$\text{Ni}_{1-x}\text{Pt}_x$ ($x=0\sim 0.12$) Hollow Spheres as Catalysts for Hydrogen Generation from Ammonia Borane

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Figure S1. Typical SEM (a, d, g) images, TEM (b, e, h) images, and EDX (c, f, i) spectra of the as-synthesized hollow sphere: $\text{Ni}_{0.97}\text{Pt}_{0.03}$ (a, b, c); $\text{Ni}_{0.94}\text{Pt}_{0.06}$ (d, e, f); $\text{Ni}_{0.91}\text{Pt}_{0.09}$ (g, h, i).

Figure S2. SEM image of commercial Ni powders. The powders are not uniform in particle sizes, which range from several micrometers to tens of micrometers and are much larger than that of the as-synthesized $\text{Ni}_{1-x}\text{Pt}_x$ hollow spheres.

Figure S3. Hydrogen generation from 50 mL aqueous NH_3BH_3 solution (1.0 wt %) in the presence of $\text{Ni}_{0.88}\text{Pt}_{0.12}$ hollow spheres at different temperatures.

Figure S4. TPD curves of the thermal decomposition of neat NH_3BH_3 (black line) and NH_3BH_3 mixed with $\text{Ni}_{0.88}\text{Pt}_{0.12}$ hollow spheres (red line). Two notable features can be observed in the curves. First, the onset temperature of hydrogen release for the mixture is much lower than that for neat NH_3BH_3 , that is, 56 °C vs. 86 °C. Second, the mixture exhibits merely one peak at approximately 100 °C. However, two peaks at the temperatures of about 110 and 150 °C were detected for neat NH_3BH_3 , which are attributed to the first hydrogen release with the formation of polyaminoborane $((\text{NH}_2\text{BH}_2)_n)$ and the second hydrogen release with the formation of polyiminoborane $((\text{NHBH})_n)$, respectively.¹⁻⁴ In addition, the intensity of the peak for the mixture is markedly higher than that for neat sample. These features indicate that $\text{Ni}_{0.88}\text{Pt}_{0.12}$ hollow spheres lead to an enhanced rate and amount of mass loss from the thermal decomposition of NH_3BH_3 .

Figure S5. XRD patterns of (a) unheated neat NH_3BH_3 and (b) the solid sample collected after heating NH_3BH_3 in the presence of $\text{Ni}_{0.88}\text{Pt}_{0.12}$ hollow spheres at 120 °C for 2h. The diffraction peak centered at $2\theta = 24.02^\circ$ is multiplied by a factor of 1/30 in order to strength other relatively weak peaks. The XRD pattern of NH_3BH_3 is in good agreement with reported data.⁵

Reference

- (1) Gutowska, A.; Li, L.; Shin, Y.; Wang, C. M.; Li, X. S.; Linehan, J. C.; Smith, R. S.; Kay, B. D.; Schmid, B.; Shaw, W.; Gutowski, M.; Autrey, T. *Angew. Chem. Int. Ed.* **2005**, *44*, 3578.
- (2) Baitalow, F.; Baumann, J.; Wolf, G.; Jaenicke-Rößbler, K.; Leitner, G. *Thermochim. Acta.* **2002**, *391*, 159.
- (3) Wolf, G.; Baumann, J.; Baitalow, F.; Hoffmann, F. P. *Thermochim. Acta.* **2000**, *343*, 19.
- (4) Sit, V.; Geanangel, R. A.; Wendlandt, W. W. *Thermochim. Acta.* **1987**, *113*, 379.
- (5) Shore, S. G.; Parry, R. W. *J. Am. Chem. Soc.* **1955**, *77*, 6084.