

# Evidence for Rh electron-deficient atoms (Rh<sup>d+</sup>) as the catalytic species for CO oxidation when supported on Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub>: a combined N<sub>2</sub>-FTIR, benzene hydrogenation and kinetic study

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## Introduction

It has been widely reported that CO oxidation was greatly promoted by the incorporation of CeO<sub>2</sub>-based oxides [1-3]. Despite Yu Yao concluded, more than 20 years ago [1], that two types of surface sites, namely zero-valent and oxidized, may be considered to explain the striking differences observed in CO-O<sub>2</sub> kinetics on CeO<sub>2</sub>-promoted supported noble metal samples compared to the non-promoted ones, few authors attributed the enhanced catalytic activity of the CeO<sub>2</sub>-promoted PGMs catalysts to the presence of oxidized species. This peculiarity may arise from the fact that in most studies both zero-valent and oxidized surfaces species co-exist on the studied catalysts and that the commonly used characterization methods usually focus on the titration of the zero-valent species only, so that the presence of the oxidized species is most often ignored. In previous studies [4], we inferred the observed differences in CO-O<sub>2</sub> kinetics of a Rh(0.29 wt%)/Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> catalyst, compared to those of a Rh/SiO<sub>2</sub> reference catalyst, to the reactivity of Rh oxidized species.

This work aims at providing additional evidence for the fact that Rh<sup>d+</sup> sites supported on CZ are the catalytic sites responsible for the enhanced CO oxidation activity of CZ-supported Rh catalysts. For this purpose, a Rh/CZ catalyst with a nominal content of Rh close to that of the material studied previously [4] was synthesized (Rh(0.32)/CZ) which, however, exhibits a greater fraction of Rh<sup>0</sup> sites than Rh(0.29)/CZ. Both of these catalysts were characterized through the benzene hydrogenation model reaction and adsorption of N<sub>2</sub> followed by FTIR (N<sub>2</sub>-FTIR). These techniques allowed characterization of the Rh<sup>0</sup> sites, whereas N<sub>2</sub>-FTIR also allows to reveal the presence of Rh<sup>d+</sup> species. Finally, CO-O<sub>2</sub> transient experiments and steady-state kinetics were performed on the newly synthesized catalyst and compared to those obtained previously on Rh(0.29)/CZ [4].

## Materials and Methods

Two Rh/CZ catalysts (0.29 [4] or 0.32 wt% Rh) were prepared by anionic exchange from an acidic solution of RhCl<sub>3</sub> · 3 H<sub>2</sub>O (Johnson Matthey) with ceria-zirconia (Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub>: CZ, ~ 200 m<sup>2</sup> g<sup>-1</sup>, Rhodia). It is worthwhile to note that Rh(0.29)/CZ was synthesized from the uncalcined CZ support, whereas the CZ support was calcined under air at 500 °C for 2 h prior to synthesis of Rh(0.32)/CZ. Experimental procedures used for benzene hydrogenation, N<sub>2</sub>-FTIR and catalytic CO oxidation have been described in previous studies [4,5].

## Results and Discussion

Both CO oxidation activity and kinetics are very similar on these catalysts despite the fact that Rh(0.32)/CZ exposes much more Rh<sup>0</sup> sites than Rh(0.29)/CZ, as revealed by benzene hydrogenation and N<sub>2</sub>-FTIR. This clearly indicates that the Rh<sup>0</sup> sites supported on CZ do not catalyze CO oxidation under the present experimental conditions. As the intensity of the band at 2295 cm<sup>-1</sup>, attributed to N<sub>2</sub> bonded to Rh<sup>d+</sup> centers, does not seem to vary to a

significant extent, it is likely that these electron deficient sites are the catalytic centers involved in CO oxidation. These conclusions are further supported by the fact that (i) CO oxidation requires higher temperatures on Rh<sup>0</sup>/SiO<sub>2</sub> than those on the Rh/CZ samples to achieve identical conversions [4], and (ii) the CO and O<sub>2</sub> reaction orders estimated on the Rh/CZ catalysts are clearly different from those expected for Rh<sup>0</sup> catalytic centers, -1 and +1 with respect to CO and O<sub>2</sub>, under experimental conditions for which the Rh<sup>0</sup> surface is mainly covered by CO adspecies [1,3].

The fact that the concentration of Rh<sup>d+</sup> sites remains almost constant on the low loaded Rh/CZ samples, whereas the concentration of Rh<sup>0</sup> sites increases dramatically on Rh(0.32)/CZ remains puzzling, as it seems that this increase in the concentration of Rh<sup>0</sup> sites does not occur at the expense of any other Rh species detectable through N<sub>2</sub>-FTIR or benzene hydrogenation. A likely explanation for this annoying observation on Rh(0.29)/CZ is the existence of Rh species that neither chemisorb N<sub>2</sub> nor catalyze benzene hydrogenation or CO oxidation.

Two hypotheses may be considered to account for the lack of reactivity of such Rh species of Rh(0.29)/CZ in benzene hydrogenation. First, the formed nanoparticles, in a zero-valent state (Rh<sup>0</sup>), are too small to catalyze benzene hydrogenation [6]. On the other hand, such a size effect of the CZ-supported Rh clusters does not account for the almost absence of N<sub>2</sub> chemisorption on Rh(0.29)/CZ, if one considers that the Rh nanoparticles are in their zero-valent form. In the case of very small clusters, an interaction with the support, with electron transfer from one to another may be also considered. Owing to the basic character of CZ, the electron density of these Rh clusters would be increased. The presence of negatively-charged clusters supported on ceria-related materials has hardly been considered [7]. In the case of a series of Pt/Faujasites catalysts, for which the electron density of the Pt clusters has been tailored by controlled addition of Na<sup>+</sup> or Cs<sup>+</sup>, de Mallmann and Barthomeuf demonstrated that the turnover frequency of benzene hydrogenation decreases as the basicity of the zeolite increases, and hence as the electron density of the Pt clusters increases [8]. An increase in the electron density of the studied CZ-supported Rh clusters would, thus, account for their much lower benzene hydrogenation reactivity. The preferential formation of electron-enriched Rh clusters on Rh(0.29)/CZ or of metallic clusters (Rh<sup>0</sup>) on Rh(0.32)/CZ will also be discussed.

## Significance

This study reveals that various Rh species may co-exist when supported on CZ and puts emphasis on the fact that only one, Rh<sup>d+</sup>, is active for the considered catalytic CO oxidation under our experimental conditions. These results are of the utmost importance in order to improve the catalytic performances and to limit the amount of noble metals of commercial catalysts.

## References

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