DOI: 10.1002/chem.200501474

A Spontaneous Combustion Reaction for Synthesizing Pt Hollow Capsules Using Colloidal Carbon Spheres as Templates

Ruizhi Yang,[a] Hong Li,*[a] Xinping Qiu,[b] and Liquan Chen[a]

Abstract: Here we report a spontaneous combustion reaction in synthesizing Pt hollow capsules. In brief, Pt nanoparticles were loaded on the surface of colloidal carbon spheres by wet-chemical impregnation. When Pt-loaded carbon spheres were taken out of an argon-filled tube furnace at room temperature and exposed to air, they underwent spontaneous combustion. The internal carbon spheres templates were removed to leave nanostructured Pt hollow capsules. There are at least two critical conditions for the occurrence of the spontaneous combustion: the Pt particle size is below 5.8 nm, and the hydrogen content in the carbon spheres is above 2.570 wt %. Such a reaction is interesting for the preparation of metal hollow spheres and is also relevant with respect to removal of accumulated carbon on catalysts and for soot oxidation at room temperature.

Keywords: carbon · hollow capsules · nanostructures · platinum · spontaneous combustion

Introduction

Hollow nanostructures of metals, such as hollow metal spheres/capsules have attracted a great deal of attention due to their potential application in many fields, owing to their high specific surface area, easy permeability, and enhanced reactivity.[1] Hollow metal spheres/capsules can be fabricated by template-assisted methods,[2] in which colloidal templates are initially coated with a thin layer of the desired material and then the template is removed selectively by calcination or wet-chemical etching.[2] Here we report that Pt hollow capsules (PtHC) can be obtained by a spontaneous combustion reaction. In brief, colloidal carbon spheres were used as template and the Pt precursor was loaded on the surface of these spheres by wet-chemical impregnation. The resulting Pt composite supported on the carbon spheres combusted spontaneously when it was taken out of a cooled tube-furnace purged with argon and exposed to air at room temperature. Removal of the carbon spheres templates left nanostructured Pt hollow capsules. There are at least two critical conditions for the occurrence of the spontaneous combustion reaction. It should be emphasized that such a reaction is interesting not only for the preparation of hollow metal capsules, but this finding is quite relevant for solving two very important but technologically difficult problems, namely, removal of accumulated carbon on catalysts, and soot oxidation at room temperature.[3]

Well-dispersed colloidal carbon spheres were chosen as templates. The colloidal carbon spheres were prepared by a hydrothermal method using sugar as the precursor. The preparation and characterization of the colloidal carbon spheres were reported previously.[4] These colloidal carbon spheres are in fact disordered microporous carbon with a smooth spherical shape. The colloidal carbon spheres coated with Pt nanoparticles were prepared by initially impregnating the Pt precursor $[Pt(NH_3)_4]Cl_2$ with the carbon spheres in aqueous ammonia solution. Then the products were reduced in H_2/Ar gas (8:92, v/v) at a certain temperature in a tube furnace for 3 h. The tube furnace was allowed to cool down to room temperature, and the product was taken out. For the samples treated at 250–600 °C, once the products were exposed to air, they burned-off spontaneously showing dark red color for a few minutes. These samples were demonstrated to be Pt hollow capsules by field-emission scanning electronic microscopy (FESEM). Whereas for the samples treated at 700–1000 °C, the spontaneous combustion did not occur. The details are described as below.

---

[a] Dr. R. Yang, Dr. H. Li, Prof. L. Chen
Institute of Physics, Chinese Academy of Sciences
Beijing, 100080 (China)
E-mail: hli@aphy.iphy.ac.cn

[b] Dr. X. Qiu
Department of Chemistry, Tsinghua University
Beijing, 100084 (China)

Results and Discussion

Figure 1a shows the FESEM image of the well-dispersed colloidal carbon spheres. The particle size of this template ranges from 800 nm to 1.5 µm. A sample the Pt nanoparticles supported on colloidal carbon spheres was reduced in H_2/Ar gas (8:92, v/v) at 400 °C for 3 h, allowed to cool down to room temperature, and taken out carefully from the tube furnace under an Ar gas flow. Then the sample was placed into a sealed Ar-filled bottle and transferred to the vacuum chamber of the FESEM microscope to investigate the morphology. The whole transfer of the sample was performed under an inert Ar gas flow.

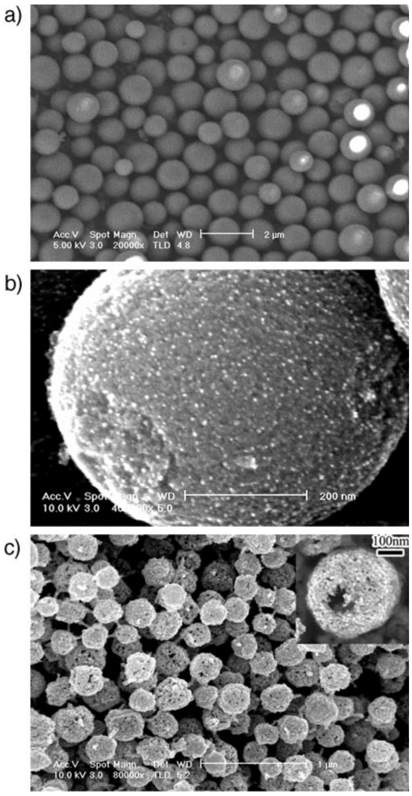

Figure 1. FESEM images of a) the colloidal carbon spheres templates, b) the Pt nanoparticles supported on the surface of the carbon spheres, treated at 400 °C, taken out from the tube furnace under the protection of an Ar gas flow, and c) the nanostructured Pt hollow capsules obtained when the sample in b) was exposed to air.

It can be seen that the Pt particles on carbon spheres are about 4.3 nm in size (Figure 1b). When the same Pt/C sample was taken out but exposed to air, it burned-off spontaneously, and Figure 1c shows the FESEM image of the final product. It can be seen that well-defined Pt capsules are formed that range in size from 250 to 400 nm. The image of a broken capsule of Pt in the inset of Figure 1c clearly shows that the capsule is hollow. The diameter of the Pt particles in the Pt hollow capsule is 9–10 nm, indicating that small Pt particles merged together after spontaneous combustion.

The X-ray diffraction (XRD) pattern of the Pt hollow capsules (corresponding to the FESEM sample in Figure 1c) is shown in Figure 2. All the peaks can be indexed to the face-centered cubic (fcc) structure. The average grain size of the Pt hollow capsules is estimated to be 11 nm by using the Scherrer formula. Raman spectra of this sample did not show the presence of any signal from carbon, indicating that carbon is removed completely (Figure 3).

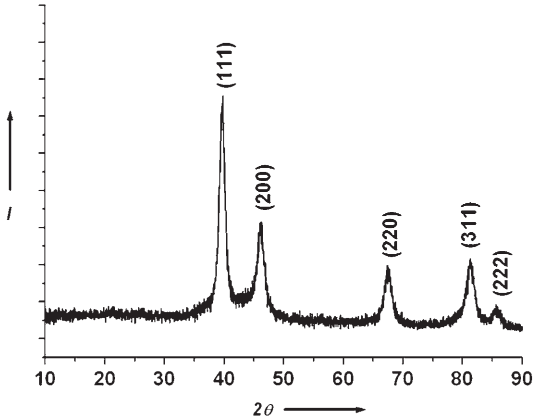

Figure 2. XRD pattern of the nanostructured Pt hollow capsules (the sample corresponding to that in Figure 1c). I = intensity, arbitrary units.

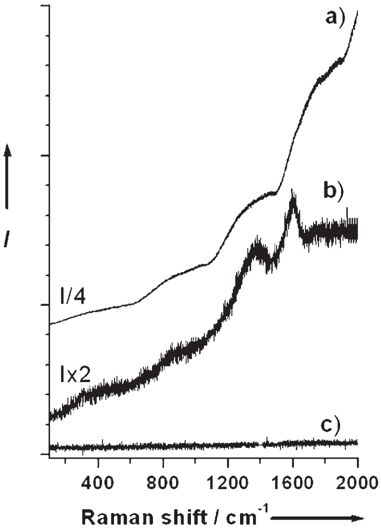

Figure 3. Raman spectra of a) the colloidal carbon spheres, b) Pt nanoparticles supported on carbon spheres reduced in H_2 and Ar at 400 °C and c) Pt hollow capsules obtained when b) was exposed to air.

The transmission electron microscope (TEM) image of the Pt capsules (corresponding to the FESEM sample in Figure 1c) further confirms the hollow nature of the capsules (Figure 4a). The electron diffraction pattern (the inset of Figure 4a) suggests that these Pt hollow capsules are polycrystalline. As shown in Figure 4b, the shell of the Pt hollow

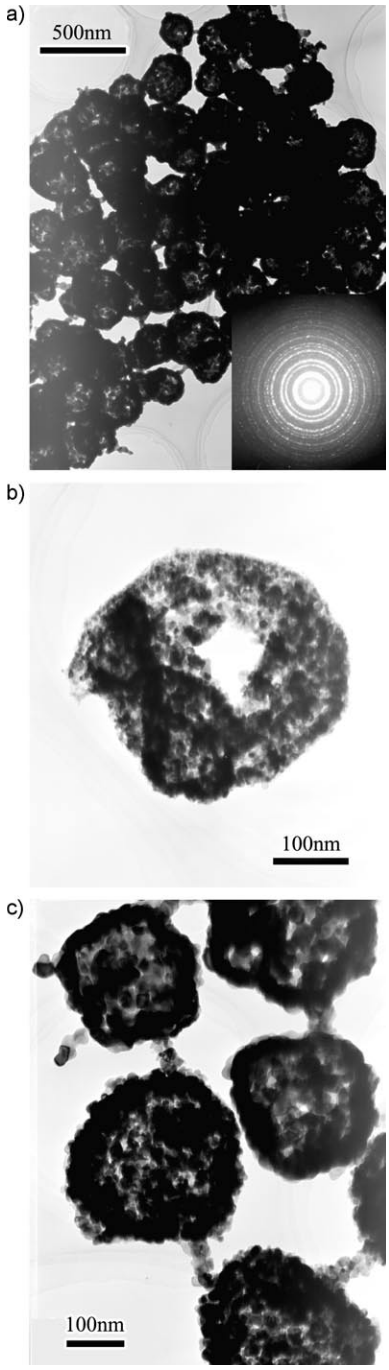

Figure 4. TEM images of the nanostructured Pt hollow capsules (the sample corresponding to that in Figure 1c).

capsules is made of discrete Pt particles with diameters of 11–12 nm, consistent with the estimation from the XRD results. In addition, the shell thickness of the Pt hollow capsules is around 30 nm, and the Pt hollow capsules are connected together through short chains (Figure 4c). Significantly, these three facts indicate that the initial small Pt nanoparticles (4.3 nm) merge during the spontaneous burn-off reaction.

The spontaneous combustion should be an oxidation reaction of carbon catalyzed by Pt at room temperature in air. Therefore, the catalytic activity of Pt could be one of the key factors to determine the occurrence of the combustion, which is always related to the particle size of Pt.

The FESEM images for the samples treated at 250–1000 °C and taken out under an Ar gas flow are shown in Figure 5. The average diameters of the resulting Pt nanoparticles supported on the surface of the carbon spheres are listed in Table 1. It can be seen that the diameter of the Pt nanoparticles increases as the treatment temperature increases. As mentioned above, the reduction temperature of less than 600 °C for the Pt nanoparticles supported on carbon spheres is the critical temperature for the occurrence of the spontaneous combustion. Therefore, a Pt particle size of less than 5.8 nm is necessary to cause spontaneous combustion of the carbon support at room temperature.

For the samples treated at 250–600 °C and taken out in air, spontaneous combustion occurred and Pt hollow capsules were obtained (Figure 6), the morphologies of which are similar to that those in Figure 1c.

For the samples treated at 700 °C, 800 °C, and 900 °C and exposed to air, the spontaneous combustion did not occur, but in contrast with the samples under the protection of an Ar gas flow (Figure 5, e, f, g), the diameters of Pt nanoparticles (Figure 7 a, b, c) increase when they are exposed to air. The diameters of the Pt particles increase from 6.5 nm (700 °C), 7.2 nm (800 °C), and 8.1 nm (900 °C) to 50.0 nm (700 °C), 24.0 nm (800 °C), and 13.5 nm (900 °C), respectively. Thus, the oxidation reaction also occurs for these cases, but not so violently to burn the internal carbon template completely. It is notable that the size of the Pt nanoparticles after exposure to air is inversely proportional to the size of the initial Pt nanoparticles. This is a further indication that the catalytic activity of small Pt nanoparticles is higher. The extent of the oxidation of the surface of the carbon spheres and the subsequent heat from the oxidation reaction should be correlated to the activity of Pt nanoparticles. It is clear that the 6.5–8.1-nm Pt particles can still catalyze the oxidation of carbon to a certain extent, but the produced reaction heat is not sufficient to allow further oxidation reactions and the reaction is limited to the surface regions.

For the sample treated at 1000 °C, the spontaneous combustion did not occur. The diameter of the Pt particles of the sample exposed to air is still 10.2 nm, which indicates that the oxidation of carbon does not occur.

It seems from the above results that the treatment temperature in the tube furnace determines the size of the Pt particles formed, and, in turn, the size of the Pt particles determines the occurrence and the extent of oxidation of carbon. It is well-known that the size of Pt particles in many commercial Pt/C catalysts is less than 5.8 nm; however, the spontaneous combustion phenomenon was not reported in those cases. In our previous study on carbon spheres as a catalyst support for the electrooxidation of methanol,[5] Pt particles with the average diameter of 4.7 nm were support-

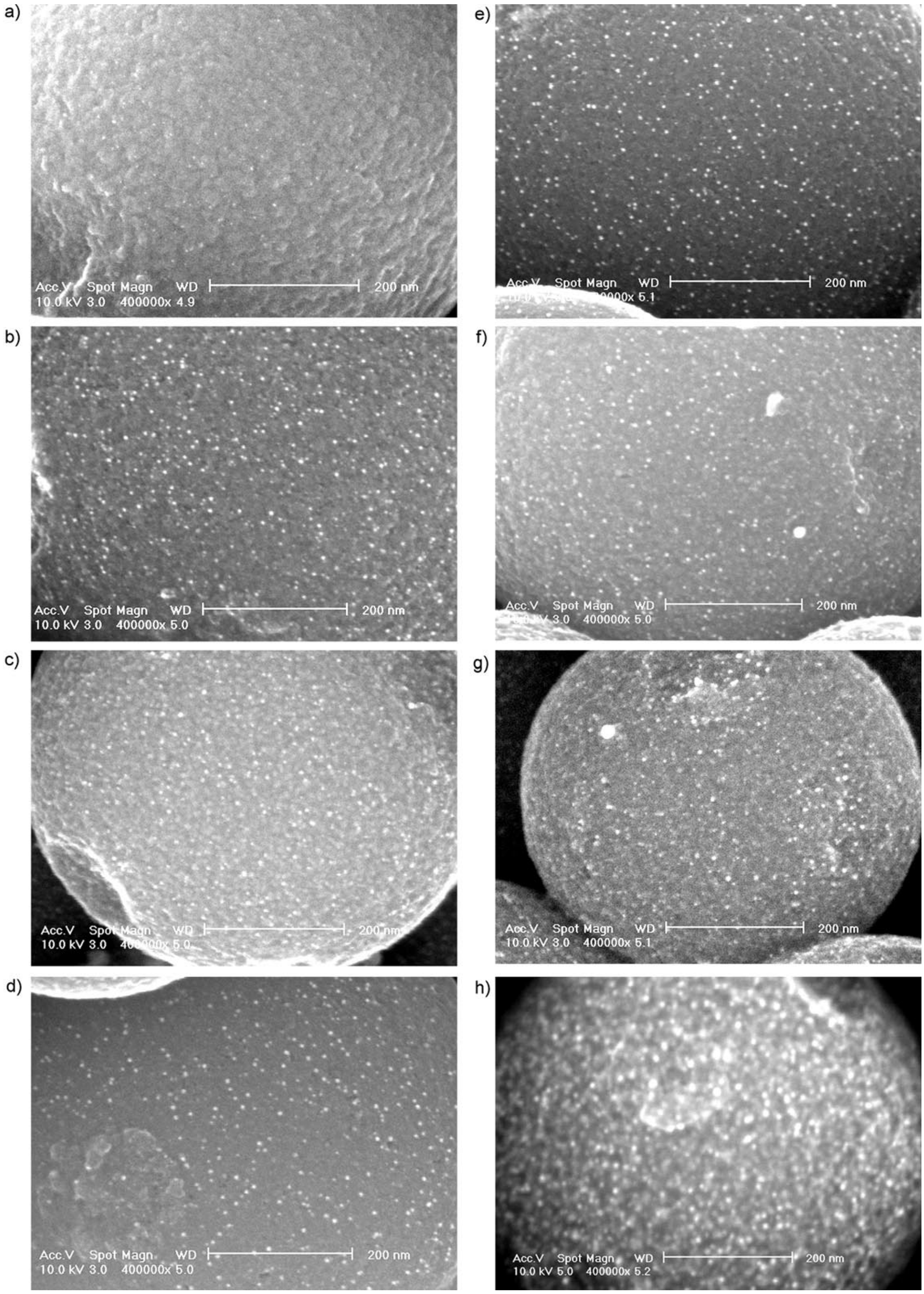

Figure 5. FESEM images of Pt nanoparticles supported on the surface of carbon spheres treated at different temperatures (samples under Ar): a) 250 °C; b) 300 °C; c) 500 °C; d) 600 °C; e) 700 °C; f) 800 °C; g) 900 °C; and h)1000 °C.

ed on carbon spheres treated at 1000 °C, and the composite did not burn-off spontaneously. Therefore, we suppose that this unusual spontaneous combustion reaction is also related to the chemical properties of the carbon substrate used in our samples.

To investigate this further, FTIR spectra of the initial colloidal carbon spheres, the initial colloidal carbon spheres loaded with $[Pt(NH_3)_4]Cl_2$, and the loaded colloidal carbon spheres that were treated at different temperatures under H_2/Ar and taken out under the Ar protection (the same

Table 1. The average diameter of Pt nanoparticles supported on the surface of carbon spheres treated at different temperatures (under Ar), the hydrogen content in carbon spheres, and the state of Pt nanoparticles supported on the carbon spheres following exposure to air.

Temperature [°C]	Colloidal carbon spheres	250	300	400	500	600	700	800	900	1000
the average diameter of Pt nanoparticles [nm]	/	2.5	2.9	4.3	5.0	5.8	6.5	7.2	8.1	10.2
the content of hydrogen in carbon spheres [wt %]	4.707	4.565	4.322	3.714	3.146	2.570	1.843	1.132	0.860	0.808
burn-off spontaneously in air?	/	yes	yes	yes	yes	yes	no	no	no	no

batch samples as in Figure 5) were recorded (Figure 8) and the bands were assigned (Table 2). In brief, the oxygen-containing group COO^- (1591–1610 cm^{-1})[6] exists in all the samples (Figure 8 c–k). Some bands for the hydrogen-containing groups COH and CCH (1300–1000 cm^{-1})[6] exist, whereas those for CH_3 or CH_2 (2968–2820 cm^{-1}, 1440 cm^{-1})[7] decrease slightly as the treatment temperature increases. To clarify this, the content of hydrogen in the carbon spheres treated at different temperatures under H_2/Ar gas (8:92, v/v) for 3 h was determined by elemental analysis (Table 1). It can be seen that the hydrogen content in the carbon spheres decreases as the treatment temperature increases. The content of hydrogen in the colloidal carbon spheres is 4.707 wt %. When the colloidal carbon spheres were treated at 250–600 °C, the hydrogen content ranged between 4.565 and 2.570 wt %, and when the colloidal carbon spheres were treated between 700 and 1000 °C, the hydrogen content ranged between 1.843 and 0.808 wt %.

For the samples that can burn-off spontaneously, the hydrogen content in the carbon spheres is above 2.570 wt % and the Pt particle size is below 5.8 nm. The Pt particle size plays an important role in the spontaneous combustion reaction as mentioned previously. However, the hydrogen content in carbon black usually used in commercial Pt/C catalysts is about 0.203 wt % (2030 ± 200 ppm).[8] The hydrogen content in the carbon spheres treated at 1000 °C used as the catalyst support of Pt for the electrooxidation of methanol in our previous study is about 0.808 wt %.[5] The spontaneous combustion of carbon did not occur although the size of the Pt particles is below 5.8 nm in these cases. The above results indicate that the hydrogen content in the carbon spheres could be another important factor that determines the spontaneous burn-off reaction.

It is well-known that soot oxidation catalyzed by Pt-based catalysts occurs above 300 °C and that the reactivity is related to the feed gas composition and substrates.[3] A recent report shows that Ru/CeO_2 as anode in a solid oxide fuel cell (SOFC) does not show coking if 10 % air was mixed with fuel in advance.[9] Our results indicate that small Pt particles and a carbon sample with a certain hydrogen content could be two critical conditions leading to the spontaneous combustion of carbon at room temperature (as also shown

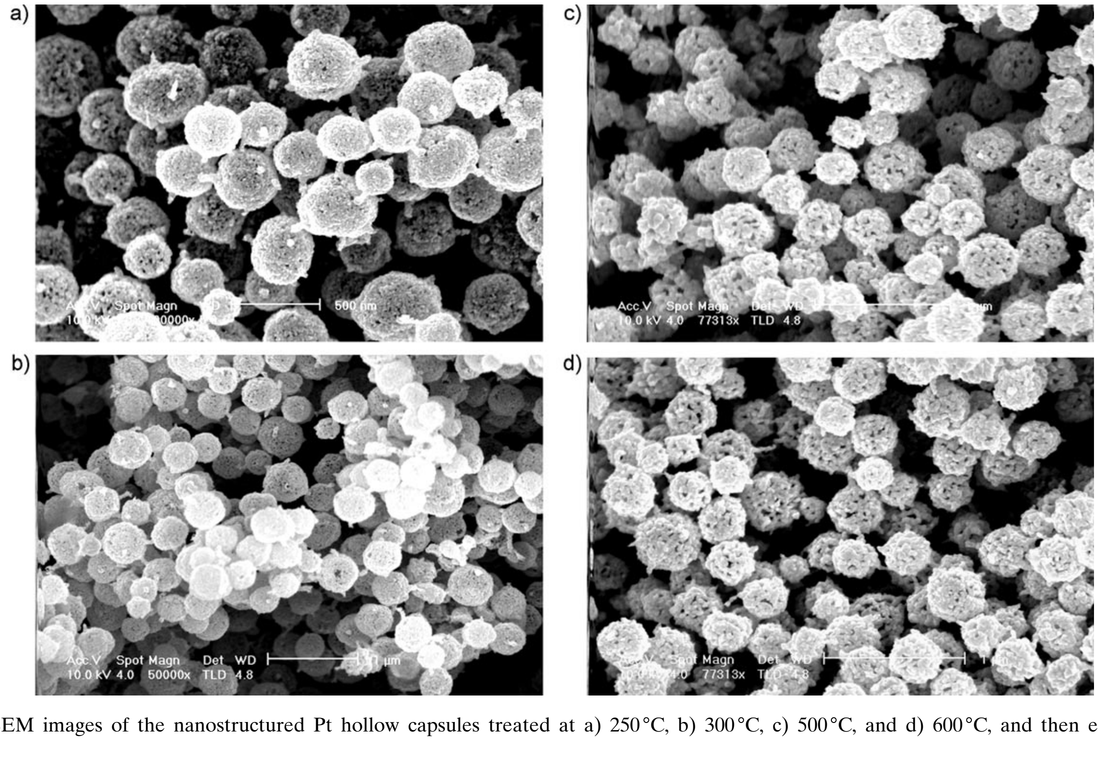

Figure 6. FESEM images of the nanostructured Pt hollow capsules treated at a) 250 °C, b) 300 °C, c) 500 °C, and d) 600 °C, and then exposed to air.

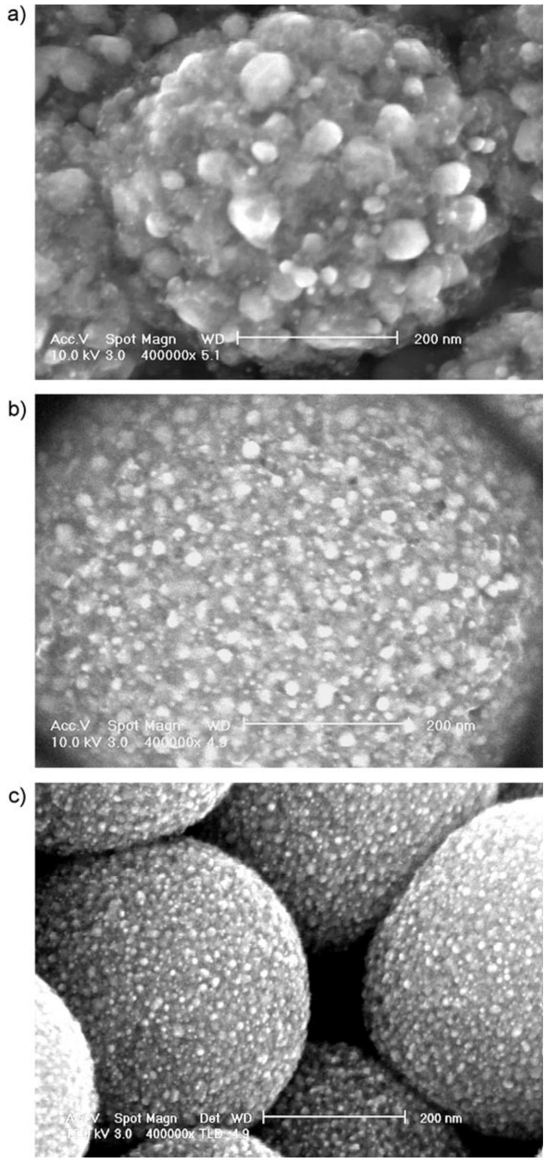

Figure 7. FESEM images of Pt nanoparticles supported on the surface of carbon spheres treated at a) 700 °C, b) 800 °C, and c) 900 °C, and then exposed to air.

in Figure 9). Clearly, the second prerequisite is applicable for most of the hydrocarbon compounds or H-containing carbon reactants. The key point for the first prerequisite is to maintain the size of the Pt nanoparticle below 5.8 nm in the reactions. Therefore, a moderate distance between each Pt nanoparticle on the substrate may be necessary to maintain the catalysis activity towards the oxidation of carbon; this aspect requires further study.

Conclusion

In summary, nanostructured Pt hollow capsules with a diameter ranging from 250 to 400 nm were obtained by using colloidal carbon spheres as templates, which were removed by a spontaneous burn-off process when the fresh Pt/C composite was exposed to air at room temperature. Two critical conditions for the spontaneous combustion reaction are a Pt particle size of below 5.8 nm and a hydrogen content of hydrogen above 2.570 wt % in the carbon spheres. These findings may lead to a method to remove accumulated carbon on catalysts and a way to oxidize soot at room temperature. This work also provides a special template method to prepare nanostructured Pt hollow spheres/capsules.

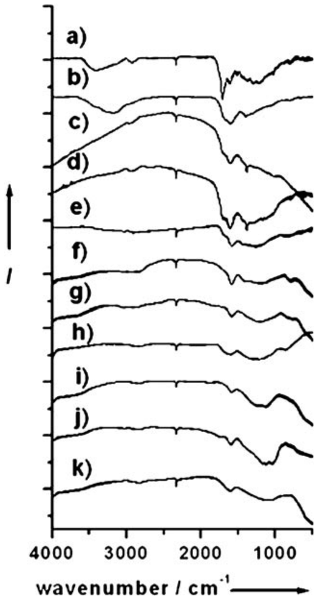

Figure 8. FTIR spectra of a) the colloidal carbon spheres, b) the colloidal carbon spheres–[Pt(NH$_3$)$_4$]Cl$_2$ composite, and c)–k) the Pt nanoparticles supported on carbon spheres, treated at different temperatures in H$_2$ and Ar (samples under Ar): c) 250 °C; d) 300 °C; e) 400 °C; f) 500 °C; g) 600 °C; h) 700 °C; i) 800 °C; j) 900 °C; k) 1000 °C. I = intensity, arbitrary units.

Experimental Section

Synthesis of Pt hollow capsules: Well-dispersed colloidal carbon spheres were used as templates. The colloidal carbon spheres were prepared by a hydrothermal method. For the preparation of Pt hollow capsules, in a typical experiment, the colloidal carbon spheres (624 mg) were added to aqueous ammonia solution (25 wt %; 30 mL) under constant stirring over 30 min to form a suspension. Then, an aqueous solution of 4 mM [Pt(NH$_3$)$_4$]Cl$_2$ (200 mL) was added slowly to the suspension. The product was rinsed with de-ionized water repeatedly. Subsequently, the dried product was treated in H$_2$ and Ar (H$_2$/Ar = 8:92, v/v) at different temperatures (250–1000 °C) in a tube furnace. When the temperature of the tube furnace had cooled to room temperature, the product was taken out. For the samples treated at 250–600 °C, it was found that once the products were exposed to air, they burned-off spontaneously showing a dark red color for a few minutes. These samples were Pt hollow capsules. On the other hand, the spontaneous combustion did not occur for the samples treated above 600–1000 °C.

Characterization: X-ray diffraction (XRD) was performed by using a Rigaku B/max-2400 X-ray diffractometer with Cu$_{K\alpha}$ radiation. The morphology of the samples was examined by using a thermal-field emission scanning electron microscope (FESEM: XL30S-FEG). Transmission elec-

Table 2. FTIR transmittance bands of the colloidal carbon spheres, $[Pt(NH_3)_4]Cl_2$-colloidal carbon spheres, and Pt/C treated at different temperatures in H_2 and Ar with a tentative assignment.

Sample	Band [cm^{-1}]	Assignment
colloidal carbon spheres	3450	ν_{OH}
	2968–2850, 1440[7]	ν_{CH_3}, ν_{CH_2} and δ_{CH_3}, δ_{CH_2}
	1710[7]	$\nu_{C=O}$
	1300–1000[6]	δ_{COH}, δ_{CCH}, ν_{CO}, ν_{CC}
$[Pt(NH_3)_4]Cl_2$-colloidal carbon spheres	3196[6]	ν_{OH}
	2968–2850, 1440	ν_{CH_3}, ν_{CH_2} and δ_{CH_3}, δ_{CH_2}
	1710	$\nu_{C=O}$
	1609 and 1396[6]	ν_{asCOO^-} and ν_{sCOO^-}
	1300–1000	δ_{COH}, δ_{CCH}, ν_{CO}, ν_{CC}
Pt/C reduced at 250 °C	2968–2850, 1450	ν_{CH_3}, ν_{CH_2} and δ_{CH_3},δ_{CH_2}
	1710	$\nu_{C=O}$
	1609 and 1378	ν_{asCOO^-} andν_{sCOO^-}
	1300–1000	δ_{COH}, δ_{CCH}, ν_{CO}, ν_{CC}
Pt/C reduced at 300 °C	2968–2850, 1444	ν_{CH_3}, ν_{CH_2} and δ_{CH_3}, δ_{CH_2}
	1710	$\nu_{C=O}$
	1608 and 1378	ν_{asCOO^-} andν_{sCOO^-}
	1300–1000	δ_{COH}, δ_{CCH}, ν_{CO}, ν_{CC}
Pt/C reduced at 400 °C	2966, 2913, 2850 and 1444	ν_{CH_3}, ν_{CH_2} and δ_{CH_3}, δ_{CH_2}
	1710	$\nu_{C=O}$
	1597	ν_{asCOO^-}
	1300–1000	δ_{COH}, δ_{CCH}, ν_{CO}, ν_{CC}
Pt/C reduced at 500 °C	2960, 2915, 2850, and 1444	ν_{CH_3}, ν_{CH2} and δ_{CH_3},δ_{CH2}
	1710	$\nu_{C=O}$
	1591	ν_{asCOO^-}
	1300–1000	δ_{COH}, δ_{CCH}, ν_{CO}, ν_{CC}
Pt/C reduced at 600 °C	2923, 2851	ν_{CH_3}, ν_{CH_2}
	1594	ν_{asCOO^-}
	1300–1000	δ_{COH}, δ_{CCH}, ν_{CO}, ν_{CC}
Pt/C reduced at 700 °C	2921, 2830	ν_{CH_3}, ν_{CH_2}
	1610	ν_{asCOO^-}
	1300–1000	δ_{COH}, δ_{CCH}, ν_{CO}, ν_{CC}
Pt/C reduced at 800 °C	2917, 2824	ν_{CH_3}, ν_{CH_2}
	1593	ν_{asCOO^-}
	1300–1000	δ_{COH}, δ_{CCH}, ν_{CO}, ν_{CC}
Pt/C reduced at 900 °C	2920, 2825	ν_{CH_3}, ν_{CH_2}
	1598	ν_{asCOO^-}
	1300–1000	δ_{COH}, δ_{CCH}, ν_{CO}, ν_{CC}
Pt/C reduced at 1000 °C	2923, 2825	ν_{CH_3}, ν_{CH_2}
	1607	ν_{asCOO^-}
	1300–1000	δ_{COH}, δ_{CCH}, ν_{CO}, ν_{CC}

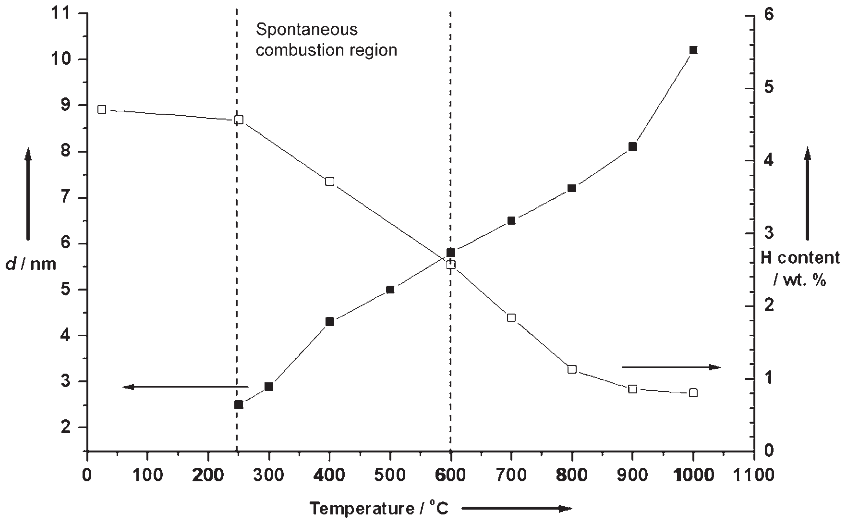

Figure 9. Temperature dependence of the Pt particle size *d*, and the hydrogen content in carbon spheres under a H_2/Ar (8:92, v/v) atmosphere for spontaneous combustion of Pt nanoparticles supported on the surface of carbon spheres.

tron microscope (TEM) images and selected-area electron diffraction (SAED) patterns of the samples were recorded on a Tecnai F20 TEM operating at 200 kV. The Fourier transformed infrared (FTIR) spectra were recorded on a FTS-60 V spectrometer between 4000 and 400 cm^{-1}. The elemental analysis was performed on a Elementar Vario EL elementalanalyzer. The samples of Pt nanoparticles supported on colloidal carbon spheres that had been treated in H_2 and Ar (H_2/Ar = 8:92, v/v) in a tube furnace were taken out and transferred to a glass bottle filled with Ar quickly under the protection of an Ar gas flow and sealed for SEM imaging and FTIR measurement. For SEM imaging, the sample was transferred to the vacuum chamber of the FESEM microscope quickly under an Ar gas flow. For the FTIR measurements, the sample was mixed with KBr in a glove box and pressed into pellets.

[1] a) S. J. Oldenburg, G. D. Hale, J. B. Jackson, N. J. Halas, *Appl. Phys. Lett.* **1999**, 75, 1063–1065; b) J. B. Jackson N. J. Halas, *J. Phys. Chem. B* **2001**, *105*, 2743–2746; c) S.-W. Kim, M. Kim, W. Y. Lee, T. Hyeon, *J. Am. Chem. Soc.* **2002**, *124*, 7642–7643; d) Y. Sun, B. Mayers, Y. Xia, *Adv. Mater.* **2003**, *15*, 641–646; e) J. Bao, H. Liang, Z. Xu, L. Si, *Adv. Mater.* **2003**, *15*, 1832–1835; f) H. Liang, H. Zhang, J. Hu, Y. Guo, L. Wan, C. Bai, *Angew. Chem.* **2004**, *116*, 1566–1569; *Angew. Chem. Int. Ed.* **2004**, *43*, 1540–1543.

[2] a) F. Caruso, R. A. Caruso, H. Möhwald, *Science* **1998**, *282*,1111–1114; b) M. L. Breen, A. D. Dinsmore, R. H. Pink, S. B. Qadri, B. R. Ratna, *Langmuir* **2001**, *17*, 903–907; c) K. P. Velikov, A. van Blaaderen, *Langmuir* **2001**, *17*, 4779–4786; d) A. B. Bourlinos, M. A. Karakassides, D. Petridis, *Chem. Commun.* **2001**, 1518–1519; e) Z. Dai, L. Dähne, H. Möhwald, B. Tiersch, *Angew. Chem.* **2002**, *114*, 4191–4194; *Angew. Chem. Int. Ed.* **2002**, *41*, 4019–4022; f) Z. Yang, Z. Niu, Y. Lu, Z. Hu, C. C. Han, *Angew. Chem.* **2003**, *115*, 1987–1989; *Angew. Chem. Int. Ed.* **2003**, *42*, 1943–1945; g) X. Sun, Y. Li, *Angew. Chem.* **2004**, *116*, 3915–3919; *Angew. Chem. Int. Ed.* **2004**, *43*, 3827-3831.

[3] a) J. O. Uchisawa, A. Obuchi, Z. Zhao, S. Kushiyama, *Appl. Catal. B: Environ.* **1998**, *18*, L183–L187; b) J. O. Uchisawa, A. Obuchi, A. Ogata, R. Enomoto, S. Kushiyama, *Appl. Catal. B* **1999**, 21, 9–17; c) J. O. Uchisawa, A. Obuchi, R. Enomoto, J. Xu, T. Nanba, S. Liu, S. Kushiyama, *Appl. Catal. B* **2001**, 32, 257–268; d) J. O. Uchisawa, S. Wang, T. Nanba, A. Ohi, A. Obuchi, *Appl. Catal. B* **2003**, 44, 207–215; e) L. Pesant, J. Matta, F. Garin, M. J. Ledoux, P. Bernhardt, C. Pham, C. P. Huu, *Appl. Catal. A* **2004**, 266, 21–27.

[4] a) Q. Wang, H. Li, L. Q. Chen, X. J. Huang, *Carbon* **2001**, *39*, 2211–2214; b) J. Hu, H. Li, X. J. Huang, *Solid State Ionics* **2005**, *176*, 1151–1159.

[5] R. Yang , X. Qiu , H. Zhang, J. Li, W. Zhu, Z. Wang, X. Huang, L. Chen, *Carbon* **2005**, *43*, 11–16.

[6] a) A. A. El-Hendawy, *Carbon* **2003**, *41*, 713–722; b) W. Tian, L. Yang, Y. Xu, S. Weng, J. Wu, *Carbohydr. Res.* **2000**, *324*, 45–52.

[7] a) H. A. El Akrami, M. F. Yardim, E. Ekinci, *Fuel* **2000**, 79, 497–504; b) A. M. Puziy, O. I. Poddubnaya, A. Martínez-Alonso, F. Suárez-García, J. M. D. Tascón, *Carbon* **2003**, *41*, 1181–1191.

[8] P. Albers, E. Auer, K. Ruth, S. F. Parker, *J. Catal.* **2000**, *196*, 174–179.

[9] Z. Zhan, S. A. Barnett, *Science* **2005**, *308*, 844–847.

Received: November 29, 2005