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Combined DFT and *operando* Spectroscopic Study of the Water-Gas Shift Reaction over Ceria-Based Catalysts: The Role of the Noble Metal and Ceria Faceting †

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Abstract: Ceria loaded with noble metals (Cu, Au) is a highly active material for the low-temperature water-gas shift reaction (LT-WGSR), but nevertheless details of the metal-support interaction as well as the role of the ceria surface termination and the metal loading are still unclear. Using *operando* Raman and UV/Vis spectroscopy combined with theoretical DFT calculations, we aim at a molecular-level understanding of LT-WGSR catalysts. In particular, by using this combined approach, we are able to draw conclusions about the reducibility state of the ceria support during reaction conditions. Our results show that the defect formation energy of the support does not play a major role for the WGSR, but rather other reaction steps like the dissociation of water or the desorption of CO_2.

Keywords: ceria; supported metals; surface termination; water-gas shift; *operando* spectroscopy; density functional theory

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1. Introduction

In the low-temperature (<200 °C) water-gas shift reaction (LT-WGSR), which is important to increase the amount of hydrogen and reduce that of carbon monoxide in fuel cell applications, supported metals like gold or copper on active supports such as ceria have been proven to be good alternatives to the conventional copper-zinc oxide catalysts used in industry.[1–4] According to the current state of research, the role of the metal and the ceria faceting during reaction remain unclear [3,5,6]. In our previous studies we could already demonstrate that for polycrystalline Au/CeO_2(111) catalysts, surface and bulk oxygen is involved in the reaction mechanism.[4] Thus, these results are consistent with a previously proposed and discussed redox mechanism [7–9]. In a very recent study, we evaluated the influence of the surface termination of Au/CeO_2 catalysts, and could show that CeO_2(111) is best suited for LT-WGSR [6].

In this study we address gold and copper loaded ceria polyhedra and sheets as well as cubes with CeO_2(111) and CeO_2(100) surface terminations, respectively, to gain new insight into the structural dynamics during reaction and the associated significance of the metal and surface termination. For this purpose, we apply an *operando*-spectroscopic approach, which combines Raman and UV/Vis spectroscopy. In addition, density functional theory (DFT) is used to calculate the vibrational frequencies, Raman activities and adsorption energies of possible reaction intermediates.

2. Methods

Ceria cubes were prepared by hydrothermal synthesis (for details see Ref. [10]), ceria polyhedra were obtained commercially (Sigma Aldrich, <25 nm (BET)), and ceria sheets were synthesized by thermal decomposition of $Ce(NO_3)_3 \cdot 6H_2O$ at 600 °C (for details see Ref. [4]). The gold loading was realized by means of an electrolyte deposition, which is described in more detail in Ref. [10]. Copper was loaded by incipient wetness impregnation using $Cu(NO_3)_2 \cdot 3H_2O$ as precursor and calcination at 500 °C. The target for all metal loadings was 0.5 wt% Au or Cu, respectively.

Operando Raman (532 nm) and UV/Vis spectra in combination with activity measurements using gas-phase FT-IR spectroscopy were recorded using an experimental setup that has been described previously.[4,6,10–12] All measurements were carried out at approx. 130 °C at the sample. Before reaction conditions (2% CO and 8% H_2O balanced in Ar) the sample was heated at the same temperature for about 1 h in Ar. After applying reaction conditions, CO is switched off and 8% water is passed over the sample. The total flow rate was always 100 mL/min.

3. Results and Discussion

Figure 1 shows the catalytic activities of various CeO_2-based catalysts loaded with 0.5 wt% gold or copper. Comparison of the copper and gold catalysts shows that all gold loaded ones have a higher catalytic activity. It is worth mentioning that samples without noble metal loading do not show any conversion of CO. Furthermore, the Au-sheets show the highest activity; likewise, among the copper catalysts the sheets are the most active, although the polyhedra also possess a $CeO_2(111)$ termination. In this context, comparison of the polyhedra and sheets shows that it is not only the surface termination of the support that matters, but also the particle shape. To this end, our previous studies have shown the presence of steps on ceria sheets.[12] These steps may have an influence on the catalytic activity, in fact earlier theoretical studies have demonstrated the increased activity of a stepped $CeO_2(111)$ facet during CO oxidation.[13] These results underline that beside the metal and the metal support interaction, also the support properties may have a strong influence on the reaction process.

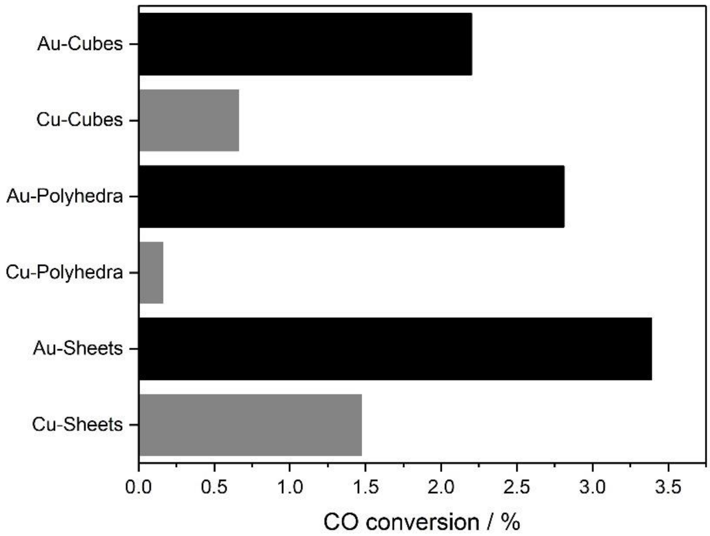
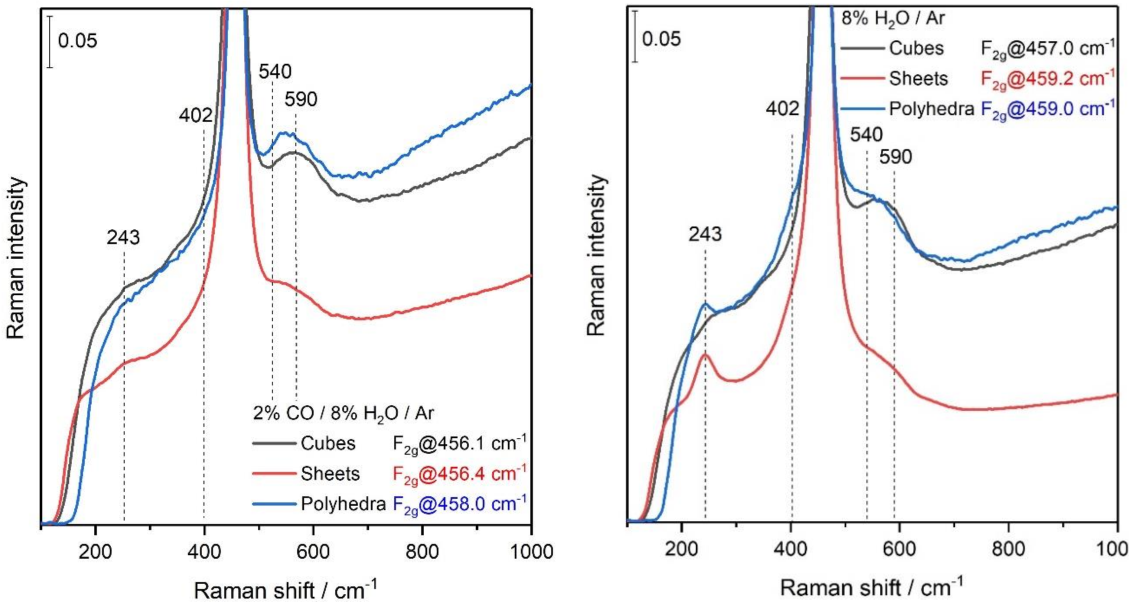


Figure 1. CO conversions (in %) during LT-WGS reaction of gold (black) and copper (grey) loaded (0.5 wt%) ceria catalysts with different morphologies. The catalytic activity was measured after at least 1 h on stream at about 130 °C under 2% CO and 8 % H_2O balanced in Ar (total flow: 100 mL/min).

In order to better understand these catalytic activities, we will now take a closer look at the Au/CeO_2 catalysts using Raman spectroscopy, since these are expected to show larger variations in their properties due to their higher catalytic activities as compared to the copper samples. To this end, Figure 2a depicts Raman spectra of the gold loaded cubes, sheets, and polyhedra during WGSR conditions, while Figure 2b shows their spectra immediately after reaction conditions in an 8 % H_2O stream. All samples show red-shifts of the F_{2g} band, which is a measure for near-surface oxygen defects [14], when switching from Ar atmosphere to reaction conditions (not shown). The observed red-shift is highest for the sheets (3.2 cm^{-1}), followed by the polyhedra (1.7 cm^{-1}) and the cubes (1.2 cm^{-1}), which correlates with the catalytic activity, i.e., sheets show the highest activity etc. This is also consistent with the UV/Vis results (not shown), which are characterized by an increase in absorption in the range above 450 nm ($Ce^{3+} \rightarrow Ce^{4+}$ charge transfer transitions)[12], when switching to reaction conditions, and an decrease under 8% H_2O after reaction conditions. However, the reduction of the support (see F_{2g} shifts and UV/Vis results) is not consistent with the oxygen defect formation energies, which is lowest on the CeO_2(100) facet.[15] These mentioned significant differences between sheets and polyhedra despite the same surface termination must be related to the presence of a stepped CeO_2(111) surface on the sheets. Hence, the defect formation energy of the support is not decisive for a high catalytic activity, but rather other factors such as the dissociation of water or the desorption of CO_2. In this context, previous studies have already shown that water dissociation is the rate-limiting step for Cu/CeO_2 catalysts during LT-WGSR [16] and that a stepped CeO_2(111) surface can reduce the CO_2 desorption energy [13]. Based on these observations, the above results are consistent with a redox mechanism that was confirmed in our previous studies [4]. In addition to the shift of the F_{2g} band, changes in the longitudinal and transversal surface modes of CeO_2(111) at 243 cm^{-1} and 402 cm^{-1} [14] disappear almost completely under WGSR conditions and reappear after switching to 8% H_2O for sheets and polyhedra. This can be explained by the removal of lattice oxygen under reaction conditions, thereby creating oxygen vacancies, which can be filled in the presence of H_2O and in the absence of CO. Furthermore, changes in the defect bands (540 and 590 cm^{-1}) are observed, which decrease again after switching from reaction conditions to 8% H_2O, which is also consistent with a blue-shift of the F_{2g} band.



(**a**) (**b**)

Figure 2. (**a**) *Operando* Raman spectra (532 nm) of ceria cubes (black), sheets (red), and polyhedra (blue) during WGSR conditions (2% CO / 8% H_2O/Ar) and at a total flow rate of 100 mL/min. (**b**) *In situ* Raman spectra (532 nm) of ceria cubes (black), sheets (red), and polyhedra (blue) in 8% H_2O balanced in Ar after WGSR conditions (total flow: 100 mL/min).

4. Conclusions

In summary, based on the above data, CeO_2 catalysts loaded with gold are more suitable for LT-WGSR than those loaded with copper. Furthermore, using a ceria support with a stepped CeO_2(111) facet yields the best catalytic performance. *Operando* Raman spectra are consistent with a redox mechanism involving lattice oxygen and therefore a Mars-van-Krevelen type mechanism. By examining different ceria facets, we could show that a low defect formation energy is not sufficient for high catalytic activities and that rather other aspects such as the water dissociation, the desorption of CO_2 or the metal-support interaction play a major role. In conclusion, the combination of *operando* Raman and UV/Vis spectroscopy is a powerful tool for studying LT-WGSR over different metal ceria catalysts.

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Conflicts of Interest: The authors declare no conflict of interest.

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