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# Efficient and recyclable catalysts for selective oxidation of polyols in $H_2O$ with molecular oxygen

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Advanced carbon materials with improved physical properties and tailored surface morphology and chemistry were developed and applied as the support for platinum nanoparticles. The carbon materials are in regular spherical form (around 100  $\mu$ m) and have a scale-like surface morphology. Platinum nanoparticles of high dispersion was achieved and detailedly characterized by EPMA, TEM, and XPS. The resulting catalysts show high activity for the selective oxidation of glycol, propylene glycol, and glycerol with molecular oxygen as the oxidant. The correlation between catalytic behaviour and the materials' surface properties (active phase dispersion, support surface morphology and chemistry, and bimetallic effect) were further investigated. The recyclability and stability of the catalysts were tested over a five-run recycling experiment. No marked deactivation was observed and the transformation of the dispersion state of platinum nanoparticles during this process was detected by XPS and TEM to address the stabilizing mechanism of the carbon support for platinum nanoparticles.

# Introduction

Molecular oxygen is a steadily available and environmentally clean reagent for chemical oxidation. There is 20% of oxygen in air and water is the only byproduct of oxidations with oxygen. In every aerobic organism in nature, various selective oxidation reactions with molecular oxygen occur every moment. However, it remains a difficult problem for molecular oxygen to be selectively activated for the synthesis of complicated molecules under mild conditions. Oxygen can be easily activated under harsh conditions and organic compound burns out quickly with the product of carbon dioxide. This quick and complete oxidation is not applicable to selective synthesis of target organic molecules. Activation of oxygen is thermodynamically favorable, but kinetically inert.<sup>1</sup> This is caused by the mismatch in the spin state of triplet dioxygen with singlet organic molecules. This limitation can be lifted by introducing transition metal catalysts for triplet molecular oxygen. Oxygen activation with transition metals received extensive attention, and it shows great promise from the standpoint of developing practical, environmentally clean oxidations.2

Selective oxidation of primary and secondary alcohols to the corresponding carbonyl compounds is a very important process in organic synthesis.<sup>3,4</sup> Classical oxidation methods use stoichiometric quantities of inorganic oxidants, chromium(VI) reagents or ruthenium or manganese salts,<sup>3</sup> which are highly toxic and environmentally polluting. Hypervalent iodine reagents<sup>5</sup> and Swern oxidation (the stoichiometric use of DMSO)<sup>4</sup> are other two classical non-green oxidation methods. However, modern oxidation methods prefer using either  $O_2$  or  $H_2O_2$  as green oxidants. Homogeneous catalysis provides powerful solutions for selective green oxidation, but the use of organic solvent and the problems related to handling, recovery, and reuse of the catalyst limit the application of these processes. Many applications of the heterogeneous oxidation of simple alcohols using O<sub>2</sub> have been well-established.<sup>6</sup> However, the selective oxidation of polyols to target compounds remains problematic in developing practical and green methods.

α or β-hydroxyl carboxylic acids are important intermediate chemicals for degradable or biocompatiable polymers and medicine. General synthesis methods involve highly toxic HCN. Selective oxidation of polyols is a powerful green method to synthesize α or β-hydroxyl carboxylic acids. Heyns *et al.* first reported that 2-keto-L-gulonic acid can be obtained in high yield by bubbling oxygen through an aqueous solution of L-sorbose and suspended finely divided platinum.<sup>7,4</sup> Heyns oxidation shows highly efficient oxidations of primary alcohols to acids under mild conditions. After the initial studies by Heyns *et al.* on the oxidation of L-sorbose, the platinum-catalyzed oxidation of

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primary alcohols with oxygen was expanded to numerous substrates by many researchers. All subsequent studies confirmed the early observations and the original protocol had not been essentially improved.<sup>4</sup> From a practical angle, Heyns oxidation is very costly for large-scale synthesis because of the expensive platinum. For best results, a generous amount of catalyst must be employed. Fine black platinum (0.6–2.1 equivalent) or 5– 10% Pt/C (95–210 g mol<sup>-1</sup> alcohol) is required for catalyzing the oxidation of one equivalent of alcohol.<sup>7,4</sup>

In this work, well-dispersed platinum nanoparticles over advanced carbon materials were prepared by incipient wet impregnation and performed as efficient and recyclable catalysts for the selective oxidation of glycol, propylene glycol, and glycerol with molecular oxygen. In our catalytic systems, the total platinum amount is only 0.05-0.1% of Heyns oxidation method for catalyzing oxidation of one equivalent alcohol, however, the activity is comparable to gold nanoparticles over activated carbon. TOF is around 1000 h<sup>-1</sup>. More appealingly, this catalyst can been separated by simple filtration and recycled batch by batch for over ten runs without marked deactivation. All these properties are attributed to the unique carbon support, which is a well-prepared polymer-derived carbon microsphere with tailored surface chemistry and morphology. In our previous works, analogous carbon microspheres have been proven to be suitable support for monodispersed metal nanoparticles<sup>8,9</sup> and the resulting materials are excellent catalysts for methanol carbonylation.9,10 Herein, green and recyclable catalysts for the oxidation of polvol are developed based on such advanced carbon supports.

#### **Results and discussion**

# Surface properties of the carbon support and the resultant catalyst

The as-synthesized carbon materials have a regular spherical shape and uniform size distribution (100–125  $\mu$ m) (Fig. 1a). Fig. 1b shows the topography of the local surface of a carbon spherule. Scale-like layers are observed and such surface morphology can offer steric restriction to confine metal nanoparticles and prevent their interaction and agglomeration.<sup>11</sup>



**Fig. 1** a) A SEM image of as-synthesized carbon microspheres; b) a SEM image of the surface morphology of a selected carbon microsphere.

X-ray photoelectron spectroscopy (XPS) was applied to detect the surface chemical composition of the carbon spherule. Fig. 2 is the XPS survey spectrum of the sample that has been treated with diluted nitric acid. Three elements can be discriminated: carbon (C1s), oxygen (O1s), and silicon (Si2s, 2p). Oxygen is introduced by partially oxidative functionalization of surface and this treatment can improve anchoring and dispersing of metal nanoparticles' precursors over carbon support surface.<sup>12,13</sup>



**Fig. 2** XPS survey spectrum of the pre-oxidized carbon microspheres. The insert is the XPS peak of Si2p and fitting of the Si2p envelope individualizes three silicon states.

The presence of silicon may be caused by application of a silica sol–gel as a dispersion agent in the preparation process. Si surface atomic mole concentration is about 5%. The insert of Fig. 2 is XPS peak of Si2p and fitting of the Si2p envelope individualizes three silicon states: silicon oxycarbide phase  $(SiO_xC_y)$  (101.2 eV, 47.88%), silicon carbide (100.5 eV, 41.07%), and silicon (97.8 eV, 11.05%).

The occurrence and transforming of silicon is evidenced by the X-ray powder diffraction patterns of the samples treated under different temperatures. Fig. 3a shows the XRD patterns of



Fig. 3 a) XRD patterns of carbon microspheres treated at different temperatures; b) the  $N_2$  adsorption isotherm and BET calculation (the insert).

the samples treated at different temperatures. With the increase of treatment temperature, three typical XRD peaks of  $\beta$ -SiC: [111], [202], and [113], are detected, and the carbon materials are graphitized gradually to a high degree. Another marked change is the disappearing of the SiO<sub>2</sub> peaks, which clearly shows the transforming of SiO<sub>2</sub> to SiO<sub>x</sub>C<sub>y</sub> and SiC. These transformations caused by thermal treatment improve physical and mechanical properties. These improvements overcome the main drawbacks of carbon materials, such as graphite, carbon black, activated carbon, pyrolytic carbon, fullerenes, and carbon nanotubes. The increase of graphitization degree ameliorates surface resistant to both acidic and basic media and structure stability at high temperatures.

Thermal treatment improves mechanical properties of the carbon spherules. The resulting materials show high resistance to mechanical crushing and abrasion in catalytic process operation. The surface chemical properties are modified to control polarity and hydrophobicity by introducing heteroatom species during thermal treatment.

Nitrogen sorption analyses were carried out to characterize the porosity properties. The isotherm of the resultant carbon materials is best described as a type I isotherm (Fig. 3b). There is especially the steep slope at low relative partial pressure, with a hysteresis loop. The isotherm and adsorption–desorption curve are typical for porous carbon materials. A BET surface area of 700  $m^2 g^{-1}$  was calculated for the carbon materials. The total pore volume is 0.394 cc  $g^{-1} (P/P_0 = 0.997)$  for mesopores and micropores.

The metal nanoparticle precursors are introduced by incipient wet impregnation. The metal nanoparticles are obtained by reducing the impregnated sample in diluted hydrogen flow under thermal treatment. The dispersion state of metal nanoparticles directly determines their catalytic performance. Electron Probe Microanalysis (EPMA) images (Fig. 4) give the global view of platinum nanoparticle dispersion over a carbon microspherule (metal load: 0.5 wt%). Fig. 4a shows the image of the selected carbon spherule, and it is clearly demonstrated that it is in a regular spherical shape and surface morphology, as depicted by Fig. 1a. Fig. 4b shows the corresponding dispersion of platinum nanoparticles. There is some background noise in Fig. 4b, but it is negligible. Bright points are platinum enriched spots.

Transmission electron microscopy (TEM) is employed to analyze the particle size and morphology of the supported platinum nanoparticles. As shown by Fig. 5a and b, platinum nanoparticles are in a monodispersed state and the particle size is under 10 nm. On closer inspection, it is found that platinum nanoparticles are located over the scale-like surface of the carbon spherule, which has been characterized by SEM (Fig. 1b). Such surface morphology provides steric restriction to stabilize the metal nanoparticles. Chemical states of supported platinum nanoparticles were measured by X-ray photoelectron spectroscopy (XPS). The binding energy of Pt  $4f_{7/2}$  is 71.3 eV (Fig. 5c), which indicates that supported platinum species are kept in a zero-valent chemical state. Herein, monodispersed platinum nanoparticles over a carbon spherule were obtained.

## Catalytic oxidation of polyols with molecular oxygen

The catalysts with different metal loads were tested. The relation between metal load and catalytic activity is shown in Fig. 6.



**Fig. 4** Electron Probe Microanalysis images of the nitrogen-doped carbon microsphere supporting platinum nanoparticles. a) The selected microsphere and b) the corresponding dispersion of platinum nanoparticles.

For a given support of noble metal nanoparticles, there is a suitable metal load range to achieve high catalytic activity with the least metal consuming. The best metal loads for Pt over the present carbon spherules are from 0.5 wt% to 0.75 wt%. In the follwing experiments the Pt metal load is 0.5 wt%. The size and dispersion of supported nanoparticles are affected by many factors, including support surface properties, preparation method, and nanoparticle precursors. It is difficult to rationalize the relation between particle size and the metal load. In our experimental observations, low metal load leads to relatively low catalytic activity.

Fig. 7 shows the results of reaction condition screening experiments. The oxidation TOF is sensitive to the oxygen pressure. The oxidation reaction can proceed smoothly over 50 °C, but the fluctuating of reaction temperature does not affect the activity as markedly as the oxygen pressure. Acidification in the oxidation of alcohol to carboxylic acid can cause very substantial decrease in oxidation speed. Base must be added to avoid acidification. In the present catalytic system, NaOH is used and its amount is 0.8–1.0 equivalents of the substrate. Excessive base can cause the decrease of oxidation selectivity, due to over oxidation and base-catalyzed decomposition of the target compound. Different carbon materials were selected as the supports for platinum nanoparticles. Pt/carbon spherule (Pt/CS) was observed as the most active catalyst with relatively



Fig. 5 a) and b) TEM images of the dispersion state of supported platinum nanoparticles; c) XPS peaks of platinum nanoparticles (Pt  $4f_{7/2}$ : 71.3 eV).



Fig. 6 Screening experiment results of Pt metal load over catalysts. Reaction conditions: 10 mmol glycol, 8 mmol NaOH, 8 ml deionized water were added to a 50 ml autoclave. 0.2 g catalyst with different metal load was used. Oxygen pressure is 1.0 MPa. Reaction temperature is 70 °C. Reaction time is 2 h. Glycol/Pt is 1950.

high selectivity for glycolic acid in catalyzing the oxidation of glycol (Table 1).

Based on the above well-established method, selective oxidation of propylene glycol and glycerol are attempted over carbon spherule supported platinum nanoparticles with molecular oxygen (Table 2). Lactic acid is an important platform chemical for biodegradable polymers and valuable compounds.<sup>14</sup> It can be obtained from glucose through fermentation or catalytic conversion.<sup>15</sup> Direct oxidation of propylene glycol to lactic acid is another powerful synthesis method. Carbon spherule



**Fig. 7** Screening experiment results of reaction temperature and oxygen pressure. Reaction conditions: 10 mmol glycol, 8 mmol NaOH, 8 ml deionized water were added to a 50 ml autoclave. 0.2 g catalyst (metal load: 0.5 wt%) was used. Reaction time is 2 h. Glycol/Pt is 1950.

 Table 1
 Comparison of supporting behavior of different carbon materials

Catalyst <sup>a</sup>	$TOF(h^{-1})$	Conversion (%) <sup>b</sup>	Selectivity (%)
Pt/Carbon Spherule	852	87.3	93
Pt/Activated Carbon	242	24.8	81
Pt/Carbon Black	206	21.1	77
Pt/Graphite	216	22.1	78
Pt/Carbon Nanotube	357	36.6	86

Reaction conditions: 10 mmol glycol, 8 mmol NaOH, 8 ml deionized water were added to a 50 ml autoclave. 0.2 g catalyst (metal load: 0.5 wt%) was used. Oxygen pressure is 1.0 MPa. Reaction temperature is 70 °C. Reaction time is 2 h. Glycol/Pt is 1950." All catalysts are prepared by the same incipient wet impregantion and reducing process and the metal load is 0.5 wt%. <sup>b</sup> Data are determined at reaction time of 2 h.

supported platinum nanoparticles exhibit excellent performance in catalyzing this conversion. The reaction TOF is 891 h<sup>-1</sup> and the selectivity to lactic acid is 90%. Glycerol, a by-product of biodiesel, has stimulated much research in transforming this inexpensive compound into valuable chemicals, due to its large availability.<sup>16,17</sup> Selective oxidation of glycerol under mild conditions is a very useful tool to convert glycerol to valueadded products.<sup>18</sup> In our research, carbon spherule supported platinum nanoparticles can oxidize glycerol to glyceric acid with a selectivity of 82% under a TOF of 645 h<sup>-1</sup>. Compared with many reported results,<sup>19</sup> our catalyst is very efficient in converting glycerol to glyceric acid, whose D-enantiomer is an anticirrhosis agent.

The catalyst can be separated from the reaction mixture by simple filtration. This allows quick recovery for reuse in the next run. The recyclability of platinum nanoparticles over carbon spherule is tested by a five-run recycling experiment (Fig. 8). The activity of the catalyst is kept constant after five-run recycling. In our practical application, the catalyst remains considerably activity after over ten batches of operation. Platinum nanoparticles over other carbon supports, such as activated carbon, carbon black, graphite, and carbon nanotubes, are not very mechanically stable and suffer from serious attrition in use. Recycling tests of the catalysts over these carbon materials show marked catalytic activity loss after three runs.

The introducing of the second metal may modify the surface chemistry and morphology of metal nanoparticles and the support. This may lead to improving or deactivation in

 Table 2
 Selective oxidation of typical polyols

Polyol	Catalyst	Conversion (%) <sup>b</sup>	TOF $(h^{-1})$	Product Selectivity (%) <sup>a</sup>
ноон	Pt/CS	87.3	852	HO OH (Glycolic acid) 93
ноон	Pt/CS	91.4	891	HO COH (Lactic acid) 90
ноон	Pt/CS	66.2	645	HO HO (Glyceric acid) 82

Reaction conditions: 10 mmol polyol, 8 mmol NaOH, 8 ml deionized water were added to a 50 ml autoclave. 0.2 g catalyst (metal load: 0.5 wt%) was used. Oxygen pressure is 1.0 MPa. Reaction temperature is 70 °C. Reaction time is 2 h. Polyol/Pt is 1950.<sup>*a*</sup> Only target products are listed. <sup>*b*</sup> Data are determined at reaction time of 2 h.



Fig. 8 The five-run recycling test. Every batch was carried out under the same reaction conditions.

catalytic activity and selectivity. The bimetallic effect of platinum nanoparticles on polyol oxidation was further investigated (Fig. 9). The second metal precursors were introduced onto the support by incipient wet co-impregnation with the platinum precursor and the final catalysts were obtained by thermal



Fig. 9 The bimetallic effect on the catalytic behavior of carbon microsphere supported platinum nanoparticles.

treatment in diluted hydrogen flow. In presence of La and Bi, the reaction TOF is increased to near 1100  $h^{-1}$ . Ce and Nd deactivate the platinum nanoparticles. It shows no marked affecti on the catalyst. The mechanistic aspect of such a bimetallic effect will be discussed in the following section.

# The correlation between surface properties and catalytic performance

In heterogeneous catalysis, carbon materials can satisfy most of the properties desired for a suitable support.<sup>20,21</sup> They have some advantages over other traditional catalyst supports.<sup>22</sup> surface resistant to both acidic and basic media, structure stability at high temperatures, the tailored pore structure and pore size distribution needed for a given application, porous carbons with a variety of macroscopic shapes (*e.g.*, granules, powder, fibers, cloths, pellets, monoliths, disks), the surface chemical properties modified to control polarity and hydrophobicity, lower cost than other conventional catalyst supports, and easy recovery of active phases by burning off carbon.

High surface area and well-developed porosity are generally considered to be very important for achieving a high dispersion of the active phase in the catalyst. However, for carbon materials, most of their surface area may be contained in narrow micropores. Such pore distribution is not suitable for mass transfer in the catalytic process involving large molecules. Some studies report the positive effect of porosity and surface area on the active-phase dispersion and the catalytic activity.23 There are also reports concluding that the surface area and porosity of carbons do not affect either the active-phase dispersion or the catalytic activity.<sup>24,25</sup> Actually, the relation between porosity and surface area on the active-phase dispersion and the catalytic activity has no fixed rule and mostly depends on the special catalyst compositions and reaction conditions. In this study, a high surface area of the carbon support may be detrimental. Polyols and the corresponding hydroxyl carboxylic acids are very viscous molecules due to hydrogen bonds and the diffusion of reactants

and products may be hindered by the narrow porosity. This has been confirmed by experimental observation (Table 1). Carbon spherules have a relatively lower surface area (nearly 700 m<sup>2</sup> g<sup>-1</sup>) than activated carbon (3000 m<sup>2</sup> g<sup>-1</sup>), but platinum nanoparticles over carbon spherules show higher catalytic activity. This is mainly attributed to the unique surface morphology of the carbon spherule. The layer-structured surface offers enough surface area to disperse and stabilize metal nanoparticles (Fig. 1b and Fig. 5). Most metal nanoparticles are located on the support surface and this exposes them directly to reactant molecules (Fig. 4) and makes them more active than metal nanoparticles embedded in micropore systems. This is the main reason that carbon spherule supported platinum catalysts show high catalytic activity even with very low metal loading.

Surface chemical properties are extremely important carbon characteristics for interpreting the catalytic behavior of carbonsupported catalysts. The common heteroatoms on carbon surface are hydrogen, oxygen, nitrogen, sulphur and phosphorus, which are in the forms of functional groups, such as carboxylic, lactonic, phenoclic, pyranes, chromene, and so on. These groups directly determine the carbon surface acid-base and hydrophilic properties. More importantly, they affect the dispersion of the active phase across the carbon support and the interaction between active phases and the support. There are many reports attempting to clarify the influence of surface functional groups on the catalytic behavior of carbon-supported catalysts.<sup>26</sup> In this work, four types of carbon spherules, which have different surface chemical compositions, are selected to address the role of surface functional groups in affecting the dispersion of platinum nanoparticles and the catalytic activity. S1 is the carbon spherules that have been treated at 1000 °C under diluted hydrogen flow and their surface oxygen atomic concentration determined by XPS is less than 0.1%. S2 is the as-synthesized carbon spherules and their XPS oxygen atomic concentration is 5.3%. S3 is the carbon spherules that have been treated with 30% nitric acid aqueous solution and their XPS oxygen atomic concentration is 12.1%. S4 is the nitrogen-doped carbon spherules that are obtained by added acrylonitrite (20%) to the precursors' polymerization process. Their XPS oxygen atomic concentration is 4.1% and nitrogen atomic concentration is 5.7%. Chemical modification of the support surfaces show little influence on the porosity properties of the carbon spherules. Surface areas of support S1-S4 have no marked difference. Supported platinum nanoparticles are prepared with the same method and metal load (0.5 wt%). Fig. 10a shows Pt/C XPS intensity ratio of the above-mentioned four types of carbon spherules (determined by XPS). The XPS intensity ratio of signals from metal particles and the support  $(I_p/I_s)$  reflects the dispersion of metal nanoparticles over the carbon support.<sup>27</sup> The well-dispersed state leads to a high intensity ratio. It is clearly demonstrated that platinum dispersion increases with the increase in concentration of surface functional groups. This tendency is very similar to the results obtained from platinum dispersed over carbon black or activated carbon.<sup>26</sup> The platinum nanoparticles dispersion state directly affects the catalytic activity. Better dispersion leads to higher catalytic activity (Fig. 10b).

The good recyclability of platinum nanoparticles over carbon spherules is partly attributed to regular physical form, high



Fig. 10 a) The XPS intensity ratio  $I_{\rm Pl}/I_{\rm C}$  of platinum nanoparticles over four types of carbon microsphere surface and b) the corresponding catalytic activity for selective oxidation of glycol.

mechanical hardness, and good resistance to attrition. The chemical stability of platinum nanoparticles and the support during the oxidation reaction is another important factor affecting the recyclability. Fig. 11a shows the Pt/C XPS intensity ratio of the catalyst after every test run in the five-run recycling experiment (Fig. 8). It is clearly revealed that the dispersed state of platinum nanoparticles is kept at a relatively high level. The chemical state of platinum nanoparticles is kept constant during the oxidation reaction, as determined by XPS (Fig. 11b).



Fig. 11 a) The XPS intensity ratio  $I_{Pt}/I_C$  of the catalysts in five runs of recycling test and b) comparison of XPS Pt peaks' binding energy of the fresh catalyst (A) and the used catalyst (B).

TEM images of Run-1 catalyst, Run-3 catalyst, and Run-5 catalyst give a direct and close view of the dispersion state of platinum nanoparticles during the oxidation reaction (Fig. 12). The characterized local surfaces are selected randomly, but the comparison indicates that there is no marked agglomeration and leaching out of platinum nanoparticles during the oxidation reaction. This confirms the result obtained from Pt/C XPS intensity ratio analysis and the five-run recycling experiment.



**Fig. 12** TEM images of the dispersion state of the catalysts in the recycling test. a) Run-1 (the largest nanoparticle: 25 nm, the smallest: 5 nm, average size: 10 nm), b) Run-3 (the largest nanoparticle: 25 nm, the smallest: 4 nm, average size: 9 nm), c) Run-5 (the largest nanoparticle: 22 nm, the smallest: 5 nm, average size: 12 nm).

The bimetallic effect also affects the catalytic activity of the supported platinum nanoparticles (Fig. 9). La and Bi show a patent promoting effect on the catalytic activity. Fig. 13a is the comparison of Pt XPS peaks between the fresh Pt-La catalyst and the used Pt-La catalyst and Fig. 13b is the comparison of La XPS peaks. Platinum nanoparticles show no chemical state changing during the oxidation. The chemical state of La is also kept constant and the XPS peaks are attributed to La<sub>2</sub>O<sub>3</sub>. This reveals that La is not involved in the catalytic oxidation reaction. Its promoting effect may result from two aspects. First, the presence of La<sub>2</sub>O<sub>3</sub> can improve the dispersion of platinum nanoparticles. Pt and La precursors were coimpregnated. The La precursors precipitate as La(OH)<sub>3</sub> and restrain agglomeration of Pt salts. In the thermal treatment, the presence of La<sub>2</sub>O<sub>3</sub> can lower the sintering of Pt nanoparticles. Second, La is the oxyphilic element and has a strong chelating ability to hydroxyl groups. The presence of  $La_2O_3$  can facilitate the chemical



**Fig. 13** a) XPS Pt peaks of the fresh catalyst (A) and the used catalyst (B); b) XPS La peaks of the fresh catalyst (A) and the used catalyst (B).

adsorption of polyols over the catalyst surface and then promote the catalytic conversion. Fig. 14a is the comparison of Pt XPS peaks between the fresh Pt-Bi (1:1) catalyst and the used Pt-Bi (1:1) catalyst and Fig. 14b is the comparison of Bi XPS peaks. The chemical states of Pt and Bi show marked changes. This indicates that Bi is involved in the oxidation reaction and meanwhile modifies the platinum nanoparticles. The bimetallic effect of Pt-Bi can be interpreted from the following three points: 1) Bi is involved in the catalytic oxidation process. Bi has oxygen storage ability and shows catalytic activity in many oxidation reactions. 2) The presence of Bi can facilitate the chemical adsorption of polyols over the catalyst surface. 3) The presence of Bi can improve the dispersion of platinum nanoparticles. An increase of the content of Bi can directly increase the adsorbed activated oxygen over the catalytic active sites and promote the catalytic process (Fig. 9). However, there is a limit to Bi content, over which the promoting effect has little fluctuation. The Bi promoting effect shows a different mechanism from the La involved promoting effect. A more elaborate model catalyst is needed to address this rising problem. Further investigation is under way.

### Conclusion

In summary, we have developed green and recyclable catalysts for selective oxidation of glycol, propylene glycol, and glycerol to the corresponding hydroxyl carboxylic acids. Advanced carbon materials with a regular spherical shape and improved mechanical properties are applied as the support for platinum





**Fig. 14** a) XPS Pt peaks of the fresh catalyst (A) and the used catalyst (B); b) XPS Bi peaks of the fresh catalyst (A) and the used catalyst (B).

nanoparticles. This makes the catalyst separation and recycling easy to operate. The tailored surface morphology and chemistry of the carbon support leads to high dispersion of platinum nanoparticles. High catalytic activity is achieved even under low metal load (0.5 wt%). All oxidation processes are carried out in water under mild reaction conditions with molecular oxygen as the oxidant. No organic solvents are used and no additives except NaOH are added. The catalyst shows high selectivity for partial oxidation products and can been recycled for five runs without any deactivation. Herein, a green route for the catalytic selective oxidation of polyols is well established.

## Experimental

#### **Chemicals and Materials**

Vinylidene chloride, azobisisobutylvaleronitrile, cetyltrimethylammonium chloride (CTAC), glycol, propylene glycol, and glycerol were purchased from Sinopharm Chemical Reagent Co. Ltd. Vinylidene chloride was distilled before using. H<sub>2</sub>PtCl<sub>4</sub> was purchased from Strem. All the reagents were used as received.

#### Preparation of the catalysts

Carbon microspherules were derived from a polymer precursor. The surfactant, cetyltrimethylammonium chloride (CTAC) and ammonium hydroxide were dissolved in deionized water at  $35 \,^{\circ}$ C. The required amount of tetraethyl orthosilicate was then

added to the solution under stirring. The mixture was kept stirring at 45 °C for 24 h and then cooled to 5 °C. Purified vinylidene chloride, with the initiator azobisisobutylvaleronitrile (1% mole ratio) dissolved, was added rapidly. A copolymer of bis(2-aminoethyl) ethylene diamine and epichlorohydrin was added to make the resultant polymer materials a good spherical shape. Such a mixture was kept at 40 °C in a water bath for 24 h under agitation of 250–300 RPM. The final solid materials were filtered and washed by a great amount of deionized water and then dried in vacuum at room temperature. The precursors were first treated in a quartz tube under argon stream at 180 °C. After complete removal of HCl, the treatment temperature was increased to 800 °C under the stream of argon at rate of 1 °C min<sup>-1</sup> and then kept at 1000 °C for 3 h. By this method, carbon microspherules were obtained.

Before introducing the metal precursors, the carbon support are treated with 30% HNO<sub>3</sub> aqueous solution at 40 °C for 12 h. The metal precursors were introduced into the support by incipient wet impregnation. The carbon spherules were immersed in metal salt methanol or aqueous solution for 40 min, followed by drying in vacuum. The solution volume is equal to total pore volume of the given support. The fresh impregnated sample was reduced at 200 °C in the stream of argon and hydrogen (4:1) for 8 h.

#### Characterization of the resultant materials

X-ray photoelectron spectroscopy (XPS) was used to detect the change of chemical states of carbon and silicon species during evolution of the composite materials. All peak positions in XPS experiments were calibrated by the binding energy of C1s as reference of 284.6 eV. Eclipse V2.1 data analysis software supplied by the VG ESCA-Lab200I-XL instrument manufacturer was applied in manipulation of the acquired spectra. The shape and surface morphology of the as-synthesized composite microspherules were characterized by scanning electron microscope (SEM) conducted over Hitachi S530. Transmission electron microscopy (TEM) was obtained by a JEOL 2010 TEM with an accelerating voltage of 200 kV. Nitrogen adsorption isotherms and textural properties of the as-synthesized materials were determined at 77.3 K using nitrogen by a Quantachrome Autosorb Automated Gas Sorption System (Quantachrome Corporation). Before analysis, the samples were dried at 300 °C under vacuum. Electron Probe Microanalysis (EPMA) (carried out on EPMA1600, SHIMADZU) was used to characterize the morphological structure of the nanocomposite spherules and the dispersion state of nanoparticles. Powder X-ray diffraction (XRD) data were recorded using a Rigaku D/max-2500.

#### Catalytic oxidation of glycol, propylene glycol, and glycerol

The catalytic oxidation was carried out in a 50 ml autoclave with magnetic stirring. To 10 mmol polyol was added 5–8 ml of deionized water containing 8 mmol NaOH. 0.2 g of catalyst (metal load 0.5 wt%) was used and the ratio of substrate to metal amount is 1950. The autoclave was flushed by oxygen three times and the reaction pressure of oxygen is 1.0 MPa. The reaction temperature is 70 °C. The substrate can be converted totally in 3 h. The catalyst was separated by simple filtration and washed by deionized water, then dried for next use. The acidified

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