Soc.*, 2008, **130**, 1402–1414.
- 20 N. A. Koryabkina, A. A. Phatak, W. F. Ruettinger, R. J. Farrauto and F. H. Ribeiro, *J. Catal.*, 2003, **217**, 233–239.
- 21 X. Wang, J. A. Rodriguez, J. C. Hanson, D. Gamarra, A. Martínez-Arias and M. Fernández-García, *J. Phys. Chem. B*, 2006, **110**, 428–434.
- 22 N. Fairley and C. S. Ltd, *CasaXPS Manual 2.3.15: CasaXPP Processing Software for XPS Spectra*, Casa Software Limited, 2009.
- 23 P. J. Chupas, K. W. Chapman, C. Kurtz, J. C. Hanson, P. L. Lee and C. P. Grey, *J. Appl. Crystallogr.*, 2008, **41**, 822–824.
- 24 B. Ravel and M. Newville, *J. Synchrotron Radiat.*, 2005, **12**, 537–541.
- 25 B. H. Toby and R. B. Von Dreele, *J. Appl. Crystallogr.*, 2013, **46**, 544–549.
- 26 A. Albinati and B. T. M. Willis, *J. Appl. Crystallogr.*, 1982, **15**, 361–374.
- 27 P. Burroughs, A. Hamnett, A. F. Orchard and G. Thornton, *J. Chem. Soc., Dalton Trans.*, 1976, 1686–1698, DOI: 10.1039/DT9760001686.

- 28 E. Bêche, P. Charvin, D. Perarnau, S. Abanades and G. Flamant, *Surf. Interface Anal.*, 2008, **40**, 264–267.
- 29 E. Paparazzo, *Mater. Res. Bull.*, 2011, **46**, 323–326.
- 30 L. Chen, P. Fleming, V. Morris, J. D. Holmes and M. A. Morris, *J. Phys. Chem. C*, 2010, **114**, 12909–12919.
- 31 F. Zhang, P. Wang, J. Koberstein, S. Khalid and S.-W. Chan, *Surf. Sci.*, 2004, **563**, 74–82.
- 32 M. C. Biesinger, L. W. M. Lau, A. R. Gerson and R. S. C. Smart, *Appl. Surf. Sci.*, 2010, **257**, 887–898.
- 33 L. A. J. Garvie and P. R. Buseck, *J. Phys. Chem. Solids*, 1999, **60**, 1943–1947.
- 34 X. Wang, J. C. Hanson, J. A. Rodriguez, C. Belver and M. Fernández-García, *J. Chem. Phys.*, 2005, **122**, 154711.
- 35 J. A. Rodriguez, J. C. Hanson, J.-Y. Kim, G. Liu, A. Iglesias-Juez and M. Fernández-García, *J. Phys. Chem. B*, 2003, **107**, 3535–3543.
- 36 S. Kumar, S. Gautam, T. K. Song, K. H. Chae, K. W. Jang and S. S. Kim, *J. Alloys Compd.*, 2014, **611**, 329–334.
- 37 X. Wang, J. C. Hanson, A. I. Frenkel, J.-Y. Kim and J. A. Rodriguez, *J. Phys. Chem. B*, 2004, **108**, 13667–13673.
- 38 X. Wang, J. A. Rodriguez, J. C. Hanson, D. Gamarra, A. Martínez-Arias and M. Fernández-García, *J. Phys. Chem. B*, 2005, **109**, 19595–19603.
- 39 A. Trovarelli, *Catal. Rev.*, 1996, **38**, 439–520.
- 40 W. Xu, R. Si, S. D. Senanayake, J. Llorca, H. Idriss, D. Stacchiola, J. C. Hanson and J. A. Rodriguez, *J. Catal.*, 2012, **291**, 117–126.
- 41 X. Wang, J. A. Rodriguez, J. C. Hanson, D. Gamarra, A. Martínez-Arias and M. Fernández-García, *J. Phys. Chem. B*, 2006, **110**, 428–434.
- 42 I.-K. Suh, H. Ohta and Y. Waseda, *J. Mater. Sci.*, 1988, **23**, 757–760.
- 43 F. C. Nix and D. MacNair, *Phys. Rev.*, 1941, **60**, 597–605.
- 44 F. Zhao, Z. Liu, W. Xu, S. Yao, A. Kubacka, A. C. Johnston-Peck, S. D. Senanayake, A.-Q. Zhang, E. A. Stach, M. Fernández-García and J. A. Rodriguez, *J. Phys. Chem. C*, 2014, **118**, 2528–2538.
- 45 C. Binet, M. Daturi and J.-C. Lavalley, *Catal. Today*, 1999, **50**, 207–225.
- 46 D. V. Curtis, J. Guild, D. A. Kriz, A. Bruix, B. Hammer, J. Llorca, W. Xu, A. El-Sawy, S. Biswas, J. A. Rodriguez and S. D. S. A. S. L. Suib, *ChemCatChem*, 2017, in review.
- 47 C. Li, Y. Sakata, T. Arai, K. Domen, K.-i. Maruya and T. Onishi, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 929–943.
- 48 C. Li, Y. Sakata, T. Arai, K. Domen, K.-i. Maruya and T. Onishi, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 1451–1461.
- 49 P. M. Albrecht, D.-e. Jiang and D. R. Mullins, *J. Phys. Chem. C*, 2014, **118**, 9042–9050.
- 50 S. Y. Yao, W. Q. Xu, A. C. Johnston-Peck, F. Z. Zhao, Z. Y. Liu, S. Luo, S. D. Senanayake, A. Martínez-Arias, W. J. Liu and J. A. Rodriguez, *Phys. Chem. Chem. Phys.*, 2014, **16**, 17183–17195.
- 51 D. Gamarra, M. Fernández-García, C. Belver and A. Martínez-Arias, *J. Phys. Chem. C*, 2010, **114**, 18576–18582.
- 52 D. Gamarra, A. L. Cámara, M. Monte, S. B. Rasmussen, I. E. Chinchilla, A. B. Hungria, G. Munuera, N. Györfy, Z. Schay, V. C. Corberán, J. C. Conesa and A. Martínez-Arias, *Appl. Catal., B*, 2013, **130–131**, 224–238.