Communication

Water-Gas-Shift over Metal-Free Nanocrystalline Ceria: An Experimental and Theoretical Study

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A tandem experimental and theoretical investigation of a mesoporous ceria catalyst reveals the properties of the metal oxide are conducive for activity typically ascribed to metals, suggesting reduced Ce^{3+} and oxygen vacancies are responsible for the inherent bi-functionality of CO oxidation and dissociation of water required for facilitating the production of H_2. The degree of reduction of the ceria, specifically the (1 0 0) face, is found to significantly influence the binding of reagents, suggesting reduced surfaces harbor the necessary reactive sites. The metal-free catalysis of the reaction is significant for catalyst design considerations, and the suite of in situ analyses provides a comprehensive study of the dynamic nature of the high surface area catalyst system. This study postulates feasible improvements in catalytic activity may redirect the purpose of the water-gas shift reaction from CO purification to primary hydrogen production.

The water-gas shift (WGS) is an important reaction for the production of high purity hydrogen, a crucial commodity utilized in the production of ammonia and fine chemicals.[1--3] Currently 95 % of hydrogen production is realized by steam reforming and preferential oxidation, which oxidizes carbon-containing molecules over a heterogeneous catalyst, concurrently reducing water to hydrogen.[4--6] The WGS is a purification reaction utilized to remove CO, and due to thermodynamic limitations is performed in a sequential high (350--450°C) and low (180--250°C) temperature regime over $Fe_2O_3{\cdot}Cr_2O_3$ and $Cu{\cdot}ZnO{\cdot}Al_2O_3$ respectively. A strong research effort is underway to develop next-generation catalysts for the process to be realized in small-scale reformers and membrane reactors.[7--10] Ceria-supported metals have emerged as promising candidates due to synergistic interactions between metal and oxide support, competitive thermodynamics in model studies and facile redox chemistry of the oxide.[11] Ceria-supported gold,[12--14] platinum,[15--17] and copper[18--21] have been extensively studied, as well as supported nickel.[14, 22--24] The metals adsorb and activate CO, while the ceria serves to dissociate water.[9, 25, 26] Nanostructured "metal-free" ceria, especially sub-10 nm nanoparticles, has recently become an interest for fundamental studies of the water-gas shift reaction over the oxide.[27--29] Herein we present a combined experimental and theoretical study of ceria in the WGS reaction, suggesting that the degree of surface reduction, specifically on the (1 0 0) facet exposed on ceria nanoparticles, has a major effect on the native activity of metal-free ceria. These results may be considered in the further development of ceria-containing catalysts for hydrogen production and purification.

We utilized a novel method to prepare a series of ceria catalysts which exhibited significant activity for the WGS reaction under CO rich conditions (Figure 1 A).[30] The activity was found to correlate to the surface area (Table S1, Scheme S2) suggesting access to the surface sites was crucial for activity. A nonporous ceria (Acros Organics) was compared and found to be active, though at a lower level, demonstrating ceria natively possesses the attributes for activity. Microscopy revealed the catalysts to be composed of spherical nanoparticle aggregates with 3--4 nm well-defined truncated octahedral nanocrystals (Figure 1 B--D) for which the (1 1 1) and (1 0 0) facets were exposed.[31] Step defects on the nanocrystal surface, indicated by arrows, reveal the presence of under-coordinated metals which may serve as active sites in the reaction.[25] The catalyst with the highest specific activity (pre-calcined to 450 °C) was selected for further investigation.

The utilization of in situ characterization techniques allows for the observation of metastable intermediates or reversible transformations of materials under reaction conditions.[32] High-resolution powder diffraction was performed under reactive conditions. (Figure 2 A) The non-thermal component of lattice constant expansion up to 300 °C is considered a relative measure of the degree of oxidation or reduction of ceria as the Ce^{3+} cation (1.143 Å) is larger than the Ce^{4+} cation (0.970 Å); thus reduction is correlated with expansion and oxidation to contraction. After an initial contraction[33] the lattice constant increased from 5.43 to 5.48 Å in incremental steps, in step with CO_2 production (Figure 2 B).[34]

Raman microscopy was utilized as a supporting technique to observe the ceria reduction in situ (Figure 2 C<xfigr2>). The spectrum is dominated by the F_{2g} vibrational mode of the fluorite lattice near 460 cm$^{<M->1}$. In the low temperature range studied (100--225 °C) a Raman shift of <M->5 cm$^{<M->1}$ was observed, as well as significant broadening.

Variation in this peak position has been correlated with vacancy formation, and simultaneous reduction of Ce^{4+}.[35] The L_3 adsorption line of the ceria observable by X-ray adsorption spectroscopy provides information about unoccupied states above the Fermi level, and can be de-convoluted into several contributing peaks related to adsorption processes associated with the 5d and 4f orbitals of ceria.[36] Up to 723 K, a 15 % contribution of Ce^{3+} was observed by XAS. This along with the previous analyses presented suggests that under WGS conditions, ceria ions may be reduced to lower oxidation states, giving rise to reduced ceria surfaces.

In situ DRIFTS is a powerful surface probe in the investigation of catalytic processes, specifically to interrogate the adsorbed intermediates formed during reaction conditions.[37] Figure 3 A presents the selected spectra collected under reaction conditions. Vibrations at 2931, 2836, and 2719 $\mathrm{cm}^{<M->1}$ are attributed to bidentate formate on the ceria surface, while a vibration at 1267 $\mathrm{cm}^{<M->1}$ (Figure S3) can be assigned to monodentate formate.[38] The behavior of the formate species suggest they are strongly bound to the ceria surface, and may be restricting surface sites. At 861 $\mathrm{cm}^{<M->1}$, a peak assigned to carbonate is observed.[39] (Figure 3 B) Recent X-ray adsorption experiments have identified a tridentate carbonate species strongly bound to ceria (1 0 0) due to reduction of the ceria surface.[40] The spectral appearance of the carbonate coincides with a significant increase in WGS activity, suggesting its association with the active site of the reaction.

DFT calculations were performed to clarify the energetics of H_2O and CO interaction with ceria substrates, to investigate the possible role of reduced ceria, and to suggest plausible reaction pathways for the WGS. The adsorption on the most stable reconstruction of the (1 0 0) surface[41, 42] leads to strongly bound CO and H_2O (Scheme S4). Furthermore, the lattice expansion observed in XRD and the presence of Ce^{3+} species revealed by XAS could be indicative of the presence of O vacancies. However, the dissociative adsorption of H_2O on an O vacancy site leads to the healing of such defects, and instead of re-oxidizing the ceria substrate, this process gives rise to a hydrogenated surface with an unperturbed number of Ce^{3+} centers[43] (Scheme S4(A)). This means that the presence of adsorbed H atoms is indistinguishable from O vacancies on the basis of XRD and XAS data. Nevertheless, the high exothermicity of the vacancy healing process by H_2O adsorption ($E_{\mathrm{ads}}(H_2O)$=<M->1.93

eV on an O vacancy, Scheme S5(A)) strongly suggests that O vacancies are not present under the water-rich conditions of WGS operation. Furthermore, the stability of hydroxyl groups also complicates their evolution to form H_2, which is an endothermic process by 2.82 eV (Scheme S5(A)). CO adsorbs strongly also on reduced CeO_2(1 0 0) in the form of a surface carbonite (E_{ads}(CO) =<M->1.87 eV, Scheme S5(B)), which can in turn exothermically interact with subsequently adsorbed H_2O to give rise to formate or very stable carbonate species (Scheme S6). Taking into account the unfavorable evolution of H_2 on ceria substrates, which is common to the different low Miller index surfaces of ceria[44], the correlation between abundance of Ce^{3+} centers and WGS-activity suggests that high concentrations of the former may facilitate the formation of H_2. This would not be surprising, since very reduced (oxidized) cerium oxide substrates are expected to more (less) favorably provide the electrons required for reducing 2 H+ to H_2. Indeed, the more facile formation of H_2 on reduced ceria substrates is clearly reflected on the calculated energy diagrams (Figure 4) for equivalent WGS mechanisms taking place on (1 0 0) ceria. Given their stability, the calculated mechanisms take place in the presence of flat-lying carbonate species. The subsequent adsorption of H_2O and another CO molecule take place on sites not occupied by $[CO_3]^{2<M->}$ species. In particular, the proposed mechanism (Figure 4) begins with the adsorption of H_2O on the under-coordinated Ce atoms of the CeO_2 (1 0 0) surface (Figure 4C). This is followed by the dissociation of an O<C->H bond (Figure 4D), giving rise to OH and H bound to the under-coordinated Ce and to one of the neighboring O atoms, respectively. Another CO molecule then adsorbs (Figure 4E) before reacting with the OH group to form COOH (Figure 4F). The transfer of H from the COOH molecule to another nearby lattice O is a very exothermic process, which gives rise to weakly bound CO_2 (Figure 4G) that can easily desorb. The last step corresponds to the reduction of 2 H+ to H_2, which is significantly less endothermic in the presence of the surface carbonate (1.50 eV, Figure 4, black lines) than for the bare surface (2.82 eV, Figure S5(B)). The carbonate species thus facilitate H_2 formation by reducing the surface and occupying sites where the H^+ species are more strongly bound. Moreover, H_2 evolution is further facilitated when the mechanism takes place on a further reduced ceria substrate, i.e. with a larger H^+ coverage. In particular, the presence of a pre-adsorbed H atom, which reduces another Ce^{4+} to Ce^{3+}, notably affects the steps involving electron transfer between the ceria surface and the adsorbates, and further reduces the energy required for forming H_2 to 1.13 eV (Figure 4, red lines). This evidences the general behavior of ceria beyond the suggested mechanism and shows how the reaction energy of redox steps on ceria-based catalysts, and by extension, the activity of the latter, can be tuned by controlling the oxidation state of ceria.

Combining the experimental and theoretical investigations leads us to obtain a mechanistic view of the water-gas shift over nanocrystalline ceria. The abundance of (1 0 0) faces adsorbed with carbonates and the higher coverage of adsorbed H atoms results in highly reduced ceria, which allows for more facile reduction of 2 H^+ to H_2. We have demonstrated the association of reduced Ce^{3+} centers with observed activity by multiple techniques, and presented a novel ceria catalyst with favorable physicochemical properties for supporting a high density of active sites for the reaction. The implications for this study extends to ceria catalysis in a wide range of applications, suggesting that with careful control of catalyst structure, function can be tuned with great applicability in relevant energy applications. The development of catalysts of suitable composition and activity for the water-gas shift reaction could serve to improve its usage in fuel cell catalysis and other relevant fields.

Experimental Section

For experimental details and methodologies please see the Supporting Information.

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Figure 1 Kinetics and microscopy studies. A) Arrhenius plot for water-gas shift on commercial ceria and nanocrystalline ceria pre-calcined at 350, 450, and 550 °C. The reactor conditions were 5 % CO/3 % H_2O/He with GHSV=45 000 $\mathrm{h}^{<M->1}$. B) SEM image of nanocrystalline ceria calcined at 450 °C. C) HR-TEM of nanocrystals showing octahedral shape oriented along {1 1 0}. D) HR-TEM of nanocrystals showing (1 1 1) and (1 0 0) faces. Several step defects are indicated with arrows.

Figure 2 A) In situ time-resolved X-Ray Diffraction of nanocrystalline ceria during heating to 400 °C under WGS reagents (5 % CO/3 % H_2O) B) Lattice parameter of ceria derived from Figure 2 (A). C) In situ Raman spectroscopy of nanocrystalline ceria showing T2g transition up to 225 °C. D) In situ XAS showing reduction of ceria. Ce^{4+} and Ce^{3+} standards are given for reference.

Figure 3 In situ DRIFTS experiment under WGS conditions over nanocrystalline ceria. The range of 3000 to 2700 $\mathrm{cm}^{<M->1}$ correlates to monodentate and bidentate formate species on the catalyst surface, while the range from 900 to 800 $\mathrm{cm}^{<M->1}$ presents evidence of carbonate formation in tandem with observed WGS activity.

Figure 4 Calculated energy diagrams and structures for a WGS mechanism taking place in the presence of an adsorbed carbonate on the (1 0 0) surface. The degree of reduction of the ceria surface influences the binding energies of the reactants, especially for redox steps involving electron transfer between adsorbates and the ceria surface. This indicates that more reduced ceria surfaces bind H reagents more weakly, allowing for more facile formation of H_2. Red, beige, grey, and white atoms correspond to outermost O, Ce, C, and H, respectively. Dark red and dark beige correspond to subsurface O and subsurface Ce, respectively. The unit cell and the position of the pre-adsorbed H atom are indicated in panel (a) by dashed lines and a blue *x*, respectively.