

Electronic Supplementary Information (ESI) for

**A High-Performance Pt-Co Bimetallic Catalyst with
Polyethyleneimine Decorated Graphene Oxide as Support for
Hydrolysis of Ammonia Borane**

Mengxiong Li[†], Jiantong Hu[†], Zhongxin Chen and Hongbin Lu*

State Key Laboratory of Molecular Engineering of Polymers, and Department of Macromolecular Science, Fudan University, 220 Handan Road, Shanghai, 200433, China. Tel/Fax: 86-21-5566 4589. To whom correspondence should be addressed: hongbinlu@fudan.edu.cn, 11307110025@fudan.edu.cn.

This PDF includes:

1. XRD Paterns of Catalysts PEI-GO/Pt_xCo_{1-x};
 2. Recycle Tests of PEI/Pt_{0.17}Co_{0.83};
 3. XPS studies of the catalyst PEI-GO/Pt_{0.17}Co_{0.83};
 4. Comparison of GO with Other Carbon Materials;
 5. Further Investigation in the Synergistic Effect between Pt with Co;
 6. XRD Patterns of PEI-GO/Pt_{0.17}Co_{0.83} Before and After Catalytic Reaction;
 7. Calculation Methods
-

1. XRD Patterns of Catalysts PEI-GO/Pt_xCo_{1-x}:

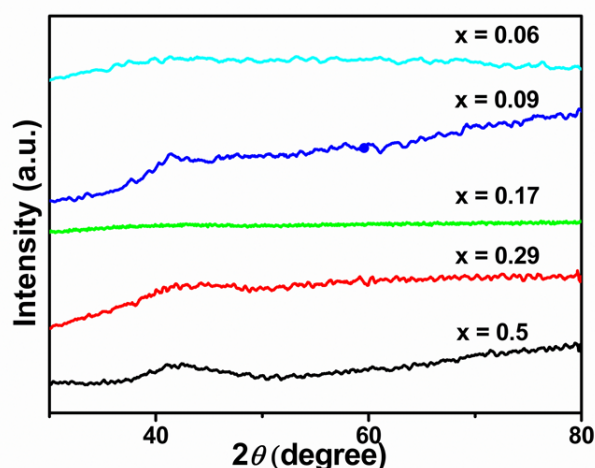


Fig. S1. XRD patterns of a series of catalysts PEI-GO/Pt_xCo_{1-x}.

XRD patterns of PEI-GO/Pt_xCo_{1-x} with different x values are shown in **Fig. S1**. The catalysts are almost amorphous.^{1,2}

2. Recycle Tests of PEI/Pt_{0.17}Co_{0.83}:

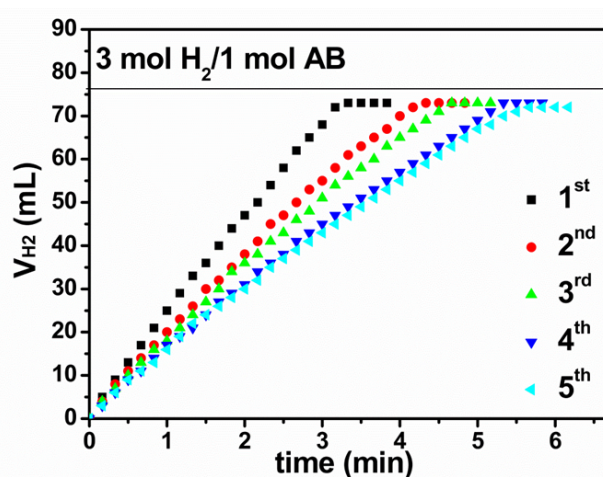


Fig. S2 Hydrogen generation from the hydrolysis of AB catalyzed by PEI/Pt_{0.17}Co_{0.83} at sequential runs at 25 ± 0.5 °C with [AB]/[metal] = 366.7. Volume of the dispersion is 10 mL.

To investigate the role of GO and PEI in the catalytic reaction, further experiments were carried out. From **Fig. 3a** we can get that GO/Pt_{0.17}Co_{0.83} has much better catalytic activity compared with Pt_{0.17}Co_{0.83}. It can be ascribed to the fact that the addition of GO improves dispersion of the small metal NPs, leading to the increased catalytic activity. In the absence of GO, PEI/Pt_{0.17}Co_{0.83} also shows good catalytic activity, which is slightly lower than that of PEI-GO/Pt_{0.17}Co_{0.83}. However, further study of PEI/Pt_{0.17}Co_{0.83} reveals poor recyclability, only ~ 60% of the initial activity is retained after 5 cycles (**Fig. S2**), while PEI-GO/Pt_{0.17}Co_{0.83} retains about ~ 80% of the initial activity after the 5th cycle (**Fig. 6a**). It can be concluded that the immobilization of amine groups on PEI molecules to metal ions improves the dispersion of metal NPs, which greatly increases the catalytic activity. Nevertheless, flexible PEI molecules can't prevent the aggregation of metal NPs.

The encapsulation of metal NPs in PEI molecules during the catalytic reaction may happen,^{3,4} which makes PEI/Pt_{0.17}Co_{0.83} show poor recyclability. With the addition of GO, PEI molecules tend to form a collapsed pancake-like structure on GO surface through hydrogen bonding and covalent bonding interactions.⁵ This can not only improve the immobilization of metal ions on PEI chains, but also mitigate the encapsulation and aggregation of metal NPs during the reaction. In this sense, GO plays an important role in controlling the morphology of PEI molecules and metal NPs, which is critical for achieving high catalytic activity and recyclability.

3. XPS studies of the catalyst PEI-GO/Pt_{0.17}Co_{0.83}:

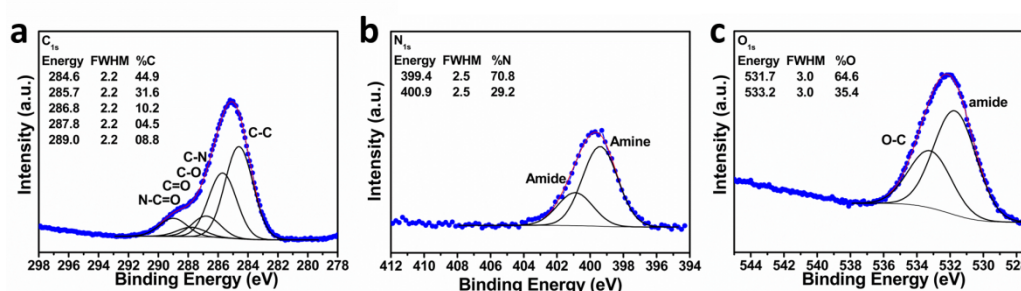


Fig. S3 XPS spectra of (a) C_{1s}, (b) N_{1s} and (c) O_{1s} core-levels for PEI-GO/Pt_{0.17}Co_{0.83}.

XPS study of PEI-GO/Pt_{0.17}Co_{0.83} was carried out and results were shown in **Fig. S3** and **Fig. 7a, b**. By comparison between **Fig. S3** and **Fig. 1a-c** it is observed that the peak values C_{1s}, N_{1s} and O_{1s} remain constant after anchoring metal NPs. This implies that there is no obvious interaction between the support matrix with metal NPs.

4. Comparison of GO with Other Carbon Materials:

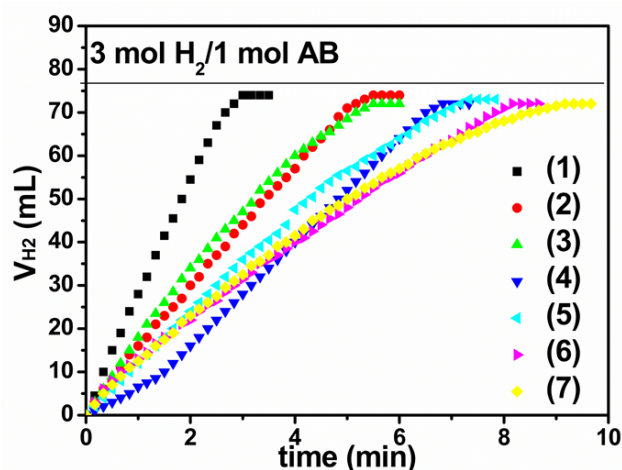


Fig. S4 Hydrogen generation of AB hydrolysis in the presence of Pt_{0.17}Co_{0.83} NPs with different support: (1) PEI-GO; (2) GO; (3) PEI-MWCNT; (4) PEI-AC; (5) MWCNT; (6) AC and (7) without support.

Activated carbon (AC) and multi-wall carbon nanotubes (MWCNT) are well-known supports in the catalysis field. They are used as control materials to clarify the advantage of GO. AC-, PEI-

AC-, MWCNT- and PEI-MWCNT-supported catalysts were prepared. AC was treated with nitric acid (2 M) to introduce oxygen groups.⁷ Carboxyl MWCNT was directly bought from Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. PEI-AC and PEI-MWCNT were then synthesized following a procedure similar to the preparation of PEI-GO. The result is shown in **Fig. S4**. AC/Pt_{0.17}Co_{0.83} and MWCNT/Pt_{0.17}Co_{0.83} show enhanced activity compared with Pt_{0.17}Co_{0.83}, but lower than that of GO/Pt_{0.17}Co_{0.83}. When PEI was introduced into the catalyst system, PEI-AC/Pt_{0.17}Co_{0.83} and PEI-MWCNT/Pt_{0.17}Co_{0.83} show improved activity, but still lower than that of GO/Pt_{0.17}Co_{0.83}. The porous structure of AC may cause spatial limitation for diffusion of reactants and the one-dimension character of MWCNT may limit the morphology control capability of PEI. In contrast, PEI-GO/Pt_{0.17}Co_{0.83} shows the best catalytic activity in all these samples. Given that GO has two-dimensional morphology, abundant oxygen functional groups, and higher specific surface areas, it is reasonable for GO to exhibit better morphology control capability of PEI and metal NPs.

5. Further Investigation in the Synergistic Effect between Pt with Co:

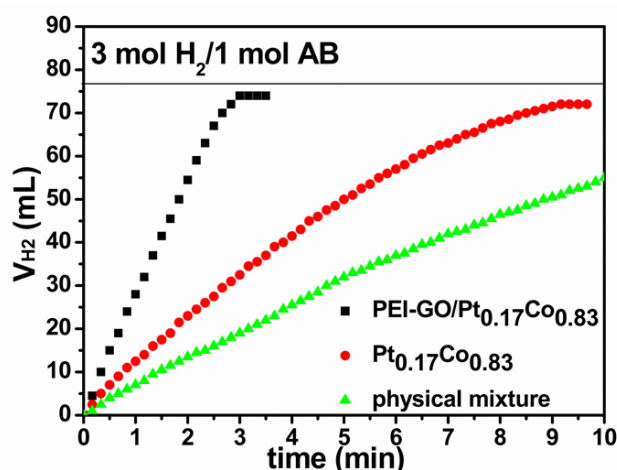


Fig. S5 Hydrogen generation from AB with different catalysts at 25 ± 0.5 °C. The physical mixture represents the mixture of PEI-GO/Pt and PEI-GO/Co. For all the catalytic reaction system, $[AB] = 110$ mM, $[Pt] = 0.05$ mM and $[Co] = 0.25$ mM. Volume of the dispersion is 10 mL.

To further illustrate the synergistic effect between these two metals, a physical mixture of PEI-GO/Pt and PEI-GO/Co was prepared for the catalytic hydrolysis of AB as shown in **Fig. S5**. PEI-GO/Pt and PEI-GO/Co were prepared in the same way described in our Experimental part. After the reduction reaction, the two catalysts were mixed together with mechanical stirring. The physical mixture reveals a much lower activity than that of PEI-GO/Pt_{0.17}Co_{0.83}, and even lower than that of Pt_{0.17}Co_{0.83} (**Fig. 3a**). Apparently, such a catalytic behaviour can be attributed to the loss of the synergistic effect between the two metals, also indicating the critical role of the synergistic effect in the catalytic activity of our catalysts.

6. XRD Patterns of PEI-GO/Pt_{0.17}Co_{0.83} Before and After Catalytic Reaction:

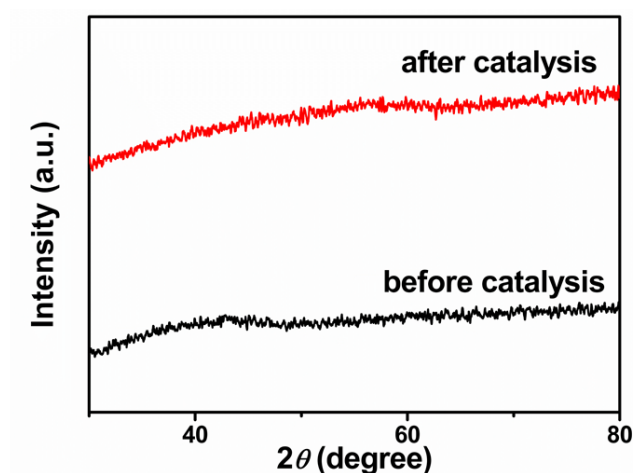


Fig. S6 XRD patterns of PEI-GO/Pt_{0.17}Co_{0.83} before and after the catalytic reaction.

Fig. S6 shows the XRD patterns of PEI-GO/Pt_{0.17}Co_{0.83} before and after the catalytic reaction. No reaction-induced crystalline phase appeared during the catalytic reaction, indicating the amorphous structure of metal NPs,² which is consistent with the result shown in **Fig. 6b**.

7. Calculation Methods

The calculation methods used in this work are given below.

(1) Conversion rate (*c*) calculation

$$c = \frac{P_{atm}V/RT}{3n_{AB}}$$

where P_{atm} is the atmospheric pressure, V is the generated gas volume, R is the universal gas constant, T is room temperature (298 K), and n_{AB} is the mole number of AB.

(2) Total TOF calculation

$$TOF = \frac{P_{atm}V_{total}/RT}{n_m t}$$

where V_{total} is the total volume of hydrogen released, n_m is the mole number of metals added (adduct of Pt and Co) and t represents the time cost by the generation of V_{total} H₂.

(3) Linear Hydrogen generation rate (*r*) calculation

$$r = \frac{V_{linear}}{m_m t}$$

where V_{linear} is the volume of hydrogen released when c reaches 30%, m_m is the mass of metals added (adduct of Pt and Co) and t is the time cost by the generation of V_{linear} H₂. r is mainly used

to calculate the activation energy in this manuscript.

References:

1. F. Y. Qiu, L. Li, G. Liu, Y. J. Wang, Y. P. Wang, C. H. An, Y. N. Xu, C. C. Xu, Y. Wang, L. F. Jiao and H. T. Yuan, *Int. J. Hydrogen Energy*, 2013, **38**, 3241-3249.
2. H. L. Jiang, T. Umegaki, T. Akita, X. B. Zhang, M. Haruta and Q. Xu, *Chem. Eur. J.*, 2010, **16**, 3132-3137.
3. M. Schneider, M. Brinkmann and H. Mohwald, *Macromolecules*, 2003, **36**, 9510-9518.
4. R. M. Crooks, M. Zhao, L. Sun, V. Chechik and L.K. Yeung, *Accounts Chem. Res.*, 2001, **34**, 181-190.
5. X. H. Zhou, Z. X. Chen, D. H. Yan and H. B. Lu, *J. Mater. Chem.*, 2012, **22**, 13506-13516.
6. A. Khelifi, M. C. Almazan-Almazan, M. Perez-Mendoza, M. Domingo-Garcia, F. J. Lopez-Dominngo, L. Temdrara, F. J. Lopez-Garzon and A. Addoun, *Fuel Process. Technol.*, 2010, **91**, 1338-1344.