	Experiment title: Effect of zirconated ceria on the structure and performance of nanoparticulate rhodium catalysts for NO and CO removal	Experiment number: CH-2553
	Beamline: ID24	Date of experiment: from: 29-09-07 to: 01-10-07
	Shifts: 18	Local contact(s): Mark Newton
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Report:

A series of rhodium catalysts on alumina were investigated by combined rapid-scanning diffuse reflectance IR and energy dispersive XAFS spectroscopy,¹ with a gas switching regime monitored by mass spectrometry.² These catalysts comprised 4 wt% Rh/Al₂O₃ with yCe(1-y)ZrO_x as a surface functionalisation (y = 0, 0.67, 0.5 and 1). The chemisorption and desorption of CO and the oxidation of CO by O₂ and by NO were monitored. The aim was to see what effect these two reducible metals would have on the reactivity of the supported rhodium.

Examples of the results are shown in Figures 1 and 2. Under H₂ at 323 K, there is a significant increase in the mean first shell coordination number after zirconation of the alumina (from 6.6 – 7.8), implying a greater mean particle size. The effect of ceriation is rather less marked, with the values for all the ceriated samples giving Rh-Rh coordination numbers of 7.3 – 7.5. This trend is maintained under CO. At low temperatures, there is a marked reduction in the first shell coordination number, with, again, the Rh/ZrO₂/Al₂O₃ maintaining the larger mean particle size. Consistent with this is the lower uptake of CO per rhodium (Figure 2) for this catalyst. The IR spectra show that the zirconated material exhibits a variety of CO sites, including those typical of metallic rhodium as well as isolated Rh^I(CO)₂ centres. As the temperature is raised these Rh(CO)₂ sites become less intense, and are lost entirely by 573 K.

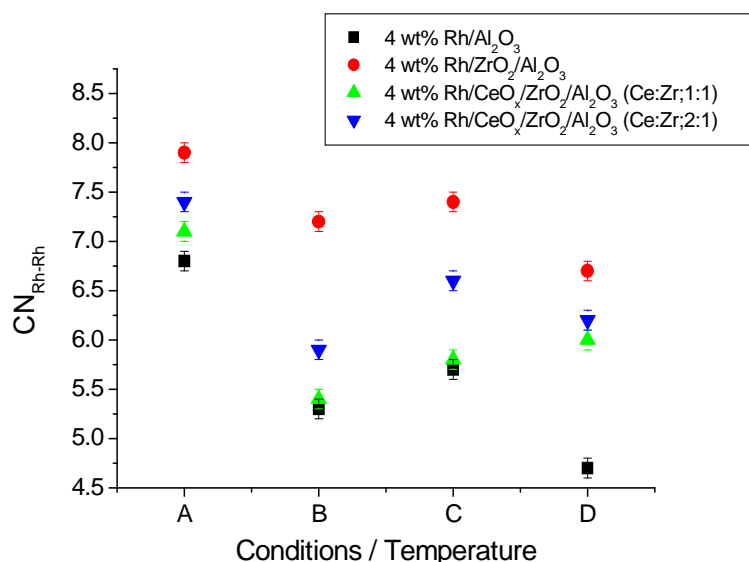


Figure 1. Variation of RhRh coordination number of 4 wt% Rh/ Al_2O_3 and Ce/Zr modified Rh catalysts under different conditions:

A: 5 % H_2/He , 323 K,

B: 5 % CO/He , 323 K,

C: 5 % CO/He , 423 K,

D: 5 % CO/He , 573 K.

These results show that the nature of the reducible oxide near supported rhodium has a significant affect on the mean particle size and the chemisorption properties of the metal sites.

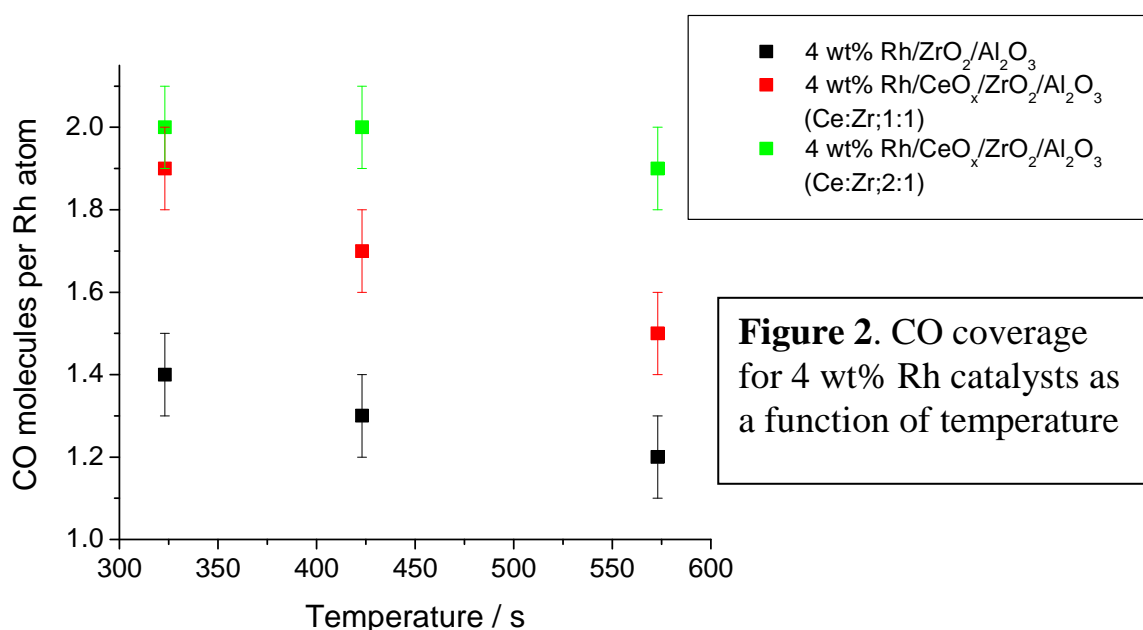


Figure 2. CO coverage for 4 wt% Rh catalysts as a function of temperature

A fuller report of these results will shortly be presented in a PhD thesis.³

We are grateful for the assistance and support of the ESRF staff in setting up these experiments.

Reference

1. Newton, M. A., Jyoti, B., Dent, A. J., Fiddy, S. G., Evans, J., *Chem Comm*, 2004, 2382-2383.
2. Dent, A.J., Evans, J., Fiddy, S.G., Jyoti, B., Newton, M.A., Tromp, M. *Angew. Chem. Int. Ed.*, 2007, **46**, 5356-5358.
3. A. B. Kroner, PhD Thesis, University of Southampton, 2008.