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Selective synthesis and characterization of metallic cobalt, cobalt/platinum, and platinum microspheres

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ABSTRACT

Metallic cobalt microspheres have been successfully synthesized via a facile hydrothermal method in the presence of poly (N-vinyl-2-pyrrolidone) (PVP), and the diameters of these spheres are in the range of 1–2 μm. Bimetallic Co/Pt microspheres and hollow noble metal Pt microspheres have also been selectively synthesized by adjusting the amount of reactants of replacement reaction in which corresponding noble metal compound and metallic cobalt microspheres are used as starting materials. The study on catalytic activities of the as-prepared metallic microspheres on hydrolysis of ammonia-borane for hydrogen generation reveals that Co/Pt (molar ratio 5:1) bimetallic microspheres are far more active than the hollow noble metal Pt microspheres.

1. Introduction

Ammonia-borane (H_3NBH_3) has attracted increasing attention as an efficient hydrogen storage material for its high hydrogen content (19.6 wt% hydrogen) and low molecular weight (30.7 g/mol). H_3NBH_3 is highly soluble in water and its solution is stable at room temperature. Unlike borohydrides, ammonia-borane solutions do not require any additional stabilization by using bases but only suitable catalyst (Eq. (1)) [1–14].

$$H_3NBH_3(aq) + 2H_2O(l) \xrightarrow{\text{catalyst}} NH_4^+(aq) + BO_2^-(aq) + 3H_2(g) \qquad (1)$$

Recently, various catalysts for promoting the hydrolysis of NH_3BH_3 have been reported. In particular, noble metal-based catalysts such as Fe@Pt core–shell nanoparticles [9], Au@Co core–shell nanoparticles [8], Pt_xNi_{1-x} nanoparticles [15,16], ruthenium supported on carbon [17], water-soluble poly (4-styrenesulfonic acid-co-maleic acid) stabilized ruthenium(0) and palladium(0) nanoclusters [18], zeolite confined palladium(0) nanoclusters [5], zeolite confined rhodium(0) nanoclusters [6], zeolite framework stabilized rhodium(0) nanoclusters [19], water soluble laurate-stabilized ruthenium(0) nanoclusters [20] have exhibited very high catalytic activity for hydrolysis of NH_3BH_3. Non-noble metal catalysts such as Co nanoparticles [21], Ni nanoparticles [7], intrazeolite cobalt(0) nanoclusters [2], cobalt chloride $CoCl_2$ [3], nanoparticle-assembled Co-B thin film [22], electroplated Co–P [1], cobalt–molybdenum–boron/nickel foam [23], water-soluble polymer-stabilized cobalt(0) nanoclusters [24], poly (N-vinyl-2-pyrrolidone) (PVP) stabilized nickel [25], nanosized Co- and Ni-based catalysts [26], zeolite confined copper(0) nanoclusters [27], hollow Ni–SiO_2 nanosphere [28], Fe–Ni alloy [29] have also shown high H_2 generation kinetics from hydrolysis of NH_3BH_3.

Various methods have been successfully applied to the synthesis of bimetallic nanoparticles and hollow noble metallic materials [15,16,30–39]. An alternative route has been reported to prepare hollow noble metal materials with different shapes by a transmetalation reaction in which suitable metal ion nanoparticles react with a sacrificial partner and finally lead to the formation of hollow spheres inheriting the morphology of the sacrificial partner, and urchinlike hollow metallic and bimetallic nanospheres have been synthesized [40–42]. Yan et al. [8] reported a rational and general strategy for preparing magnetically recyclable Au@Co core–shell nanoparticles through the one-step seeding-growth route at room temperature under ambient atmosphere within a few minutes. The resultant magnetically recyclable Au@Co nanoparticles exerted excellent catalytic activity and longterm stability toward the hydrolytic dehydrogenation of aqueous NH_3BH_3. Yi et al. [42] demonstrated that hollow metallic microspheres (e.g., Ni, Ni/Au, Ni/Pt, Ni/Pd, Pt, Pd, etc.) could be successfully synthesized based on the reduction and replacement reaction and revealed that the catalytic activity of hollow bimetallic microspheres was much higher than those of pure noble metal microspheres. Those studies have successfully expanded the catalyst materials for hydrogen generation from noble metal such as Pt and Rh to more abundant and economical first-row metals.

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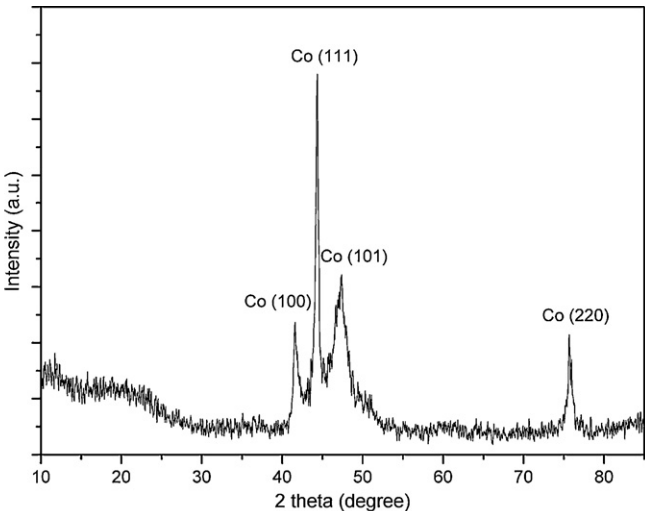


Fig. 1. XRD patterns of the as-prepared metallic Co spheres.

Herein, we demonstrate a facile synthesis strategy for fabricating metallic cobalt microspheres via a direct reduction of cobalt(II) chloride by hydrazine hydrate in the presence of poly (N-vinyl-2-pyrrolidone) (PVP) stabilizer in ethylene glycol solution. PVP-stabilized cobalt(0) nanoclusters are found to be stable in solution, highly active and long-lived in hydrolyses of ammonia-borane. The direct reduction route provides a new method for large-scale synthesis of metallic cobalt spheres and other metallic spheres. On the basis of replacement reaction, bimetallic (Co/Pt) and noble metal (Pt) spheres have also been obtained as corresponding noble metal compounds interacting with as-prepared metallic cobalt spheres. The investigation on catalytic activities of hollow noble metal and bimetallic spheres reveals the superior catalytic activities of Co/Pt bimetallic spheres for hydrogen generation, respectively.

2. Experimental

2.1. Chemicals

Ammonia-borane (NH_3BH_3) was of 90% grade from the Aldrich, cobalt(II) chloride hexahydrate ($CoCl_2{\cdot}6H_2O$) was of analytical reagent grade and obtained from the Beijing Chemical Reagents Factory, chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$), hydrazine hydrate, ethylene glycol and poly (N-vinyl-2-pyrrolidone) (PVP) were of analytical grade and purchased from the Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as starting materials without further purification. Deionized water was used throughout the experiment.

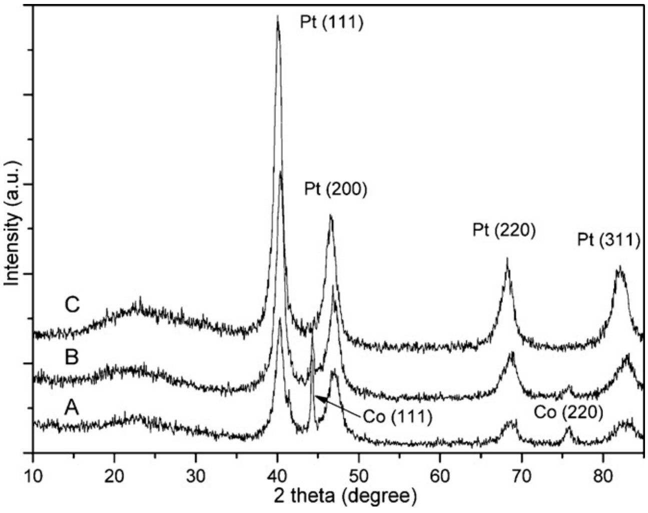


Fig. 3. XRD patterns of the as-prepared spheres: (A) Co/Pt (molar ratio 10:1), (B) Co/Pt (molar ratio 5:1) and (C) Pt.

2.2. Synthesis

1 mmol of $CoCl_2{\cdot}6H_2O$ and 0.5 g of poly (N-vinyl-2-pyrrolidone) (PVP) were put into a beaker of 100 mL and dissolved in 30 mL of ethylene glycol before the beaker was sealed and stirred vigorously for 1 h at room temperature. Then 2 mL of hydrazine hydrate was added into the beaker and stirred for 1 h in confined conditions at room temperature. After that, the solution was sealed in a 50 mL Teflon-lined autoclave, and was maintained at 200 °C for 4 h without shaking or stirring, and then the system was cooled to room temperature naturally. The resulting products were collected by filtration and washed with absolute ethanol and distilled water in sequence several times. The final product was dried in a vacuum box at 60 °C.

As-prepared metallic Co spheres (1 mmol) were suspended in deionized water by ultrasonic treatment. Afterward, a freshly prepared HCl solution (5 wt%) was added slowly to remove the oxidation layer on metallic Co spheres. The upper solution was decanted immediately when continuous bubbles were observed, indicating metallic Co started to react with HCl to release H_2 and the removal process of oxidation layer was complete. The Co powders were washed with distilled water several times by centrifugation and then freshly processed Co powders were added to a certain amount of the chloroplatinic acid ($H_2PtCl_6{\cdot}6H_2O$) solution according to the designed molar ratio of Co: Pt (10:1, 5:1 and 2:1, M). The replacement reaction was allowed to proceed for 6 h without stirring and shaking at room temperature. Finally, the obtained products were collected and washed with absolute ethanol and distilled water in sequence several times and then dried in vacuum box at 60 °C for 30 min.

2.3. Catalyst study

The hydrolysis of ammonia borane (NH_3BH_3) was carried out at 35 °C. A 0.0012 g sample of catalyst (metallic Co, Pt spheres and Co/Pt bimetallic spheres) was kept in a round-bottom flask with the opening connected to an inverted, water-filled graduated burette. The reaction was started and proceeded under constant stirring with the addition of aqueous NH_3BH_3 solution (50 mL, 0.25 wt%). The volume of generated H_2 was recorded per minute.

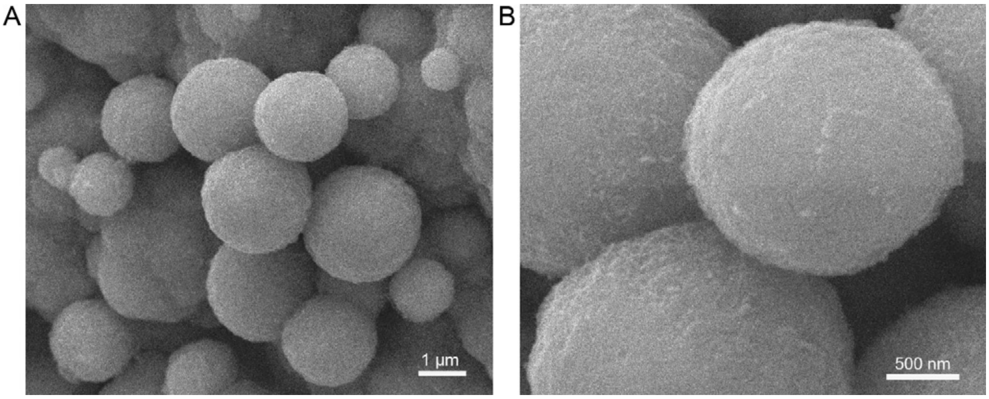


Fig. 2. SEM images of the as-prepared metallic Co spheres.

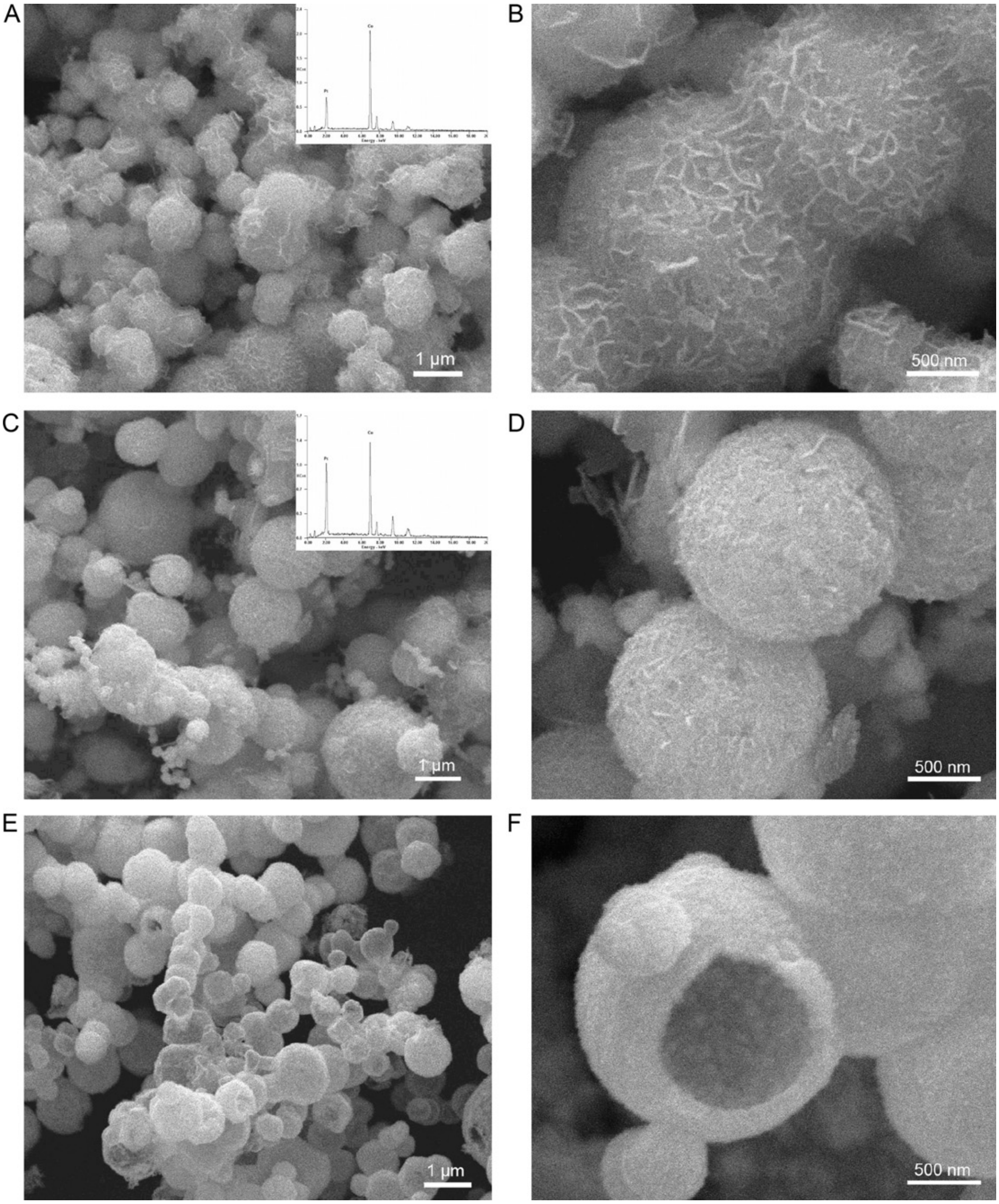


Fig. 4. SEM images of the as-prepared the Co/Pt bimetallic spheres: (A and B) Co/Pt (molar ratio 10:1), (C and D) Co/Pt (molar ratio 5:1) and (E and F) Pt. EDS spectrum of the as-prepared the Co/Pt bimetallic spheres: (insert of A) Co/Pt (molar ratio 10:1) and (insert of C) Co/Pt (molar ratio 5:1).

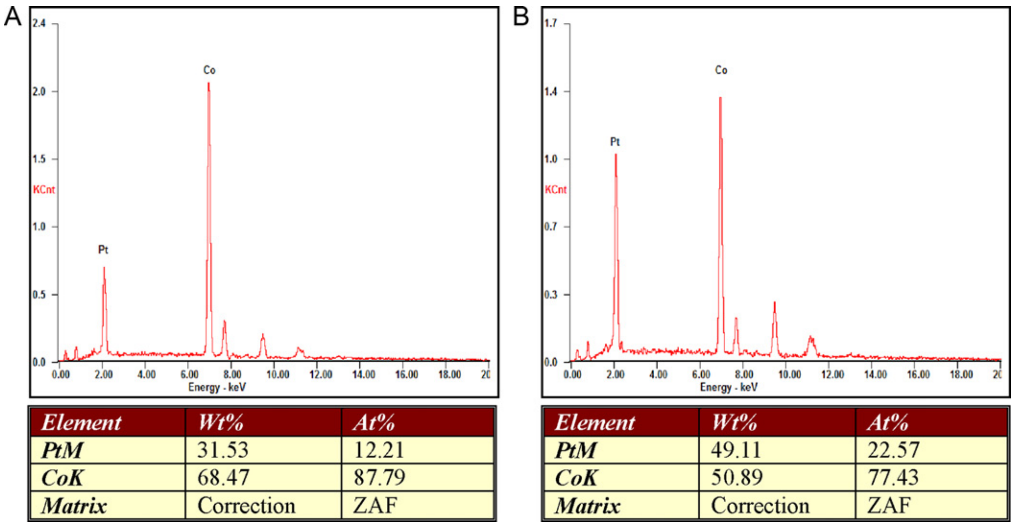
2.4. Characterization

The obtained samples were characterized on a Rigaku Dmax-2000 X-ray powder diffractometer (XRD) with Cu Kα radiation (λ = 1.5418 Å). The operation voltage and current were kept at 40 kV and 40 mA, respectively. The size and morphology of the as-synthesized products were determined at 20 kV by a XL30 S-FEG scanning electron microscope (SEM). Energy-dispersive X-ray spectroscopy (EDS) was taken on the SEM. The specific surface area of the cobalt/platinum and platinum microspheres was detected by Brunauer–Emmett–Teller (BET) nitrogen adsorption–desorption measurements (NOVA-1000). Before the analysis, the samples were outgassed at 90 °C under vacuum.

3. Results and discussion

X-ray diffraction (XRD) was carried out to determine the chemical composition and crystallinity of the as-prepared products. Fig. 1 shows the typical XRD pattern of Co spheres. Two characteristic diffraction peaks can be indexed as (1 1 1) and (2 2 0) crystal planes of face-centered cubic Co, in good accordance with the reported data (space group *Fm*3*m* (2 2 5), PDF# 15-0806, *a* = 3.5477 Å), and two characteristic diffraction peaks can be indexed as (1 0 0) and (1 0 1) crystal planes of hexagonal Co, in good accordance with the reported data (space group *P63*/*mmc* (1 9 4), PDF# 05-0727, *a* = 2.0531, *c* = 4.0605 Å). Moreover, the sharp and narrow diffraction peaks indicated the well-crystallinity of the Co spheres. The peaks of any impurities were not detected, which indicated that the metallic Co was successfully obtained with high purity.

Scanning electron microscopy (SEM) analysis (Fig. 2A) shows metallic cobalt microspheres synthesized via a direct reduction of cobalt(II) chloride by hydrazine hydrate in the presence of poly (N-vinyl-2-pyrrolidone) (PVP) stabilizer in ethylene glycol solution. More details of those spheres can be obtained from the high-magnification SEM image (Fig. 2B). The diameters of these spheres



Element	*Wt%*	*At%*
PtM	31.53	12.21
CoK	68.47	87.79
Matrix	Correction	ZAF

Element	*Wt%*	*At%*
PtM	49.11	22.57
CoK	50.89	77.43
Matrix	Correction	ZAF

Fig. 5. EDS spectrum of the as-prepared the Co/Pt bimetallic spheres: (A) Co/Pt (molar ratio 10:1, insert of Fig. 4A) and (B) Co/Pt (molar ratio 5:1, insert of Fig. 4C).

are in the range of 1–2 μm, and the surface of the Co spheres is very tight. The diameter of metallic cobalt microspheres (secondary particles) is far larger than the particle size based on X-ray diffraction (XRD) analysis, which indicates that the microspheres are composed of individual nanoparticles (primary particles) with an average size of about 28 nm.

The Co/Pt bimetallic spheres and hollow Pt spheres are obtained by replacement reaction between metallic Co spheres and the chloroplatinic acid. The driving force of those reactions comes from the large standard reduction potential gap between the Co^{2+}/Co redox pair (−0.280 V vs standard hydrogen electrode (SHE)) and the $PtCl_6^{2-}/Pt$ redox pair (0.74 V vs standard hydrogen electrode (SHE)). Fig. 3A and B displays XRD patterns of the as-prepared Co/Pt bimetallic spheres. The characteristic diffraction peaks of Co ((1 1 1) and (2 2 0)) and Pt ((1 1 1), (2 0 0), (2 2 0) and (3 1 1)) are also found in the patterns of the Co/Pt bimetallic spheres sample, indicating the successful replacement of non-noble metal. Fig. 3C displays XRD patterns of the as-prepared hollow Pt spheres. Prominent peaks ((1 1 1), (2 0 0), (2 2 0) and (3 1 1)) in the XRD patterns correspond to the reflections of the face-centered cubic structure of Pt, in good accordance with the reported data (space group *Fm*3*m* (2 2 5), PDF# 87-0647, $a = 3.878$ Å). The sharp and narrow diffraction peaks indicate the well-crystallinity of the as-prepared Co/Pt bimetallic spheres and hollow Pt spheres (Fig. 3).

Fig. 4A–D shows the SEM images of Co/Pt bimetallic spheres. The diameters of these spheres are in the range of 1–2 μm. The diameter of the Co/Pt bimetallic spheres microspheres (secondary particles) is far larger than the particle size based on X-ray diffraction (XRD) analysis, which indicates that the microspheres are composed of individual nanoparticles (primary particles) with an average size of about 28 nm Co nanoparticles and 11 nm Pt nanoparticles. It is known that the bimetallic nanoparticles prepared by using solid templates could be alloy nanoparticles in which the two constituent metals are mixed at the atomic level [43–45] or core/shell nanoparticles in which the two components are separated by distinct phase boundaries [46,47] or even core/shell nanoparticles with an alloy shell and a pure core [48]. However, all the peaks of the Pt and Co can be observed without shift compared with those of pure Pt and Co in our work (Figs. 1 and 3), distinct from the XRD pattern of a Co–Pt alloy [42]. Meanwhile, many flakes are in the surface of Co/Pt bimetallic spheres (Fig. 4A–D), which indicate that the $PtCl_6^{2-}$ may react with Co atoms on the surface, in the case of the formation of the core/shell structure. As the molar ratio of cobalt to platinum decreases, the surface of spheres becomes smoother. The result of EDS analysis (Fig. 5) reveals the sample mainly consists of Co and Pt, therefore, it indicates that the Co/Pt bimetallic spheres have been successfully obtained, which is in good accordance with XRD results.

The SEM images of the as-prepared Pt samples are shown in Fig. 4E and F, in which some broken spheres can be clearly seen, exhibiting the hollow structure of the obtained Pt spheres. The hollow Pt spheres are obtained by replacement reaction between metallic Co spheres and the chloroplatinic acid because the Pt lattice constant ($a = 3.878$ Å) is larger than the Co lattice constant ($a = 3.5477$ Å), and two Co atoms are replaced by one platinum atom. Furthermore, the surface of the hollow Pt spheres with a diameter range of 1–2 μm is very tight, resembling those of metallic Co spheres. The diameter of the hollow Pt spheres (secondary particles) is far larger than the particle size based on X-ray diffraction (XRD) analysis, which indicates that the microspheres are composed of individual nanoparticles (primary particles) with an average size of about 11 nm.

The catalytic activities of the as-prepared spheres for hydrogen generation from ammonia borane (NH_3BH_3) were investigated and the results are shown in Fig. 6. In comparison, the catalytic activities of products containing Pt are favorable, among which Co/Pt

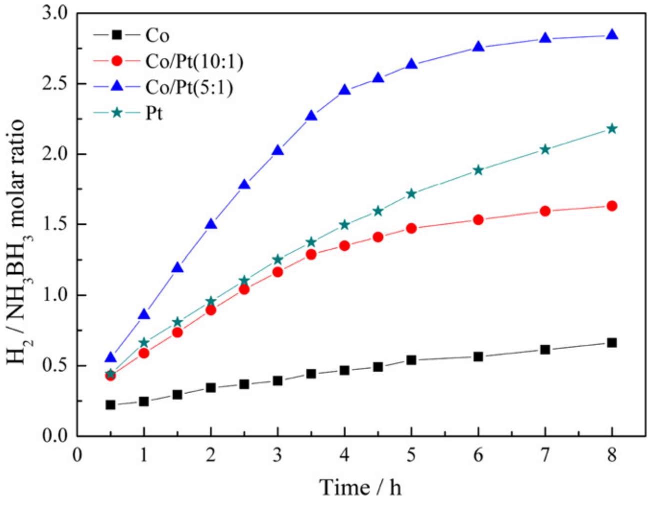


Fig. 6. Hydrogen release from the hydrolysis of aqueous NH_3BH_3 solution (50 mL, 0.25 wt%) in the presence of various as-prepared catalysts (12 mg) at 35 °C.

(molar ratio 5:1) bimetallic spheres show the highest activity. It is noteworthy that Co/Pt (molar ratio 5:1) bimetallic spheres can catalyze the hydrolysis of NH_3BH_3 at 35 °C, and about more than 2.5 out of 3.0 (H_2/NH_3BH_3, molar ration) can be generated over 4 h. BET nitrogen-adsorption measurements show that the specific surface area of the Co/Pt (molar ratio 10:1) bimetallic spheres, Co/Pt (molar ratio 5:1) bimetallic spheres and hollow Pt spheres is 3.50 m^2/g, 3.21 m^2/g and 2.43 m^2/g, respectively, which is in good accordance with the spheres surface features in Fig. 4. According to the results presented above, Co/Pt (molar ratio 5:1) bimetallic spheres exhibit higher catalytic activity than that of Co/Pt (molar ratio 10:1) bimetallic spheres and hollow Pt spheres for the hydrolysis of NH_3BH_3 and the interpretation of the reason follows. First, the BET surface area of the Co/Pt (molar ratio 5:1) bimetallic spheres is much larger than that of the hollow Pt spheres, exposing more active sites for the catalytic reaction to happen. Second, the hollow Pt spheres have inevitably collapsed after complete replacement reaction, making the surface area decrease to some extent and further weakening the catalytic activities. Third, the BET surface area of the Co/Pt (molar ratio 5:1) bimetallic spheres is smaller than that of the Co/Pt (molar ratio 10:1) bimetallic spheres, but the Co/Pt (molar ratio 5:1) bimetallic spheres have much more Pt than that of the Co/Pt (molar ratio 10:1) bimetallic spheres, making more active sites for the catalytic reaction. Due to their relatively higher catalytic activities and much lower cost compared to hollow Pt spheres, Co/Pt (molar ratio 5:1) hollow bimetallic spheres may have potential applications in portable hydrogen generation systems.

4. Conclusions

In summary, metallic cobalt microspheres have been successfully synthesized via a facile hydrothermal method in the presence of poly (N-vinyl-2-pyrrolidone) (PVP), and the diameters of these spheres are in the range of 1–2 μm. Bimetallic Co/Pt microspheres and hollow noble metal Pt microspheres have also been obtained via a replacement reaction route using metallic Co microspheres as sacrificial templates. The catalytic activities of the as-prepared metallic microspheres for hydrogen generation by hydrolysis of ammonia borane have been investigated; the results show much enhanced favorable catalytic performance of Co/Pt (molar ratio 5:1) bimetallic microspheres with the larger BET surface area comparing with the hollow Pt spheres, providing a new possible alternative in the making of portable fuel cells. This strategy provides an effective method for the fabrication of other pure and composite hollow spheres.

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