Preparation and characterization of hydrophobic platinum-doped carbon aerogel catalyst for hydrogen isotope separation

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Abstract. We report preparation of hydrophobic platinum-doped carbon aerogel (PtCA) catalyst and its characterization for catalytic exchange reactions between hydrogen isotopes. The PtCA powder was synthesized by sol–gel polymerization method, mixed with colloidal PTFE solution, and coated on Dixon rings to obtain hydrophobic catalyst. The Pt cluster size in PtCA powder was observed to vary from 3 to 5 nm for a change in resorcinol to alkali molar ratio in synthesis solution from 20 to 200. Transmission electron microscopy of powder showed that the Pt clusters were uniformly dispersed and Pt^0 metallic content estimated by X-ray photoelectron spectroscopy (XPS) was found to be of ~ 70%. The catalytic activity was found to depend on Pt cluster size and was higher for smaller cluster size. For the smallest achieved Pt cluster size of 3 nm, catalytic activity of ~ 0·8 m^3 (STP) s^{-1} m^{-3} was obtained for hydrogen isotope exchange in atmospheric pressure conditions.

Keywords. Hydrophobic catalyst; carbon materials; sol–gel preparation; nanoparticles; hydrogen isotope exchange.

1. Introduction

Liquid phase catalytic exchange (LPCE) reaction between water and hydrogen gas has received considerable attention for both tritium separation and deuterium enrichment. While, tritium separation is required to reduce radiation hazard in heavy water-based nuclear reactors (Kim *et al* 2007; Popescu *et al* 2008), deuterium enrichment by LPCE for heavy water production is an attractive process, since it is more energy efficient and environmetal friendly (Izawa 1979) compared with existing 'girder sulphide' and 'ammonia-hydrogen' processes (Aprea 2002). In the LPCE process, hydrogen isotope exchange reactions take place on active sites of platinum (Pt) between gaseous reactants and these sites loose catalytic activity, when covered with liquid water. Therefore, a primary requirement in the catalyst for LPCE process is that it should be hydrophobic (Stevens 1972). Further, to have a good catalytic activity and throughput, a uniform dispersion of Pt particles in a large surface area substrate is required.

Over the years, different support materials such as alumina (Belapurkar *et al* 1988), silica (Wanke 1985) and activated carbons (Butler 1980) have been investigated for dispersing Pt nanoparticles. Activated carbon supports, in addition to high surface area, help in lowering of activation energy of Pt as compared with alumina and silica

supports (Sagert and Pouteau 1975). However, it has the drawback of inaccessible micropores and mineral impurities. More recently, there has been interest in the use of carbon aerogel as host substate for dispersing Pt, because it offers a good surface area, high level of purity and a possibility of tailoring of the pore sizes (Dawidziuk *et al* 2009). These Pt-doped carbon aerogels (PtCAs) have primarily been investigated for use as electrocatalyst for fuel cell applications (Kim *et al* 2008; Guo *et al* 2011). It is also pertinent to note that several synthesis methods like conventional wet impregnation, electroless deposition and sputtering have been used for uniformly dispersing Pt nanoparticles on high surface area carbon supports. While the wet impregnation and electroless deposition do not provide adequate control of particle size and distribution, sputtering method poses technical challenges for mass scale production (Esmaeilifar *et al* 2010).

We describe in this paper, the use of *in situ* sol–gel method for dispersing platinum on carbon aerogel. This method not only leads to a uniform dispersion of platinum in carbon aerogel, but also provides some control on the particle size by adjusting the process parameters like pH, pyrolysis temperature and concentration. This control on particle size is desirable because a lower mean particle size for Pt, helps in achieving the same catalytic activity with less quantity of Pt thus, reducing the cost of the catalyst. PtCA powder was synthesized by sol–gel polymerization method, mixed with colloidal PTFE solution, and coated on Dixon rings to obtain hydrophobic

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catalyst. After describing the synthesis and characterization of the catalyst, we also present results of its use for H/D exchange reactions in atmospheric pressure conditions.

2. Experimental

2.1 *Catalyst preparation*

PtCA powder was prepared by ambient pressure drying process reported earlier by us (Singh *et al* 2010). In this process, platinum precursor was added to the synthesis solution before polymerization of gel. As described in our previous work, PtCA powder was synthesized by poly-condensation of resorcinol (R) and furfuraldehyde in iso-propyl-alcohol. Hydrogen-hexachloroplatinate was used as platinum precursor. Potassium hydroxide (KOH) was added to the solution in different molar ratios to obtain R/KOH of 20, 50, 100, 150 and 200. The solution was kept in a sealed vial at 60 °C for 72 h for complete gela-tion. The gel was dried under ambient conditions and pyrolysed in argon atmosphere at 500 °C employing heat-ing rate of 4 °C/min to obtain 7% PtCA powder.

Catalyst was prepared by coating the slurry of PtCA powder and PTFE on Dixon ring support to achieve hydrophobicity and mechnical strength. PTFE binder was selected among other hydrophobic binders like SDBC and PVDF, since it has better hydrophobic property owing to high contact angle (108°), high temperature sustainability and long time stability (Huang and Meng 2010). Coated Dixon rings were cured at 370 °C in argon atmosphere to obtain hydrophobic catalyst (contact angle ~ 150°).

2.2 *Physiochemical characterizations*

The surface morphology of PtCA powder and the coated film of PTFE and PtCA on Dixon rings were examined using scanning electron microscope (SEM) (Carl Zeiss, Zigma). Surface area and pore volume of PtCA powder were measured by BET surface area measurement system (Micromeritics ASAP2020). Pt cluster size and its distribu-tion on carbon aerogel support were analysed by trans-mission electron microscopy (TEM Philips CM 200) and X-ray (RIGAKU) diffractometer. The distribution of Pt cluster size was estimated from histograms obtained using TEM images. X-ray photoelectron spectroscopy (XPS) analysis was carried out on ESCA lab250 spec-trometer to determine the chemical states of Pt.

2.3 *Measurement of catalytic activity*

Catalytic exchange reaction between deuterated water and hydrogen occurs according to the following reversi-ble reaction

$$H_2 + HDO \xleftrightarrow{\text{Catalyst}} HD + H_2O.$$
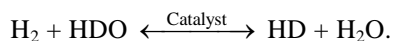
The complete reaction mechanism is well documented in literature (Sagert and Pouteau 1974). The catalytic activ-ity was measured in terms of volume transfer rate, *Kya*, as described in literature (Butler 1980), which defines the net amount of deuterium transferred from isotopically-enriched liquid water to the hydrogen stream in a unit volume of packed catalyst bed under conditions of unit displacement. *Kya* is expressed as m^3 (STP) s^{-1} m^{-3} of cata-lyst bed, and can be evaluated using follwing expression

$$Kya = (F_{H_2}*A/V)(-\ln(1 - \eta)),$$

where F_{H_2} is the superficial flow rate of hydrogen gas, *A* and *V* the cross-sectional area and volume of catalyst packed bed, respectively, and η the isotope exchange efficiency.

Catalyst performance tests were performed in a glass column with internal diameter of 25 mm and height of 1000 mm. The column was filled with coated Dixon rings to a height of 220 mm. Water having ~ 2000 ppm D/H was fed at the top of the column and natural hydrogen gas (~ 50 ppm D/H) was fed from bottom of the column. The operating conditions were as follows: temperature – 32 °C, H_2O flow rate – 3 kg/h and H_2 gas flow rate – 14 lpm. The D/H concentration in the hydrogen gas at inlet and outlet of the column were analysed with D/H mass spectrome-ter. Experimental conditions were selected in such a way that it leads to a concentration of D/H which will be in the measurable range with the mass spectrometer.

3. Results and discussion

The morphology of PtCA powder and the coated Dixon ring catalyst are shown in SEM images (figure 1(a) and (b)). Figure 1(a) shows highly porous open structure of PtCA powder. SEM image of coated Dixon ring film shows that PTFE covers the open structures of PtCA powder (figure 1b). The PTFE film is permeable to gaseous reactants, but prevents water penetration to active Pt sites. Surface area and pore volume of PtCA powder were measured to be 605 m^2/g and 0·24 cm^3/g, respectively.

In figure 2, we show the representative TEM images and corresponding histograms of particle size distribution for PtCA powder prepared with varying molar ratios of R/KOH. Figure 2(a) shows highly dispersed Pt nanoparticles with almost no agglomeration for R/KOH of 100. It has mean particle size of 3·01 nm with standard deviation of 0·39 nm. Bigger particle size and agglomeration were observed for lower and higher values of R/KOH (figure 2(b) and (c)).

Figure 3 shows XRD spectra of PtCA powder, where the major diffraction peaks of Pt can be seen at $2\theta = 39·6°$, 46·1°, 67·4°, 81·2° and 85·6° corresponding to the reflection planes of (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2). The peaks are in consistent with the face-centered cubic (*fcc*) structure of platinum (JCPDS card no. 04-0802). The *fcc* phase of crystalline platinum demonstrates a successful
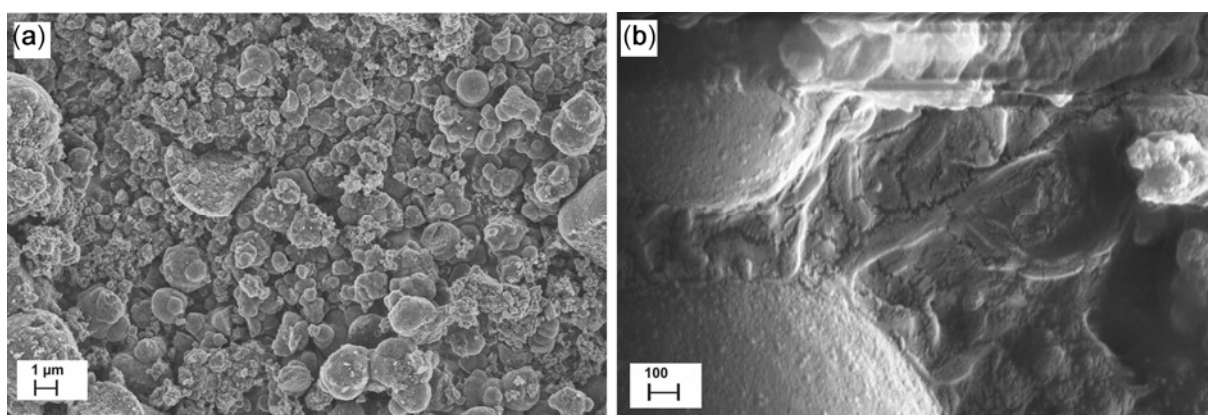
Figure 1. SEM image of (**a**) PtCA powder and (**b**) coated film of PTFE and PtCA on Dixon ring.
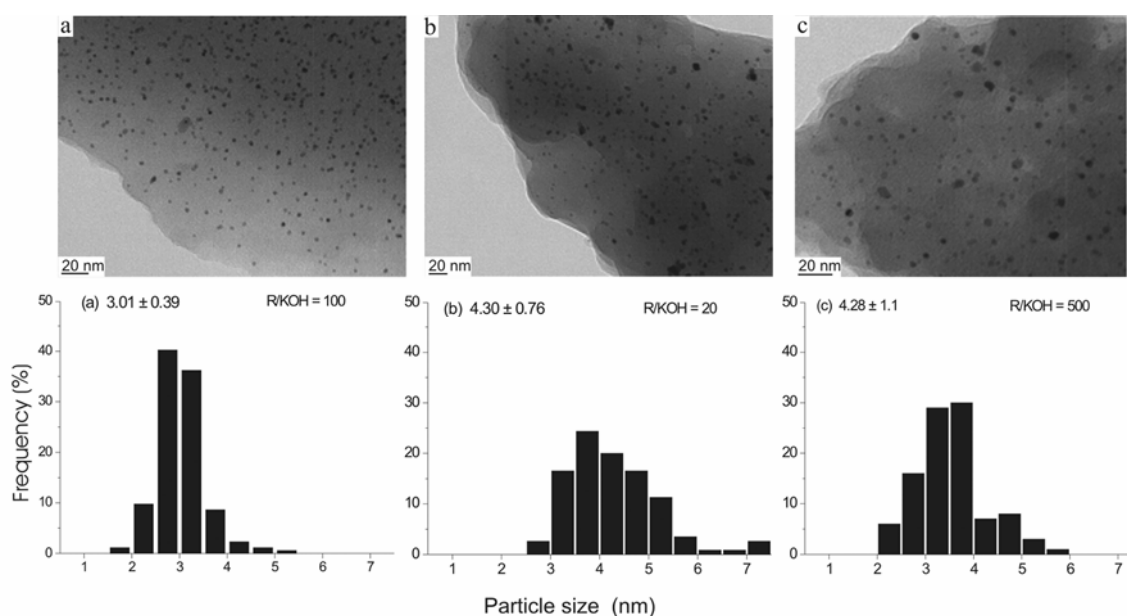

Figure 2. (**a**)–(**c**) TEM images of Pt cluster on carbon aerogel and their corresponding histograms for varying molar ratios of R/KOH.
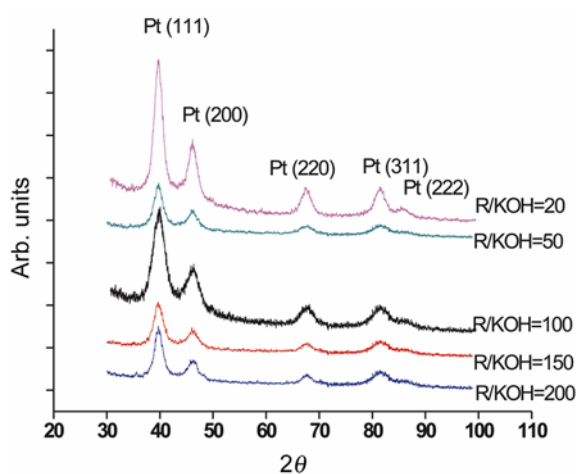

Figure 3. XRD spectra of PtCA powder for varying molar ratios of R/KOH.
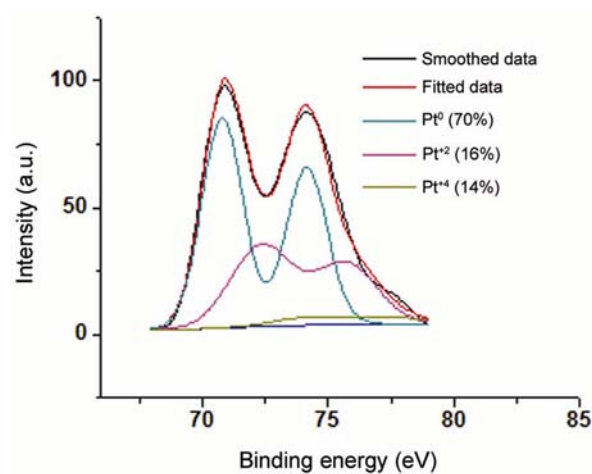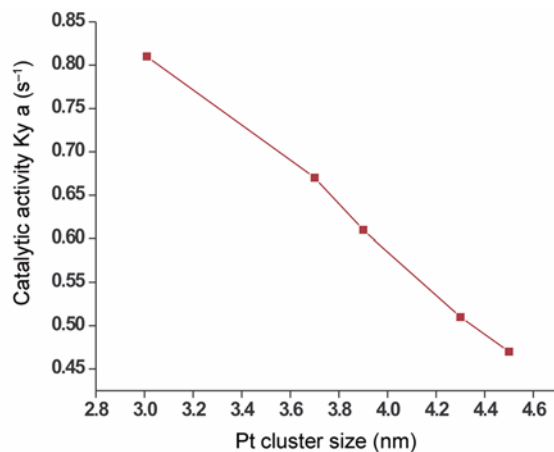
Figure 4. XPS spectra for Pt $4f$ region with relative intensities for different Pt states.

Table 1. Catalytic activity in terms of *Kya* for different Pt cluster sizes having varying R/KOH molar ratios.

R/KOH ratio	Pt cluster size (nm)	*Kya* (m^3 (STP) s^{-1} m^{-3})
20	$4\cdot3 \pm 0\cdot76$	$0\cdot51$
50	$3\cdot7 \pm 0\cdot68$	$0\cdot67$
100	$3\cdot01 \pm 0\cdot39$	$0\cdot81$
150	$3\cdot9 \pm 0\cdot63$	$0\cdot61$
200	$4\cdot5 \pm 1\cdot1$	$0\cdot47$

Figure 5. A plot of Pt particle size vs catalytic activity.

reduction of platinum precursor to the metallic form. Particle size calculated using the Scherrer equation is in close agreement with the results obtained from TEM analysis.

In figure 4, we show XPS spectra for Pt 4f region, which was de-convoluted to three pairs of doublets by XPSPEAK software with their relative intensities. Reasonably high metallic Pt^0 content $\sim 70\%$, suggests that synthesis process effectively reduces platinum salt into Pt^0 metallic state, which is desirable for good catalytic activity (Hu *et al* 2011).

3.1 *Catalytic performance of the hydrophobic catalysts*

Measurement of catalytic activity was carried out under test conditions as explained earlier in §2.3. Results of the measurements made on catalytic activity of catalysts prepared using different molar ratios of R/KOH are presented in table 1.

The results show that the best activity is obtained for R/KOH ratio of 100, for which the Pt cluster size is lowest ($3\cdot01 \pm 0\cdot39$ nm). The result of higher activity for smaller particle size (figure 5) is in agreement with previous reports (Hu *et al* 2011), where a similar dependence of activity on Pt cluster size has been reported.

Measurements of catalytic activity over a period of one month at atmospheric pressure conditions show that loss in activity was less than 5%.

4. Conclusions

Hydrophobic catalyst for hydrogen isotope exchange reactions was prepared using PtCA powder and PTFE binder. This study shows that resorcinol to alkali ratio in synthesis solution has effect on Pt cluster size and lowest Pt cluster size of $3\cdot01 \pm 0\cdot39$ nm was obtained for R/KOH of 100. Physiochemical characterization shows that PtCA powder has high surface area, well-dispersed Pt nanoparticles and high Pt^0 metallic state. This catalyst has shown good catalytic activity and stable performance in atmospheric conditions for LPCE process. The catalytic activity was found to depend on Pt cluster size and was higher for smaller cluster size. For the smallest achieved Pt cluster size of 3 nm, catalytic activity of $\sim 0\cdot8$ m^3 (STP) s^{-1} m^{-3} was obtained for hydrogen isotope exchange in atmospheric pressure conditions.

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