

# Molecular sieving platinum nanoparticle catalysts kinetically frozen in nanoporous carbon†

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Highly active shape selective catalysts with excellent thermal stability are synthesized by entrapping well dispersed platinum nanoparticles in a polyfurfuryl alcohol derived nanoporous carbon matrix; these nanocomposites are excellent candidates for new catalytic applications including fuel cells, pharmaceutical synthesis and biomass conversion.

There has been considerable interest in developing well dispersed platinum nanoparticles on carbon due to their applications in fuel cells, catalytic converters and catalytic burners.<sup>1–5</sup> There are excellent reviews in the literature on this topic.<sup>6–8</sup> Carbon-supported platinum catalysts are usually synthesized by one of a few methods: (a) impregnation of an activated carbon support with a platinum salt precursor solution such as chloroplatinic acid, (b) adsorption of platinum oxide, platinum metal or colloids on the carbon surface<sup>9,10</sup> or (c) by ion exchange at the surface with a platinum amine complex. These steps are followed by reduction of platinum species to Pt<sup>0</sup> by heating in the presence of hydrogen at 300–500 °C. Each method can result in the formation of initially well dispersed platinum nanoparticles typically ranging in size from 2–4 nm. However, these nanometer-sized particles on such a surface are unstable and as a result seek to minimize their surface chemical potential through agglomeration and sintering at higher temperatures.

In this communication, we report a novel synthesis‡ for the creation of a highly active and thermally stable platinum–carbon catalyst that also shows shape selective properties. We find that platinum nanoparticles of dimensions ranging from 2–4 nm can be dispersed well with high stability towards agglomeration in a glassy nanoporous carbon matrix. The essential feature underlying this stability is that the diameter of the platinum nanoparticles are six to ten times larger than the pore size of the carbon (0.4–0.5 nm). Hence, it is impossible for the particles to move through the matrix, thereby preventing their agglomeration and sintering even under forcing conditions (*i.e.* at 800 °C in flowing hydrogen). However, since the matrix of carbon is nanoporous, reactants and products are able to diffuse to and from the surfaces of the embedded platinum nanoparticles. Furthermore, since the pore dimensions in the carbon are comparable to the molecular dimension of alkenes, we find that the global reactivities of these alkenes are strongly dependent upon their size. This molecular sieving effect arises from restricted or configurational diffusion in the nanopores. It shows that the nanoporosity extends from the carbon matrix to the platinum nanoparticle surfaces.

Platinum nanoparticles were prepared by reduction of platinum(II) acetylacetonate in the presence of furfuryl alcohol under reflux. There are several reports on the use of alcohols as reducing agents to prepare platinum nanoparticles<sup>11,12</sup> and our investigation shows that furfuryl alcohol is a very good reducing agent for this purpose. The reduced platinum nanoparticles are dispersed in excess furfuryl alcohol using TritonX-100 as a surfactant. The monomer–nanoparticle mixture is polymerized

using *p*-toluenesulfonic acid monohydrate at 15–20 °C for 24 hours. The resultant polymer composite was redissolved in acetone, ultrasonicated for 1 hour and pyrolyzed at 800 °C for 8 hours under an argon atmosphere. All the results discussed in this paper are based on 6.4 wt% platinum loaded nanoporous carbon.

HRTEM and STEM images were used to study the size and distribution of platinum nanoparticles. The particle sizes range between 2–4 nm and were very well dispersed in the nanoporous carbon matrix.§ Closer inspection shows that the platinum particles are clearly embedded in the carbon and thus are accessible only through the pores of the nanoporous carbon (Fig. 1). The total pore volume and pore size distribution of the sample were measured using methyl chloride porosimetry described elsewhere in detail.<sup>13</sup> The pore size distribution of 6.4 wt% platinum loaded carbon is essentially of nanopore dimensions centered at 0.4–0.5 nm.¶ These micropores are characteristic of nanoporous carbon derived from polyfurfuryl alcohol, however pores larger than 1.5 nm were also evident. The presence of pores larger than 1.5 nm is not typical of nanoporous carbon derived from polyfurfuryl alcohol alone and may be a consequence of the presence of platinum during pyrolysis. These pores also aid in the transport of reactants through the carbon and undoubtedly increase catalyst effectiveness.

Alkene hydrogenation test reactions were carried out in a tubular quartz reactor. The catalyst amount for each run was kept at 0.2 g and the mole ratio of the carrier gas (argon) to hydrogen to alkene was 2 : 1 : 1 respectively. The total flow rate of the gas mixture was kept at ~60 ml min<sup>-1</sup>. Pretreatment of the catalyst involved heating the sample in argon and hydrogen to 800 °C over a 30 minute period and maintaining at 800 °C for 1 hour. Reaction products were analyzed by gas chromatography using a flame ionization detector. Ethylene hydrogenation was tested using a 10 m Porapak column maintained at 50 °C, while hydrogenations of propene, 1-butene and isobutene were tested using a 30 m Chromosorb column kept at 30 °C (propene) and 80 °C (1-butene and isobutene) respectively. Hydrogenation reactions were studied at reaction temperatures ranging from 25–200 °C using a 6.4 wt% Pt/C sample (Fig. 2). The results indicate that the catalyst was active for ethylene and propylene hydrogenation even at 25 °C. Conversion at equivalent conditions was strongly dependent

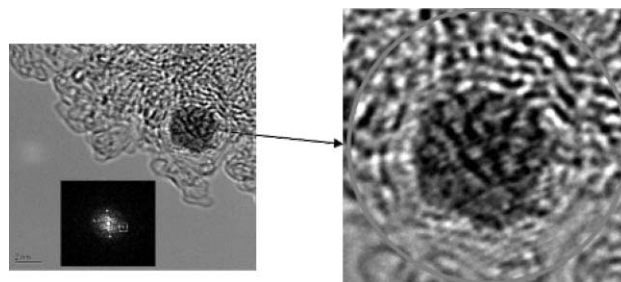
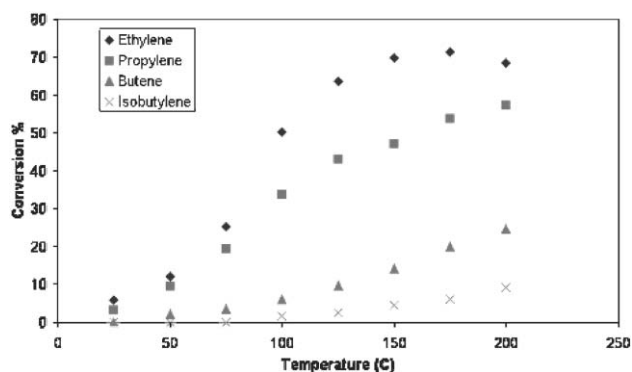


Fig. 1 HRTEM image of a platinum nanoparticle embedded in the nanoporous carbon matrix.

† Electronic supplementary information (ESI) available: Appendix A, B, C and D. See <http://www.rsc.org/suppdata/cc/b4/b407854c/>



**Fig. 2** Conversion of alkenes to alkanes as a function of reaction temperature using a 6.4 wt% platinum loaded nanoporous carbon catalyst.

upon the molecular size of the alkene (molecular sieving property) and this effect becomes especially obvious at high temperatures.

The sample subjected to multiple reductions in hydrogen at 800 °C followed by hydrogenation reactions showed no significant change in the size or dispersion of the platinum nanoparticles.¶ The formation of nanoporous carbon around the preformed platinum nanoparticles takes place *via* the synthesis of a thermosetting polymer such as polyfurfuryl alcohol that arrests the free transport and agglomeration of the particles. As the polymer starts to crosslink, it solidifies and all particle motions are hindered; in this way, the platinum nanoparticles are kinetically “frozen” in the carbon matrix. Agglomeration and sintering of platinum particles may also be diminished to some extent by chemical as well as physical means through the strong interaction of the metal with the carbon. It has been shown that the basicity of electron rich graphene sheets can interact with and stabilize platinum nanoparticles.<sup>14,15</sup> So, this effect is likely responsible for the strong adhesion of the nanoporous carbon matrix *via*  $\pi$ -bonding to platinum nanoparticle surfaces. We think that the strong interaction of platinum nanoparticles with the carbon in addition to the physical entrapment of the particles in the glassy carbon matrix provides the high temperature stability.

The robust pore structure of carbon prepared at 800 °C allows the material to maintain its structural integrity resulting in a catalyst that can be reused indefinitely without any significant loss of activity. This method of stabilizing high surface area platinum nanoparticles in carbon may be general enough to be useful in a variety of platinum carbon catalysts including fuel cells, hydrogenation and dehydrogenation reactions. This method may also be

extended in preparing shape selective catalysts with other transition metals.

## Notes and references

‡ A mixture of platinum(II) acetylacetonate (Pt(acac)), furfuryl alcohol and TritonX-100 was mixed in the ratio of 1 : 5 : 5 by weight and refluxed overnight. This resulted in a black colloidal solution of platinum nanoparticles dispersed in furfuryl alcohol. An additional amount of furfuryl alcohol (5 ml) was then added to the solution and polymerized using an acid catalyst (*p*-toluenesulfonic acid monohydrate (0.1 M)) for 24 hours. The polymer solution was then ultrasonicated for 1 hour and pyrolyzed at 800 °C for 8 hours in a tube furnace under an argon atmosphere. The pyrolyzed sample was weighed and the amount of platinum loading was calculated using the weight of the final product and the amount of initial platinum(II) acetylacetonate added to the furfuryl alcohol.

§ An HRTEM image of 6.4 wt% platinum dispersed in nanoporous carbon and particle size distribution calculated using STEM is attached as Appendix A; see ESI.†

¶ The pore size distribution of 6.4 wt% platinum dispersed in nanoporous carbon studied using methyl chloride adsorption tests is attached as Appendix B; see ESI.†

|| An HRTEM image of 6.4 wt% platinum dispersed in nanoporous carbon repeatedly reduced under hydrogen at 800 °C for 1 hour followed by alkene hydrogenation is attached as Appendix C; see ESI.†

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