

## Combustion synthesized $Ce_{1-x}Pt_xO_{2-\delta}$ ( $x = 0.005, 0.01$ and $0.02$ ; $\delta \sim 0.07$ and $0.1$ ): A novel room-temperature $H_2-O_2$ recombination catalyst

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**Pt-substituted ceria,  $Ce_{1-x}Pt_xO_{2-\delta}$  prepared by the combustion of aqueous solution containing calculated amounts of  $(NH_4)_2Ce(NO_3)_6$ ,  $H_2PtCl_6$  and oxalyldihydrazide has been shown to be an excellent catalyst for hydrogen–oxygen recombination to water at room temperature. The activity of catalyst is much more than that reported for Pt/SiO<sub>2</sub> or Pt/Al<sub>2</sub>O<sub>3</sub>. Platinum ions, Pt<sup>2+</sup> and Pt<sup>4+</sup>, rather than Pt<sup>0</sup> atoms dispersed on ceria are the active sites for  $H_2-O_2$  recombination at room temperature.**

SEARCH for an efficient room-temperature  $H_2-O_2$  recombination catalyst forming water is still an important area of research. For certain applications, lowering of  $H_2$  content requires an efficient hydrogen reducer via a catalyst that works at room temperature under wet conditions. While charging lead acid batteries,  $H_2$  and  $O_2$  are produced and if they are recombined to give water, the batteries can be sealed and there is no need of replenishing water.  $H_2-O_2$  recombination via polymer electrolyte fuel cell produces power. In the literature, formation of water from  $H_2 + O_2$  over noble metal catalysts, especially Pt, has been a subject of interest since 1921 (refs 1–12). Fine Pt metal particles supported on Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> are known to convert  $H_2 + O_2$  to H<sub>2</sub>O. Levy and Boudart<sup>13</sup> reported WC as a possible alternative for Pt, but its efficiency is much lower than that of Pt. Here we report a new, extremely efficient room-temperature  $H_2-O_2$  recombination catalyst, namely Pt/CeO<sub>2</sub> prepared by solution combustion method, where Pt<sup>2+</sup> and Pt<sup>4+</sup> ions are substituted for Ce<sup>4+</sup> site on CeO<sub>2</sub> nano crystallites. The aim of this study is to use every Pt atom as the catalytic site by way of dispersing platinum in the form of ions, so that cost of this catalyst can be reduced substantially and also to achieve higher activity.

The combustion mixture for the preparation of 1% Pt/CeO<sub>2</sub> contained  $(NH_4)_2Ce(NO_3)_6$ ,  $H_2PtCl_6$  and  $C_2H_6N_4O_2$  (oxalyldihydrazide, ODH) in the mole ratio of 0.99:0.01:2.33 ODH was used as the fuel. In a typical preparation, 10 g of  $(NH_4)_2Ce(NO_3)_6$  (Fluka, 99.9%), 0.095 g of  $H_2PtCl_6$  (Ranbaxy Laboratories Ltd, 99%)

and 5.175 g of ODH were dissolved in minimum volume of water in a borosilicate dish of 130 cm<sup>3</sup> capacity. The dish containing the redox mixture was introduced into a muffle furnace maintained at 350°C. Initially the solution boiled with frothing, foaming and then it ignited to burn with a flame (~1000°C), yielding a voluminous solid product within 5 min. Similarly, 0.5 and 2% Pt/CeO<sub>2</sub> have been prepared by this method. 0.5 and 1% Pt/CeO<sub>2</sub> samples are light grey and 2% Pt/CeO<sub>2</sub> sample is grey in colour. Details of preparation, characterization and catalytic properties of the catalysts have already been reported<sup>14</sup>.

XRD patterns (Siemens D5005, CuK $\alpha$ ) of 1 and 2% Pt/CeO<sub>2</sub> show that the diffraction lines agree well with CeO<sub>2</sub> in fluorite structure and there are no reflections corresponding to Pt metal<sup>14</sup>. Crystallite sizes of CeO<sub>2</sub> calculated from Debye–Scherrer method are in the range of 15–25 nm. The composition of the catalyst can be written as  $Ce_{1-x}Pt_xO_{2-\delta}$  ( $x = 0.005, 0.01$  and  $0.02$ ;  $\delta \sim 0.07$  to 0.1). Thus, in addition to Pt ion substitution for Ce<sup>4+</sup> ions, oxygen ion vacancy to the extent of 3 to 5% is observed. High resolution X-ray diffraction study shows that lattice parameter  $a$  of pure CeO<sub>2</sub> is 5.4112(4) Å and that of 1% Pt/CeO<sub>2</sub> is 5.4104(4) Å. Although there is a small variation, it is not so significant. XPS (ESCA-3 Mark II spectrometer, VG Scientific Ltd, England, AlK $\alpha$ ) of Pt(4f) core level region in the 1 and 2% Pt/CeO<sub>2</sub> samples shows peaks due to multiple oxidation states which could be resolved into sets of spin-orbit doublets (Figure 1). Accordingly, Pt(4f<sub>7/2, 5/2</sub>) peaks at 71.7, 74.9 and 74.0, 77.2 eV in 1% Pt/CeO<sub>2</sub> can be attributed to Pt<sup>2+</sup> and Pt<sup>4+</sup> oxidation states.<sup>15</sup> Similarly 2% Pt/CeO<sub>2</sub> also contains Pt<sup>2+</sup> and Pt<sup>4+</sup> peaks. Pt(4f<sub>7/2, 5/2</sub>) peaks at 71.0 and 74.2 eV corresponding to Pt metal (Pt<sup>0</sup>) are not observed. Relative intensities of Pt<sup>2+</sup> to Pt<sup>4+</sup> in 1% Pt/CeO<sub>2</sub> are about 0.75 to 0.25 and as the Pt concentration is increased, Pt<sup>2+</sup> ion intensity increases. Ce(3d) core level spectrum corresponds Ce in +4 oxidation state. The surface concentration of Pt in 1% Pt/CeO<sub>2</sub> is calculated from relative intensities of Pt(4f) and Ce(3d) core level peaks. Surface concentration of Pt ion is 15% against 1% by molar ratio taken in the preparation. Surface concentration of platinum ions in 2% Pt/CeO<sub>2</sub> is 28%. From structural parameters of CeO<sub>2</sub>, the number of Ce<sup>4+</sup> ions in 15 nm CeO<sub>2</sub> crystallites terminated with Ce<sup>4+</sup> ions can be calculated. Accordingly, about 20% Ce<sup>4+</sup> ions can be substituted by Pt ions, if all the Pt ions are dispersed from 1% molar Pt/CeO<sub>2</sub> on the surface. Observation of 15% surface Pt concentration in 1% Pt/CeO<sub>2</sub> and 28% concentration in 2% Pt/CeO<sub>2</sub> suggests that all the Pt salt used in the preparation is dispersed mostly on the surface of CeO<sub>2</sub> as ions. In contrast to Pt/CeO<sub>2</sub>, fine metal Pt particles of 5–8 nm size are dispersed over the Al<sub>2</sub>O<sub>3</sub> surface<sup>16</sup>. Similarly, Pt metal particles are dispersed on SiO<sub>2</sub>.

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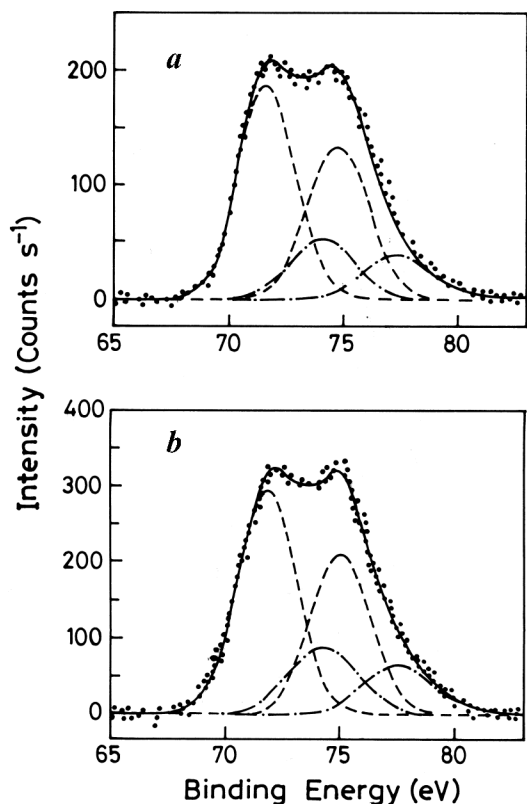


Figure 1. XPS of Pt(4f) core level region of (a) 1% Pt/CeO<sub>2</sub> and (b) 2% Pt/CeO<sub>2</sub>.

The as-prepared catalyst (~0.1 g) was loaded in a quartz reactor tube of length 20 cm and diameter 6 mm and evacuated to 10<sup>-5</sup> Torr. H<sub>2</sub> was passed over the catalyst at a flow rate of 25 μmol s<sup>-1</sup> at room temperature. There was no H<sub>2</sub>O (*m/z* = 18) formation as seen from the quadrupole mass spectrometer (QXK300, VG Scientific Ltd, England), indicating lattice oxygen is not reduced by H<sub>2</sub> (*m/z* = 2). The moment feed O<sub>2</sub> (*m/z* = 32) was leaked through the reactor, huge amount of H<sub>2</sub>O was observed in the mass spectrometer and the entire amount of O<sub>2</sub> could be utilized. However, temperature did rise to 40–50°C due to exothermicity of the reaction. Realizing the potential of this catalyst, a detailed study on the rate, conversion efficiency and turnover frequency was undertaken.

In order to obtain the rate and turnover frequency, H<sub>2</sub> + O<sub>2</sub> reaction was performed with an electrolyzer containing Ni plaques as electrodes in 6 M KOH solution. The evolved H<sub>2</sub> and O<sub>2</sub> gases from the electrolyzer in 2:1 ratio were passed through a glass tube reactor containing different amounts of the catalyst. The length and diameter of the reactor tube were 20 cm and 6 mm, respectively. Increase in the catalyst bed temperature due to exothermicity was measured by a fine chromel–alumel thermocouple immersed in the catalyst. The tube was cooled by water circulation so that recombination can be carried out at around 30–35°C. The amount of

gas escaping from the catalyst bed after recombination was measured and accordingly H<sub>2</sub>–O<sub>2</sub> recombination efficiencies (% conversion) were calculated for different flow rates.

From the flow rate and the recombination efficiency for H<sub>2</sub> and O<sub>2</sub> to give H<sub>2</sub>O, absolute rate of the reaction is calculated from the equation<sup>17</sup>,

$$\text{Rate} = FX/vW,$$

where *F* is the flow rate of O<sub>2</sub>, *X* is fractional conversion of O<sub>2</sub>, *v* is stoichiometric coefficient and *W* is the weight of the catalyst. Rate and turnover frequencies (TOF) are expressed in μmol g<sup>-1</sup> s<sup>-1</sup> and s<sup>-1</sup>, respectively. Figure 2 shows the plots of rate and TOF vs oxygen flow rate at 33°C. High conversion rate and TOF at room temperature are noteworthy. H<sub>2</sub> + O<sub>2</sub> reaction has been carried out over Pt/SiO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> to compare activity with Pt/CeO<sub>2</sub>. We find that Pt/CeO<sub>2</sub> catalyst is at least 10 times more efficient than Pt/SiO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub> for the same Pt concentration. Even at room temperature, 100% conversion can be achieved employing Pt/CeO<sub>2</sub> catalyst. The Pt/CeO<sub>2</sub> catalyst does not need any pretreatment such as vacuum drying, heat treatment and hydrogen reduction. Higher catalytic activity of Pt/CeO<sub>2</sub> in relation to Pt/SiO<sub>2</sub> or Pt/Al<sub>2</sub>O<sub>3</sub> can

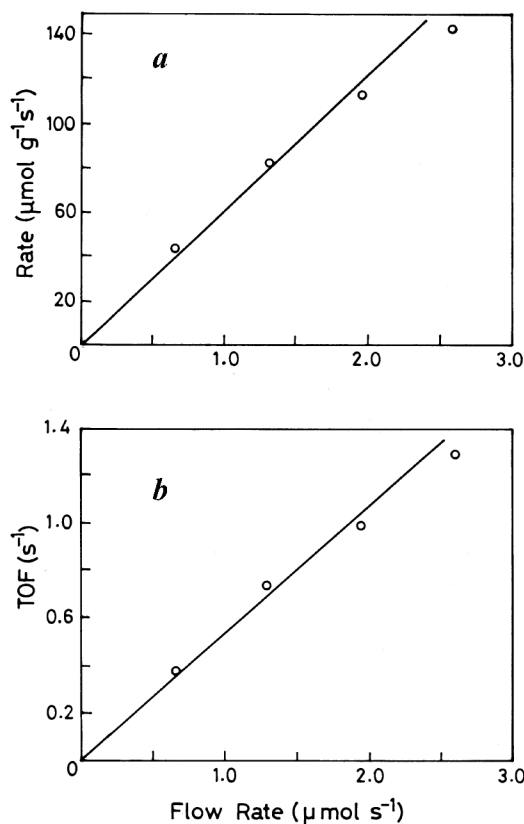


Figure 2. (a) Rate and (b) TOF of water formation over 2% Pt/CeO<sub>2</sub> catalyst as a function of O<sub>2</sub> flow rate at 33°C.

be rationalized as follows:  $H_2 + O_2$  recombination reaction occurs on Pt atom sites on the surfaces of Pt particles in Pt/SiO<sub>2</sub> or Pt/Al<sub>2</sub>O<sub>3</sub>. Average size of Pt metal particles is in the range of 4–6 nm. Considering 5 nm Pt particles, the ratio of the total number of Pt atoms to the number of surface Pt atoms is about 6. If all the atoms in the same 5 nm Pt particle are available as the active sites, the rate of  $H_2 + O_2$  reaction should be at least 6 times higher. For the same Pt concentration,  $H_2 + O_2$  reaction rate over Pt/CeO<sub>2</sub> is about 10 times more than Pt/SiO<sub>2</sub>. Therefore, increase in reaction rate from 6 to 10 times seems to originate from the metal–ceria interaction in Pt/CeO<sub>2</sub> catalyst, in addition to all the Pt atoms dispersed in the form of Pt ions. Pt-substituted CeO<sub>2</sub> shows 3 to 5% oxide ion vacancy which increases oxygen storage capacity<sup>18</sup>. Therefore, CeO<sub>2</sub> support plays an additional role on the catalytic activity.

Two salient features of this novel catalyst are that Pt ions are well separated and they are stabilized to  $-Pt^{2+}-O^{2-}-Ce^{4+}-$  kind of linkages in the  $Ce_{1-x}Pt_xO_{2-\delta}$  solid solution. The active sites for the catalytic  $H_2 + O_2$  reaction are Pt ions rather than normally believed Pt metal (Pt<sup>0</sup>). Operationally, Pt/CeO<sub>2</sub> has many advantages over Pt/SiO<sub>2</sub> and Pt/Al<sub>2</sub>O<sub>3</sub>, such as absence of flashing, hot spot and wetness. The role played by oxygen defects in this catalyst needs further study and is being investigated.

In conclusion, we have shown that Pt ions dispersed over CeO<sub>2</sub> nanocrystallites synthesized by the solution combustion method act as an efficient and cheap catalyst for  $H_2-O_2$  recombination reaction at room temperature. This catalyst has already been successfully employed for  $H_2 + O_2$  reaction in a sealed lead acid battery to prolong its life and efficiency<sup>19</sup>.

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## Intrachain defects in $n-C_{60}H_{122}$ hydrocarbon: A low angle powder XRD study

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**An analysis based on the information obtained from the first reflection (the low-angle reflection) of powder XRD pattern, in case of longer ( $C_{60}H_{122}$ ) and shorter ( $C_{15}H_{31}OH$ ) alkane chains is made. The study is akin to small-angle X-ray scattering (SAXS) studies. Occurrence and increase in the density of intrachain defects in case of long chains and their absence in shorter chains are noticed. The results indicate that the defect formation is a chain length-dependent process, in a sense that longer chain molecules respond to thermal variation and can adopt systematic chain defects, whereas short chains ( $C \leq 15$ ) appear to be immune to such defects in the temperature range investigated.**

THE small angle X-ray scattering (SAXS) studies made by Strobl<sup>1</sup> indicated the formation of intrachain defects in  $n-C_{33}H_{68}$  hydrocarbon with increasing temperature. Kim *et al.*<sup>2</sup> made spectroscopic studies on  $n-C_{60}H_{122}$ ,  $n-C_{50}H_{102}$  and established the occurrence of kink defects. We took up a study on hydrocarbons of different chain lengths, ranging from  $C_{10}H_{22}$  to  $C_{60}H_{122}$ , and certain fatty acids and fatty alcohols. The study covers aspects related to phase transitions, phase strength and inter-chain and intra-chain defects and interface morphology<sup>3–13</sup>. As a part of such programme, we investigated the intrachain defects in case of orthorhombic  $n-C_{60}H_{122}$  hydrocarbon. Linear chain pentadecanol was also investigated to gain information on shorter hydrocarbon chains that are in solid state at room temperature.

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