A practical demonstration of electronic promotion in the reduction of ceria coated PGM catalysts†

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When ceria is deposited over supported PGM catalysts its reducibility is dependent on the work function of the underlying metal.

The technological importance of ceria, CeO_2, is widely recognised, especially in three-way catalytic converters,[1] solid oxide fuel cells,[1] water gas shift catalysis[2] and CO oxidation.[3] Its widespread use as a catalyst support material is in part due to its ability to stabilise metal dispersion, but also to other effects such as its propensity to sustain a high mobility of lattice oxygen and an ability to promote the activation of water. The combination of PGMs (platinum group metals) with ceria is known to lower the ceria reduction temperature.[4] Although the precise role of the PGM in facilitating the ceria reduction is not known, two apparently alternative explanations for this phenomenon have been proposed: (i) hydrogen spillover from the PGM to the ceria surface,[5] and (ii) an electronic interaction between the PGM and the ceria.[3,6] By depositing ceria over supported PGM catalysts we have been able to demonstrate a direct correlation between PGM promotion of the ceria surface and the work function of the metal, inferring that an electronic interaction plays a crucial role in the metal–ceria interface. From our experience, this correlation is difficult to detect in simple PGM-impregnated catalysts.

1 wt% PGM catalysts were prepared by impregnation of silica or alumina with a solution of platinum (IV) nitrate, palladium (II) nitrate, rhodium (III) nitrate, ruthenium nitrosyl nitrate, silver nitrate or chloroauric acid. The PGM treated support was dried at 105 °C for 4 h and then calcined in static air at 500 °C for 2 h. This preparation method yielded typically 1–15 nm metal particles. Each PGM catalyst was coated with ceria (to a loading of 15 wt%) using a deposition precipitation technique where the ceria source was cerium (IV) nitrate in nitric acid and the precipitating base was 0.5 M aqueous sodium carbonate solution. Precipitation was performed at pH 7.5 ± 0.5 and a stirring rate of 200 rpm. The precipitate was filtered and washed until the conductivity of the washings was less than 10 μS, and then dried at 105 °C for 4 h and calcined at 500 °C for 2 h.

The catalysts were characterised using sub-ambient temperature programmed reduction (TPR) using a 10% H_2–90% N_2 gas mixture over the temperature range −25 to 900 °C. Fig. 1 shows example reduction profiles for supported and unsupported ceria and for ceria-coated Pt supported on silica and alumina. Unsupported ceria and ceria supported on PGM free silica and alumina show two reduction features, one at intermediate and one at high temperature which are attributable to surface (●) and bulk ceria (■), respectively.[4] Deposition of ceria over the PGM catalysts leads to the appearance of up to two additional peaks in the TPR profile: firstly, in some cases, a low temperature feature attributable to the reduction of the metal (+), which is closely followed by the reduction of ceria species in close proximity to the PGM (*i.e.* promoted surface ceria, ○).[7]

An intermediate temperature peak due to the reduction of surface ceria distant from the PGM (unmodified surface ceria, ●)[7–9] is also present, as well as a high temperature peak due to unmodified bulk (■) ceria being reduced to Ce_2O_3.[7,8] Table 1 shows the reduction temperatures for the promoted surface ceria feature for the Pt, Pd, Rh, Ru, Ag and Au catalysts supported on SiO_2 and Al_2O_3.

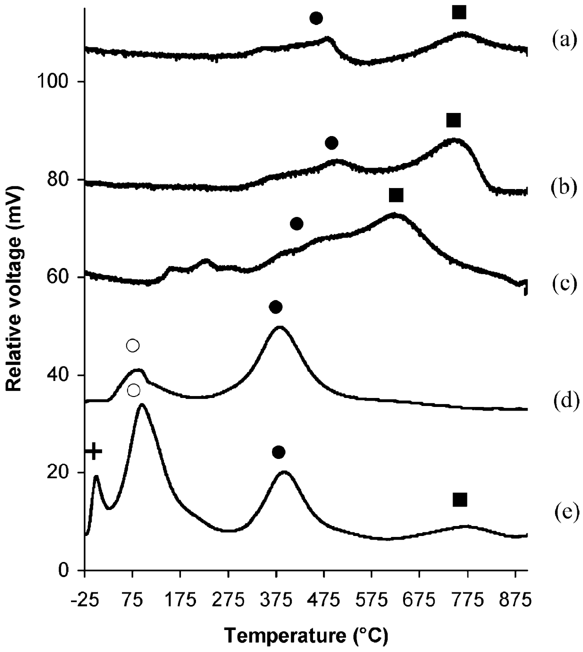

Fig. 1 TPR profiles of: (a) CeO_2, (b) 15%CeO_2/SiO_2, (c) 15%CeO_2/Al_2O_3, (d) 15%CeO_2/0.85%Pt/SiO_2, (e) 15%CeO_2/0.85%Pt/Al_2O_3. Symbols: ■ = bulk ceria, ● = surface ceria, ○ = surface ceria promoted by PGM, and + = PGM.

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Table 1 Promoted surface ceria reduction temperatures

Metal	Supported on SiO_2/°C	Supported on Al_2O_3/°C
Pt	80	110
Pd	100	140
Rh	125	200
Ru	155	220
Ag	173	200
Au	—	140

The spillover model provides a physical mechanism by which molecular hydrogen dissociation on the PGM surface generates highly mobile atomic hydrogen, which reduces the ceria by abstracting O^{2-} from its surface.[10]

In the electronic promotion model, the PGM perturbs the electronic band structure of ceria without invoking the exchange of surface chemical species. Significantly, we observe that the reduction temperature of the promoted surface ceria correlates well with the tabulated work function[11] of the bulk PGM, (Fig. 2 and Fig. 3), indicating that the fundamental mode of interaction between the PGM and the ceria is an electronic one.

Interestingly, we found the same trend for both silica and alumina supports, namely, that the reduction temperature for the promoted surface ceria is inversely proportional to the work function of the underlying PGM. Only rhodium and ruthenium supported on alumina deviate significantly from the linear relationship (Fig. 3). The known ability of both metals to interact strongly with alumina[12,13] may explain why they exert less of an effect on the reducibility of the ceria overlayer. The observed correlation between work function and reduction temperature for silica and alumina catalysts provides compelling evidence to suggest that an electronic interaction between the PGM and ceria plays an important role in facilitating the ceria reduction. Quantum size effects could be important in determining whether the PGM particles are metallic, and hence in influencing charge transfer between the ceria and the PGM. However, it might expected that this would be more important in coprecipitated PGM–ceria catalysts (which don't show the work-function correlation), where a narrow distribution of very small metal particles could well be present.

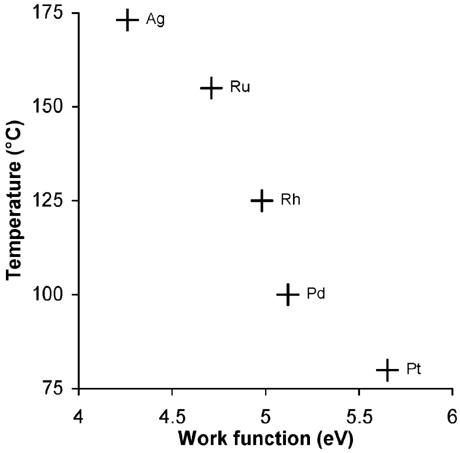

Fig. 2 Plot of work function *vs.* promoted ceria reduction temperature for silica supported catalysts.

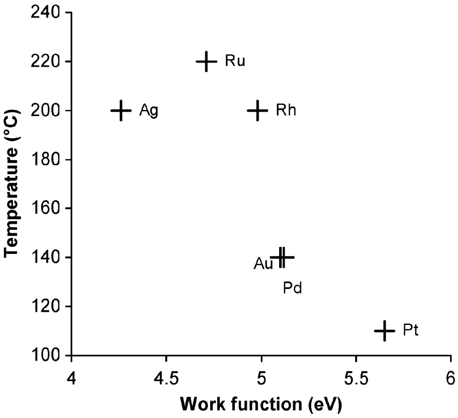

Fig. 3 Plot of work function *vs.* promoted ceria reduction temperature for alumina supported catalysts.

We believe that the mechanism by which the PGM electronically promotes the ceria can best be rationalised using the "junction effect" theory.[14] This theory, postulated in the late 1980s, attempted to explain the performance of methanol synthesis catalysts in terms of electronic interactions between copper and zinc oxide.[14] This caused some controversy at the time and was not universally accepted,[15] however, the model itself was never repudiated, only its application to methanol synthesis. Its use in our case is justified since it is based on earlier traditions of semiconductor models in heterogeneous catalysis[16] and the physics of semiconductors.[17] It predicts that if a metal with high work function is in intimate contact with a semiconducting oxide with a high band gap, an equilibrium can be established in which the electrons produced by ionizing the oxygen vacancies are distributed between the oxide conduction band states and the states available at the Fermi level of the metal. These criteria are met in our case by having a PGM and ceria in close proximity. The conduction band edge for ceria is significantly higher in energy than the PGM Fermi level, so there is a net transfer of charge from the oxide to the metal. The metal promotes the formation of oxygen vacancies, and therefore ceria reduction, by allowing electrons to move across to the metal Fermi level, thereby lowering the enthalpy of formation of the doubly ionized oxygen vacancy. This stabilisation perturbs the defect equilibrium in favour of increased oxygen vacancy concentrations. As the work function is increased, by changing the metal, the barrier for oxygen-vacancy formation is effectively lowered, and the neighbouring ceria becomes even more reducible. This does not exclude the possibility of hydrogen spillover, but may provide the driving force for its occurrence, especially in catalysts where there are exposed PGM sites.

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