

Activation of Rh,Pd/CeO₂ nano-catalyst

M. Scott, G. Waterhouse, T. Söhnle

Department of Chemistry, University of Auckland, Auckland, New Zealand.

The activity of Rh,Pd/CeO₂ nano-catalyst can be understood by the metal-support interaction. X-ray analysis and junction theory of the nano-catalyst are here presented describing the onset of catalytic activity.

1. Introduction

In the implementation of the Hydrogen economy current efforts are employed at the devise of a viable Hydrogen storage technique of which water and biomass appear as most practical. Ethanol Steam Reforming has impetus as a renewable energy process of Hydrogen production for fuel cell purposes and efforts are aimed at design of an efficient catalyst. Catalyst design incorporates the necessity of ethanol decomposition with methane reforming and water gas shift reaction. Ceria supported bimetallic Rh,Pd nanoclusters exhibit high activity in ESR at the interfacial periphery. A high activity with a selectivity of 84% stoichiometric for Hydrogen can be obtained with a bimetallic 1/2%Rh,1/2%Pd/CeO₂ nanocatalyst. The activated catalyst attains a full conversion of ethanol at (11.5 mL/hr inlet; 6:1 molar ratio water:ethanol) with 150 mL/min/g_{cat} H₂ outflow[1]. Rh/CeO₂ catalysed ethanol decomposition occurs via interfacial dehydrogenation of the bridging oxametallacycle[2] and although Rhodium metal is favourable in the low energy ethanol decomposition it also exhibits unfavourable properties at steps and edges in the dissociation of CO by bridging adsorption[3]; effectively a route for methanation in the Hydrogen environment. Production of methane is rescinding the stoichiometric selectivity for Hydrogen. The discovery of the high activity of low loadings of Rh and Pd on ceria highlights a practical top down approach of nanotechnology for synthesis of an efficient catalyst. The activity of the catalyst is inherent of the synthesis technique and the reaction environment; the catalyst effectively self activates. The stability of the metal nanoclusters on the ceria is fundamental to the efficiency of the nano-catalyst and ultimately dictates the high catalytic activity by maintaining a high proportion of the active peripheral boundary. It has been shown the method of preparation plays the defining factor in the strong interaction of the metal-support interface essentially forming the active site[4,5]. The Pd/CeO₂ interaction produced by precipitation deposition using the chloride precursor is the foundation of the activity. High temperature Hydrogen reaction environment effects the reduction of metal oxide particles and formation of the bimetallic clusters[1]. The as prepared catalyst consists of distinct Pd and Rh₂O₃ clusters where XPS characterization has identified the presence of the chloride species remaining after the calcinations and persisting still after activation in steady state reaction. This indicates a reduced activity due to poisoning of active sites by the chloride ion. The role of the support contributing to the activity of this catalyst is the capacity for oxygen migration and abstraction at the peripheral interface facilitated by the redox capability and junction properties. The interfacial contact is a region of complex electronic structure consisting of various electronic fluctuations and the underlying quantum dipole pinning, an electronic equilibrium is maintained that is a combination of reduction of the support, metallic bonding, junction effects, contribution from f states and is stabilised by quantum tunnelling. The catalyst is an ideal metal support combination for ESR and the nanostructure contributes to the efficiency of the catalysis. Nano-catalyst are known to exhibit enhanced activity by higher

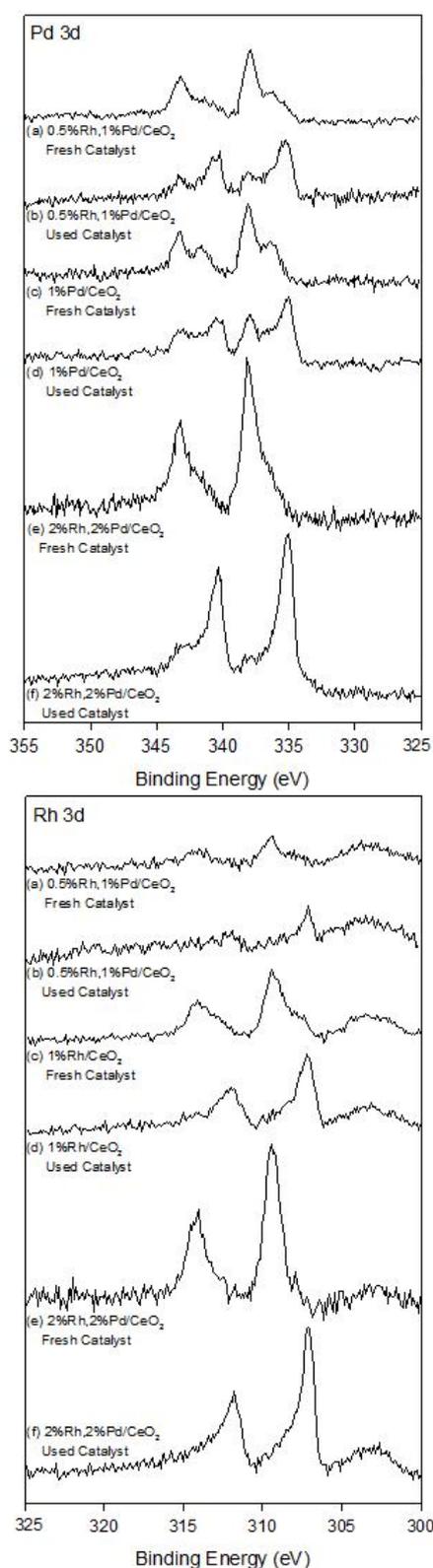


Fig. 1. Pd and Rh 3d XPS spectra for various catalysts before and after Ethanol Steam Reforming

respectively) that is characteristic for Rh metal, and also a weaker doublet at 308.2 and 313.0 eV is probably Rh_2O_3 . For Pd the intense doublet at 338.0 and 343.3 eV ($3d_{5/2}$ and $3d_{3/2}$, respectively) is likely due to PdCl_4^{2-} or a surface PdO_xCl_y species, while the weaker doublet at

surface to volume ratio and quantum confinement effects due to boundary conditions, essentially nanostructures contain higher Fermi energy.

Theoretically improved catalytic activity is achievable by overcoming the persistence of chlorine and the unwanted geometries of the Rh surface. The catalyst displays a paradox in methane oxidation activity due to undesirable processes occurring on surplus Rh sites. Manipulation of the nanostructure by applied electric field is theorised to alleviate the superfluous processes by vanquishing the unwanted active sites. Electric field induced transformation of nanoclusters from three dimensional to planar has recently been attained in a similar system[6]. Similar field induced increased wetting is known to cause deactivation in nanostructured carbon fuel cell electrodes by agglomeration of the active metal[7]. When synthesized by the precipitation deposition method or reduced in Hydrogen electric field induced effects are proposed to yield increased catalytic activity and selectivity for Hydrogen due to the stability of the Pd/CeO₂ interface[4]. A planar cluster has a huge impact on catalysis, the advantages include lower desorption of activated species; excess strain at the metal surface lowering activation energy, lower interface coordination raising activity and a significantly higher interfacial periphery. The possibility of hyper-activation by applied field is currently being investigated with the Vienna Ab-initio Simulation Package.

2. Experimental

$\frac{1}{2}\text{wt.}\% \text{Rh} \frac{1}{2}\text{wt.}\% \text{Pd/CeO}_2$ catalyst samples are prepared by the precipitation deposition method. CeO₂ was precipitated from $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ by dropwise addition of ammonia until a pH of nine was attained. The resulting white gel was filtered, washed and dried overnight at 60°C. The product was then calcined at 500°C for 6 hours. The metal chloride precursor were added in HCl then heated to evaporation, dried overnight at 60°C, then calcined at 400°C for 3 hours.

XPS measurements were performed on pellets pressed from as prepared and post-reaction powdered samples using about 300 mg in a 13mm die set. From Fig. 1. fresh catalysts show an intense doublet at 309.3 and 314.1 eV ($3d_{5/2}$ and $3d_{3/2}$, respectively) that is typical for RhCl_3 (or a surface RhO_xCl_y species), and the weaker doublet at 308.2 and 313.0 eV due to Rh_2O_3 . Used catalysts show a main doublet at 307.2 and 312.0 eV ($3d_{5/2}$ and $3d_{3/2}$, respectively) that is characteristic for Rh metal, and also a weaker doublet at 308.2 and 313.0 eV is probably Rh_2O_3 .

336.35 and 341.6 ($3d_{5/2}$ and $3d_{3/2}$, respectively) is likely due to PdO[8]. The main doublet at 335.1 and 340.3 eV ($3d_{5/2}$ and $3d_{3/2}$, respectively) is typical for Pd metal. In all cases evidence for chlorine was found in the survey spectra. Rh and Pd loadings determined by XPS are in reasonable agreement with nominal metal loadings. Atomic % chloride ion was found to be around 4% in the fresh catalysts and persist in the Pd only used catalyst, Rh only catalyst was found to lose chloride more readily (2% in the used catalyst) where in bimetallic used catalysts only 1% was detected.

For XAS measurements the as prepared catalyst was ground to fine powder and reduced in a 15 mL/min flow of H_2 at the specified temperature. Reduced catalyst samples of 150 mg were pressed in the 13mm die set without binder; 60mg BN binder was used for the 20mg reduced Rh metal standard. EDS/SEM performed at the University of Auckland was used in confirmation of the Rhodium concentration. XAS performed at the Australian Synchrotron show the behaviour of Rh over the activation period (Fig.2.). Recent studies of the Rh/ CeO_2 interaction using H_2 Temperature Programmed Reduction indicate the reduction of the Rh_2O_3 occurs at temperatures as low as 60°C[9]. In this system it is believed the metal support interaction maintains cationic Rh^{3+} until the composite cluster has formed. It has been reported at 300°C the Rh_2O_3 has diffused into the reduced Ce_2O_3 structure under Hydrogen atmosphere[9]. $CeRhO_x$ type intermetallic compounds have been identified by XPS and

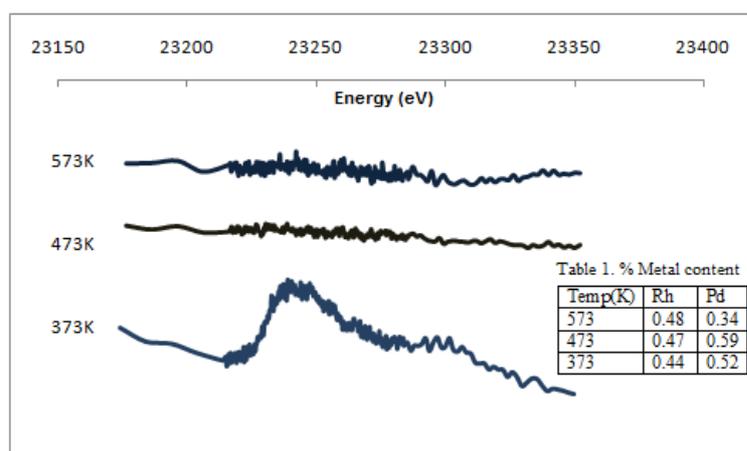


Fig. 2. XANES spectra at the Rhodium K edge of samples reduced in H_2 for 4 hours.

EXAFS[10] this type of compound is proposed to be present during the activation period. Fig. 2 confirms that on reduction at elevated temperature Rhodium sesquioxide nanoparticles dissipate over the ceria surface becoming dissolved in the support and undetectable in transmission mode. Although the metal loading is low for transmission detection higher local concentrations are detected at 373 K. The signal/noise ratio is due to sample inhomogeneity, such concentrations are more suited to fluorescence. Metal quantification by Energy Dispersive Spectroscopy (inset) shows consistency in the Rhodium content of the samples. XANES at 373 K shows a distinct Rh K edge adsorption evidencing the presence of Rh aggregates, however at higher temperatures Rh has dispersed and integrated into the support.

3. Discussion

The two metals exhibit distinct interactions with the support due to the degree of reduction of the support by the metal; Pd metal prefers d^{10} configuration whilst Rh finds stability in a full t_{2g} subshell as Rh^{3+} and as a metallic shell on Pd[1]. It is assumed chloride in the synthesis plays the role of oxidising the surface hydroxyls of the support. The Pd- CeO_2 interaction results in a Ce-Pd bimetallic bond with the d band of Pd shifted to the lanthanide; a strong interaction in conservation of d band occupancy. A Pd chloride species persists indicating an encapsulation of Cl at the Pd-Ce interface disturbing both the strength of the interface and the catalytic activity. Rh chloride species do not show the same persistence as Pd, it is believed in the migration to bimetallic clusters chloride is lost from Rh. It also appears that Rh facilitates the loss of chlorine from Pd. Altering the synthesis technique by

excluding the calcination of bare ceria should resolve the persistence of chlorine[11]. Palladium reduces the proximal cerium on contact due to lowering of the energy of freed electrons by the Schottky barrier[12,13]. The charge balance at the interface forms the Schottky barrier; the higher polycrystalline workfunction of Pd (5.22 eV) than Rh (4.98 eV) displays a higher Schottky junction barrier; additionally implying more facile oxygen abstraction and a more stable M-Ce interface. Rhodium has more oxygen neighbours in its Rh₂O₃ form than PdO and Rh³⁺ ‘dissolves’ in the oxygen rich support which at the surface is reduced to the structurally analogous Ce₂O₃. Cationic rhodium exhibits solubility in the reduced ceria surface at elevated temperature[14] and finds stability once it has migrated to its periodic neighbour Palladium. This is theorised to be due to the extra stability of the greater d band occupancy of the Pd clusters and low energy mixing of Rh and Pd. Reduced Rh metal forms a shell on the Pd clusters[1] and the greater d character of Pd influences the action of Rh at the peripheral boundary.

DFT + U calculations[13] have shown Rh doping of the ceria lattice lowers the reduction energy by up to 1.62 eV with the Metal Induced Gap States falling below the Fermi energy. For Pt the reduction energy falls by 2.03 eV and the MIGS are pinned above the Fermi energy directly facilitating electron transfer to the metal. The MIGS are reported to be formed from M4d – O2p hybridisation and in the reduced surface are occupied by electrons present in the oxygen vacancy. It is postulated the difference in Pd and Rh metal-support interaction at 273-573 K is due to RhCeO_{3-x} compound formation that displays degeneracy in the Fermi level of Rh due to contribution from the f states of Cerium thus lowering oxygen abstraction capacity. At 673 K the bimetallic clusters are formed[1].

Acknowledgements

The authors are indebted to the Australian Synchrotron.

References

- [1] Idriss H, Scott M, Llorca J, Chan S C, Chiu W, Sheng P-Y, Yee A, Blackford M A, Pas S J, Hill A J, Alamgir F M, Rettew R, Petersburg C, Senanayake S D and Barteau M A 2008 *ChemSusChem* **1** 905
- [2] Chen H, Liu S and Ho J 2006 *J. Phys. Chem. B* **110** 14816
- [3] Mavrikakis M, Baumer M, Freund H-J and Norskov J K 2002 *Cat. Lett.* **81** 153
- [4] Shen W-J, Ichihashi Y, Okumura M and Matsumura Y 2000 *Cat. Lett.* **64** 23
- [5] Zerva C and Philippopoulos C 2006 *Appl. Catal. B Env.* **67** 105
- [6] Yoon B and Landman U 2008 *Phys. Rev. Lett.* **100** 1
- [7] Vaivars G, Ndungu P and Linkov V 2007 “Catalyst Degradation in PEM Fuel Cells – Modelling Aspects”. In: *Proceedings of the COMSOL Users Conference* (Grenoble)
- [8] Moulder J F, Stickle W F, Sobul P E and Bomben K D 1992 “Handbook of X-Ray Photoelectron Spectroscopy”, Perkin-Elmer Corporation
- [9] Cai W, Wang F, Veen A C V, Provencor H, Mirodatos C and Shen W 2008 *Cat. Today* **138** 152
- [10] Gayen A, Priolkar K R, Sarode P R, Jayaram V, Hegde M S, Subbanna G N and Emura S 2004 *Chem. Mat.* **16** 2317
- [11] Mukherjee P, Patra C R, Ghosh A, Kumar R and Sastry M 2002 *Chem. Mat.* **14** 1678
- [12] Frost J C 1988 *Nature* **334** 577
- [13] Yang Z, Luo G, Lu Z, Woo T K and Hermansson K 2008 *J. Phys.* **20** 035210
- [14] Inamura S, Yamashita T, Hamada R, Saito Y, Nakao Y, Tsuda N and Kaito C 1998 *J. Mol. Cat. A* **129** 249