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Flame made ceria supported noble metal catalysts for efficient H$_2$ production via the water gas shift reaction

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Abstract. *Rh/ceria catalysts were synthesized by flame spray pyrolysis for high temperature water gas shift (WGS) reactions. These catalysts show a high specific surface area due to a high degree of nanocrystallinity. X-ray absorption spectroscopy (XAS) unraveled the formation of small Rh particles under WGS reaction conditions. The catalytic activity was examined at atmospheric pressure by measuring CO conversion as a function of temperature. Some methane formation was observed above 310 °C.*

1. Introduction

Hydrogen is a feedstock used for diverse industrial applications, but also a clean fuel for fuel cells and a key element for chemical storage of renewable energy. The WGS reaction is important for hydrogen production and purification and an essential step in many industrial processes. In industry, different catalysts and reaction conditions are applied for this reaction [1].

Hydrogen production over commercial (copper and ferrochrome) catalysts requires two reaction stages for WGS, which need a large volume reactor. Due to their volume, long treatment time, limited durability and susceptibility to reaction conditions, industrial copper (low temperature) and ferrochrome (high temperature) WGS catalysts are not suitable for one stage reactions and fuel cell applications [1, 2]. Furthermore, conventional WGS catalysts are pyrophorous, require time-consuming reduction, and they are sensitive to sulfur and chloride poisoning. In recent years noble metals (mainly Pt, Au and Pd) supported on reducible oxides (ceria, zirconia, titania) have been extensively studied as promising catalysts for high temperature WGS reactions [2, 3]. These catalysts should exhibit high stability, activity and poisoning resistance and convert CO at a single stage at high temperature [2, 4]. Rather little is known about Rh-based catalysts up to now. For this study, Rh/CeO$_2$ catalysts were prepared by flame spray pyrolysis and characterized during WGS by X-ray absorption spectroscopy.

2. Experimental

X-ray Absorption Near Edge Structure (XANES) and Extended X-ray Absorption Fine Structure (EXAFS) measurements at the Rh K-edge (23220 eV) were performed at BM25 (the Spanish CRG Beamline) at the European Synchrotron Radiation Facility (ESRF, Grenoble, France) in transmission mode using a Si(111) double crystal monochromator and ionization chambers.

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4.3 wt.% Rh/CeO_2 catalysts were prepared by flame spray pyrolysis (FSP) [5], using solutions of the corresponding initial precursor in xylene (VWR chemicals). Precursor solutions were prepared by dissolving specified amounts of metal acetylacetonate $(Rh(acac)_3$, 99% (25% Rh), abcr GmBH & Co. KG), and cerium (III) 2-ethylhexanoate 49% 2-ethylhexanoic acid (12%Ce, Alfa Aesar). The concentration of the noble metal precursor was 1 mol/L. At first, X-ray diffraction (XRD) patterns of the catalysts were recorded in a 2Θ range of 10°–90° (2 s/step, step size 0.016°) using Cu K_α radiation (λ=0.15406 nm), a nickel filter and a graphite monochromator (D8 Advance Diffractometer by Bruker). For *in situ* XAS measurements, a 100–200 µm sieve fraction of the catalyst was filled into a quartz glass capillary (outer diameter 1.5 mm, wall thickness 20 µm) between quartz wool plugs. The capillary was placed on top of a gas blower (FMB Oxford). First the catalysts were characterized by *in situ* temperature programmed reduction (TPR) during heating from room temperature to 450 °C at 5 °C/min in 5% H_2/He (flow 50 mL/min) while recording XANES spectra in Quick-EXAFS mode (recorded at SNBL/ESRF).

Table 1. 4.3 wt.% Rh/CeO_2 in capillary at BM25 beamline at ESRF.
EXAFS spectra were recorded at each gas atmosphere and temperature.

RT	200 °C	300 °C	400 °C	RT
He	CO	$CO + H_2O$	$CO + H_2O$	CO
CO	H_2O			He
	$CO + H_2O$			

Most importantly, the effect of different feed gas compositions and temperature on the catalyst structure was investigated (Table 1). The first series of XAS spectra were recorded at room temperature, first under He, then in 8% CO/He. Afterwards the capillary reactor was heated to 200 °C in 8% CO/He. Further series of XAS spectra were recorded at 200 °C in 8% CO/He, 12% H_2O/He, and CO/H_2O (8% CO, 12% H_2O and 80% He), respectively. Afterwards the capillary reactor was heated to 300 °C and 400 °C in the WGS gas mixture. Finally the reactor was cooled to room temperature and further XAS spectra were recorded. Absorption data were analyzed using the IFEFFIT software package [6].

3. Results and Discussion

The X-ray diffraction pattern of the 4.3 wt.% Rh/CeO_2 catalyst, shown in Figure 1(a), corresponds to crystalline CeO_2 in fluorite phase. At 2θ = 41.1° a reflection matching the Rh(111) plane appears. However, it is rather broad, and so weak in intensity that it can hardly be distinguished from the background. Further analysis of ceria reflections at 2θ = 28.6° and 33.0° using the Scherrer equation [7] unraveled CeO_2 crystallite sizes of 7.5 nm and 6.3 nm, respectively.
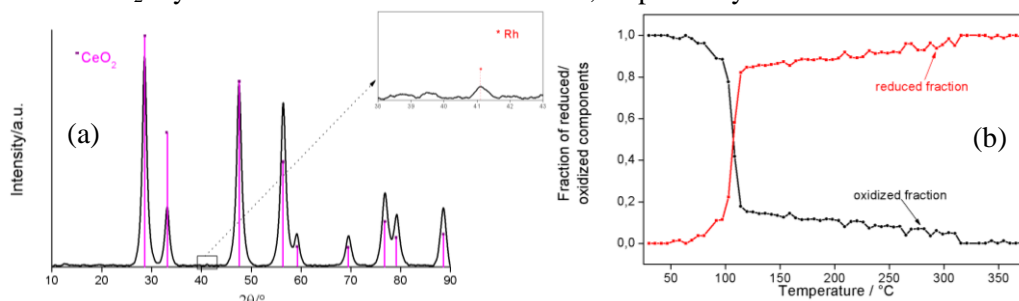

Figure 1. (a) XRD pattern of flame made 4.3 wt.% Rh/CeO_2 with characteristic ceria reflections (2θ = 28.6°, 33.0°, 47.5°, 56.5°, 59.1°) and an extremely weak Rh peak (2θ = 41.1°). (b) Linear combination fitting results of Rh K-edge XANES spectra recorded during TPR, revealing changes in relative concentrations of oxidized and reduced Rh species.

The specific surface area, determined by BET, amounted to 142 m^2g^{-1}, in line with the smaller crystallite size of the support compared to two previously investigated flame made 1.9 wt.% and

3.1wt.% Rh/CeO_2 catalysts with crystallite sizes of 11 and 17 nm (reflection at $2\theta = 28.6°$) and surface areas of 125 and 105 m^2g^{-1}, respectively. Next the catalyst was reduced during TPR. The relative concentrations of oxidized and reduced Rh species, determined by linear combination fitting using the initial and final spectrum of the TPR series as reference spectra, are shown in Figure 1(b). The results show that the 4.3 wt.% Rh/CeO_2 catalyst is reduced at ca. 114 °C. A previously characterized flame made 3.1 wt.% Rh/CeO_2 catalyst was completely reduced at 75 °C [8]. These results show that Rh in contrast to Pt [9] is reduced at rather low temperature.

Figure 2 (a) shows normalized Rh K-edge XANES spectra of the 4.3 wt.% Rh/CeO_2 catalyst in different gas atmospheres and at different temperature. At room temperature under He and in CO the catalyst is obviously in an oxidized state. The decrease in white line intensity after *in situ* reaction at higher temperature and in different reaction gas mixtures indicates reduction of the catalyst.
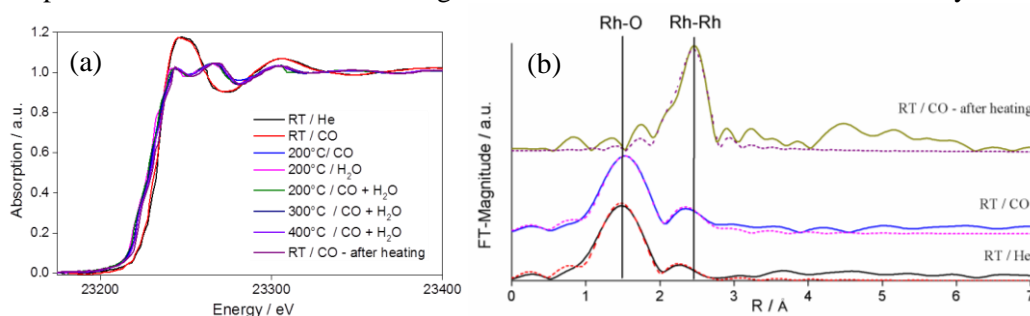

Figure 2. (a) Rh K-edge XANES spectra of the 4.3 wt.% Rh/CeO_2 catalyst recorded at room temperature under He and in 8% CO/He, at 200 °C in 8% CO/He and in 12% H_2O/He, and in CO + H_2O (8% CO, 12% H_2O, 80% He) at 200 °C, 300 °C and 400 °C. (b) k^3–weighted Fourier transformed EXAFS data of the catalyst at room temperature under He and in CO, and at room temperature in CO after the WGS reaction (solid lines) and fitting results (dashed lines).

Structural parameters were derived from fitting the k^3–weighted Fourier transformed EXAFS data in R-space. Representative spectra and the corresponding fits are shown in Figure 2(b). The chemical environment of Rh at room temperature under He and in CO is similar; the absorber atoms are surrounded by ca. 6 oxygen atoms at 2.01 Å, similar to the first coordination sphere (Rh – O) in Rh_2O_3. At a larger distance (ca. 2.2 Å in Figure 2(b)) the contribution of a second shell is observed, but this peak is so weak that the coordination number cannot be extracted. After *in situ* WGS reaction the contribution of the Rh – O shell disappears and a Rh – Rh shell clearly dominates. The Rh absorbers are now coordinated by ca. 4 neighboring Rh atoms at 2.71 Å. This low coordination number compared to the coordination number in bulk state (12) indicates a very small Rh particle size, probably due to disruption of the particles, e.g. by Rh carbonyl formation. A similar effect was observed by Grunwaldt et al. [10] for Rh/Al_2O_3 catalysts for catalytic partial oxidation of methane. Obviously at higher temperature Rh is reduced to metallic Rh, in accordance with the XANES results (Figure 2(a)). At higher temperature EXAFS analysis was not possible due to the high noise level.

Catalytic activity measurements were performed at atmospheric pressure with a space velocity of 150,000 ml/g h^{-1} for 10.5 wt% Rh/CeO_2 (R1) and 50,000 ml/g h^{-1} for 10.5 wt% Rh/CeO_2 (R2,R3 and R4) and for 4.3 wt% Rh/CeO_2 (R4 and R5). The H_2O/CO ratio was also varied from 1.5 (R1, R2 and R4) to 4 (R3 and R5). Figure 3 shows the effect of the space velocity on the conversion of CO. With a H_2O/CO ratio of 1.5 feed the CO conversion is ca. 77% at 330 °C and 92% at 350 °C at a space velocity of 150,000 ml/g h^{-1}, whereas 50,000 ml/g h^{-1} leads to ca. 93% at 330 °C and 97% at 350 °C. The H_2O/CO ratios as well as the partial pressures affect the CO conversion. For 10.5 wt.% Rh/CeO_2 CO conversion increased from 15.2% to 26.8%, for 4.3 wt.% Rh/CeO_2 from 17.6% to 28.3% at 250°C at a space velocity of 50,000 ml/g h^{-1}. The thermodynamic WGS equilibrium was calculated using the Gaseq program [11] and is at 350 °C 92.9% for a S/C ratio of 1.5, and 98.5% for a S/C ratio of 4. Obviously, both catalysts show high activity at high temperature and reach almost equilibrium concentrations, which can be circumvented using membrane reactors [12]. A disadvantage of Rh/CeO_2

is the formation of methane (CH_4) starting at 310 °C, which has been previously reported [13]. CH_4 selectivity (S_{CH4}) was calculated by relating the outlet CH_4 concentration to the total outlet concentration of carbon containing species [8]. Note that with increasing Rh loading the conversion to CH_4 increases.
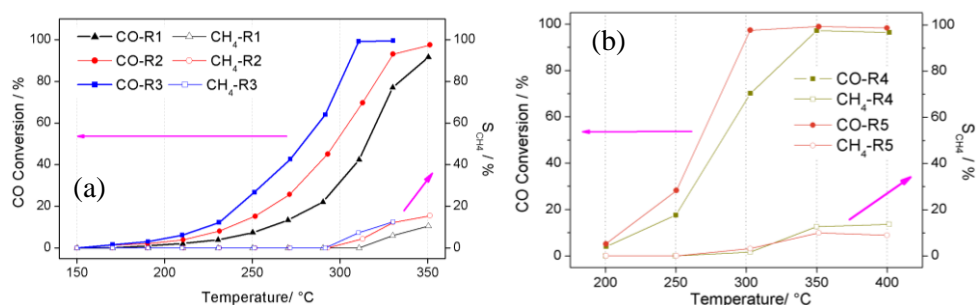

Figure 3. Effect of temperature and H_2O/CO ratio on CO conversion over a 10.5 wt.% Rh/CeO_2 catalyst (a) and a 4.3 wt.% Rh/CeO_2 catalyst (b). For R1, R2 and R4 the H_2O/CO ratio is 1.5, and for R3 and R5 the ratio is 4.

4. Conclusion

Nanocrystalline Rh/CeO_2 catalysts with high surface area were prepared in one step by flame spray pyrolysis. *In situ* XAS studies combined with linear combination fitting of the XANES data recorded during TPR showed that the flame made 4.3 wt.% Rh/CeO_2 catalyst was reduced at rather low temperature (114 °C). Moreover, EXAFS analysis uncovered rather small Rh particles after *in situ* WGS reaction (coordination number around 4), probably forming mobile Rh carbonyl species under reaction conditions. FSP made catalysts are promising candidates for high temperature WGS reactions in membrane reactors.

5. Acknowledgement

6. References

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