

# NANOSTRUCTURING MIXED CE/LA OXIDES FOR WATER-GAS-SHIFT CATALYSIS

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## Summary

Recent advances in materials chemistry allow for unprecedented control over reactive properties of materials via controlling size, shape, and composition. Here, we are demonstrating this exceptional control for pure and mixed Ce- and La-oxides for the Water-Gas Shift reaction. Pure and mixed CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> nanoparticles and nanorods were prepared via reverse microemulsion-templating and a hydrothermal synthesis route. In this way, we were able to fine-tune the reducibility of the oxides through simultaneous control of composition and structure. After embedding Au nanoparticles, we obtain excellent WGS catalysts, whose activity can be directly correlated with the properties of the supporting oxides.

## Keywords

Water-gas shift, hydrogen production, nanostructured catalysts, metal oxides

## Introduction

The water-gas shift (WGS) reaction is one of the most fundamental reactions for both fossil and renewable fuel processing in the current industry, and current efforts towards a 'hydrogen-base economy' will only further increase the importance of this reaction. However, current commercial catalysts, such as Cu-based catalysts, suffer from several disadvantages such as pyrophoricity and the requirement of careful pre-activation. In recent years, gold on ceria and other oxides has been investigated as the alternative to the WGS commercial catalysts<sup>1, 2</sup>. Unlike other, inert, oxide support, ceria is known to play an active role in the reaction. The redox processes of Ce<sup>4+</sup>/Ce<sup>3+</sup> couple enable the release and uptake of oxygen, which is supplied to CO oxidation<sup>3</sup>. Recent studies showed that the activity of CeO<sub>2</sub> is shape-dependent or structure sensitive<sup>4, 5</sup>. However, very little is known about the shape-dependence of mixed ceria and other oxides. For example, mixed lanthana/ceria have been very little studied to-date, in spite of the well-known capability of that La<sup>3+</sup> cations to introduce oxygen vacancies into the ceria lattice and thus enhance the reducibility of CeO<sub>2</sub>.

In the present work, we employ different synthesis methods to prepare pure and mixed oxides, and demonstrate how nanoscale control of composition and morphology allows to tailor activity of these mixed oxides in WGS.

## Experimental Section

Ceria and mixed lanthana-ceria were prepared by two different methods, reverse microemulsion templating and a hydrothermal synthesis path. Au was added via deposition-precipitation. The materials were characterized via X-ray powder diffraction (XRD), transmission electron microscopy (TEM and HRTEM), nitrogen sorption (BET & BJH for total surface area and pore size distribution), and temperature-programmed reduction (TPR). Catalytic tests for water-gas-shift were carried out in a fixed bed reactor.

## Results

Ceria and mixed lanthanum cerium oxides nanoparticles were prepared by a reverse-microemulsion templating approach, which allows for fine control of synthesis conditions and hence highly homogeneous mixed oxide nanoparticles. The XRD patterns of pure and mixed oxides after calcination at 750 °C are shown in fig.1. It is noticed that the mixed lanthanum cerium oxides (fig. 1 (b)-(f)) all show the cubic crystalline structure of pure CeO<sub>2</sub> (fig. 1 (a)). No indication for the formation of a second phase can be found, suggesting formation of homogenous La<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub> solid-solution. This is further supported by the continuous shift of the X-ray diffraction peaks as a

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function of lanthanum content, which indicates a continuous increase in the lattice parameter due to the embedding of the larger lanthanum cations into the  $\text{CeO}_2$  lattice. The peak broadening further indicates that the La-doping also results in a decrease in particle size (since HRTEM shows that the samples are still highly crystalline).

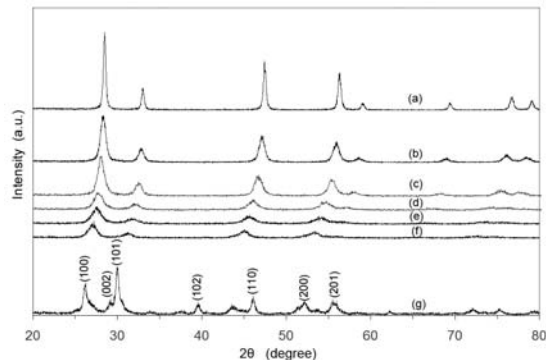


Fig. 1 XRD of  $\text{La}_x\text{Ce}_{1-x}\text{O}_{2-x/2}$  calcined at  $750^\circ\text{C}$  with La content (a) =0%; (b) =0.1; (c) =0.2; (d) =0.25; (e) =0.5; (f) =0.75; (g) =0.9; (h) =1.

The compositional tailoring of these metal oxides not only affects particle size and lattice parameter, but also significantly changes catalytic activity. Fig. 2 shows the WGS activity of a pure and a mixed oxide after addition of Au. While the Au-Ce $2\text{O}$  nanoparticle (“NP”) catalyst shows fairly poor activity (black squares), addition of 25at% La in the Au-La $_{0.25}$ Ce $_{0.75}$ O $_x$  catalyst (blue diamonds) strongly increases activity, reaching comparable activity with a commercial Cu-based low-T WGS catalyst. A systematic series of experiments (not shown here) allows to demonstrate a direct correlation between the reducibility of the oxides, tailored via La doping and quantified via TPR, and WGS activity of the respective Au-based catalyst.

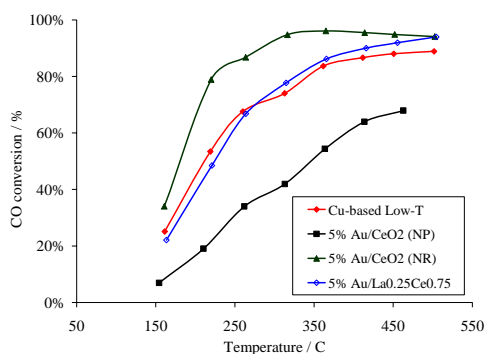


Fig. 2 Catalytic activity of gold on ceria nanoparticles, lanthana-ceria nanoparticles, and ceria nanorods in comparison to a commercial Cu-based low-temperature WGS catalyst

Beyond composition, the morphology of the oxide support also affects the activity of the catalysts. Ceria nanorods were prepared by a hydrothermal synthesis route, which enables good control of morphology. Ceria nanorods with a width of 10-20 nm and a length of 50-200 nm were synthesized (see TEM in fig. 3 (a)). After addition of Au, the activity of ceria nanorod-based catalysts shows a strong improvement over the commercial Cu- and the

nanoparticle Au-catalysts (see fig. 2, black triangles). The outstanding activity of the nanorod-based catalysts is attributed to the different crystal planes exposed to the reactants: Ceria nanoparticles expose mostly {111} surfaces, which are thermodynamically most stable. High-resolution TEM (fig. 3 (b)) shows that ceria nanorods expose mostly {110} surfaces which are less stable, but much more active.

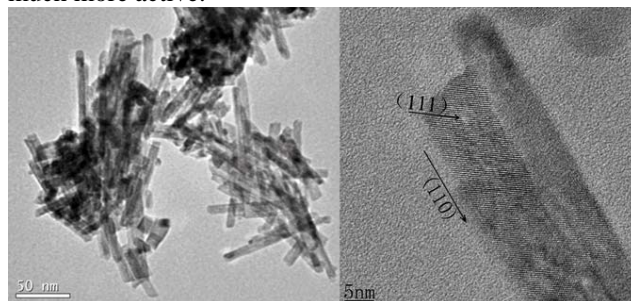


Fig.3. TEM (a) and HRTEM (b) image of ceria nanorods

## Conclusion

In summary, we have prepared water-gas shift catalysts based on ceria and mixed lanthana-ceria. By tailoring the composition and morphology of the oxides supports, we can significantly improve the WGS activity. These changes in activity can be directly correlated with the change in reducibility of the oxides upon La-doping and change in morphology. We are currently extending the presented work onto the simultaneous control of composition and morphology via synthesis of mixed lanthana-ceria nanorods.

## References

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