



Development of ultrafine metal nanoparticles for catalytic hydrogen generation from liquid chemical hydrides

Yang, Xinchun

(Degree)

博士 (工学)

(Date of Degree)

2018-03-25

(Date of Publication)

2020-03-25

(Resource Type)

doctoral thesis

(Report Number)

甲第7197号

(URL)

<https://hdl.handle.net/20.500.14094/D1007197>

※ 当コンテンツは神戸大学の学術成果です。無断複製・不正使用等を禁じます。著作権法で認められている範囲内で、適切にご利用ください。



Doctoral Dissertation

Development of ultrafine metal nanoparticles for catalytic
hydrogen generation from liquid chemical hydrides

(水素発生用超微細な金属ナノ粒子触媒の開発)

January, 2018

Graduate School of Engineering,

Kobe University

YANG XINCHUN

楊 新春

Acknowledgements

This dissertation is dedicated to all the people who have helped me until now.

The work described in the present doctoral dissertation has been carried out in the Cooperative Division (located at Kansai Centre, National Institute of Advanced Industrial Science and Technology (AIST)) at the Department of Chemical Science and Engineering, Graduate School of Engineering, Kobe University during 2014.10-2018.03.

I would like to express my deepest gratitude to Professor Qiang Xu for his powerful guidance, inspiring ideas, constructive suggestions, valuable discussions, kind consideration, and for his carefully reading of this dissertation.

I sincerely thank Professor Minoru Mizuhata, Professor Satoru Nishiyama and Professor Tsutomu Ioroi for valuable supports and critically reading of this dissertation.

I am grateful to Ms. Hitomi Fujii, Ms. Naoko Yamawaki and other members in our group for their valuable suggestions and supports.

I thank for financial supports from MEXT, AIST and Kobe University.

Finally, I appreciate my family for their constant supports and mental encouragements.

YANG XINCHUN

January, 2018

Osaka, Japan

Contents

Abstract.....	I
Chapter 1	1
Recent Advances in Hydrogen Generation from Liquid Chemical Hydrides by Metal Nanoparticle Catalysts.....	1
1.1 Introduction.....	1
1.2 Hydrogen generation from formic acid	2
1.3 Hydrogen generation from ammonia borane.....	6
1.4 Conclusions.....	11
Chapter 2	16
Immobilization of Highly Catalytically Active bimetallic AuPd NPs on Reduced Graphene Oxide for Hydrogen Generation from Formic Acid	16
2.1 Introduction.....	16
2.2 Experimental details.....	17
2.3 Results and discussion	19
2.4 Conclusions.....	31
Chapter 3	34
Encapsulation of Highly Catalytically Active Pd Nanoclusters inside Porous Organic Cages for Hydrogen Generation from Ammonia Borane	34
3.1 Introduction.....	34
3.2 Experimental details.....	35
3.3 Results and discussion	40
3.4 Conclusions	62
Chapter 4	66
Solid Solution Alloying of Classically Immiscible Au and Rh for Highly Efficient Catalytic Hydrogen Generation from Formic Acid	66
4.1 Introduction.....	66
4.2 Experimental details.....	68
4.3 Results and discussion	69
4.4 Conclusions.....	78
Chapter 5	81
Conclusions	81
List of Publications.....	84

Abstract

Our common future calls on chemists to make great efforts to establish a more sustainable world. Hydrogen, as a clean, effective, renewable and promising energy carrier, has received great attention. The present dissertation focuses on the development of ultrafine metal nanoparticles (MNPs) for catalytic hydrogen generation from liquid chemical hydrides. Chapter 1 describes the recent advances in hydrogen generation from liquid chemical hydrides using heterogeneous MNP catalysts. In the subsequently chapters, the findings gained during the Ph.D. program are presented, which include the synthesis and characterization of newly-developed MNPs and their applications as heterogeneous catalysts for hydrogen generation from liquid chemical hydrides, including formic acid (FA) and ammonia borane (AB). Reduced graphene oxide (rGO)-supported bimetallic Au-Pd alloy NPs have been synthesized using a non-noble metal sacrificial approach (*NNMSA*), which exhibit excellent catalytic performance for the dehydrogenation of FA. Organic molecular cage-encapsulated Pd nanoclusters (NCs) have been synthesized using a reverse double solvents approach (*RDSA*), which are highly efficient for the methanolysis of AB. In addition, bimetallic Au-Rh nanoclusters composed of classically immiscible Au and Rh metals have been synthesized using a functionalized carbon, which show great promising for the dehydrogenation of FA. The main findings of this dissertation are summarized as follows:

(I) Immobilization of highly catalytically active bimetallic AuPd NPs on rGO for hydrogen generation from formic acid

Highly dispersed bimetallic Au-Pd alloy NPs have been successfully immobilized on rGO using a facile *NNMSA*. The $\text{Co}_3(\text{BO}_3)_2$ co-precipitated with Au-Pd NPs and subsequently sacrificed by acid etching effectively

prevents the primary Au-Pd NPs from aggregation. The obtained ultrafine Au-Pd NPs show efficient catalytic activity for hydrogen generation from FA with extremely high turnover frequency (TOF) of 4840 h^{-1} at 323 K, and possess high selectivity, durability and stability.

(II) Encapsulation of highly catalytically active metal nanoclusters inside porous organic cages for hydrogen generation from ammonia borane

The creation of metal NCs with dimensions ranging from sub-nanometer to $\sim 2\text{ nm}$ for heterogeneous catalysis has received substantial attention. Herein, for the first time, we report an innovative *RDSA* that enables encapsulation of highly catalytically active Pd NCs inside the newly emerging discrete organic molecular cage, RCC3. By encapsulating within the open cavities of soluble RCC3 cages, the obtained Pd NC cores are well dispersed with precisely controlled size ($\sim 0.72\text{ nm}$), extremely high solubility, excellent dispersibility and accessibility in solution, presenting significantly enhanced catalytic activities toward various liquid-phase catalytic reactions including AB methanolysis, nitroarenes hydrogenation and dyes reduction. Moreover, owing to the effective confinement of cage cavities, the as-prepared Pd NCs possess excellent stability and durability. The strategy of encapsulation of metal NCs within soluble porous organic cages is promising for developing advanced catalysts.

(III) Solid solution alloying of classically immiscible Au and Rh for highly efficient catalytic hydrogen generation from formic acid

Solid-solution alloying opens enormous possibilities for various applications. However, a great many metals are immiscible with each other even above their melting points. Synthesizing such unknown but promising alloy consisting of the immiscible metals is particularly desirable. Herein, we report a relatively simple, effective and general approach for alloying the entirely immiscible Au and Rh at room temperature. The obtained Au-Rh clusters are ultrafine (~ 1.65 nm), highly dispersed and well-alloyed, possessing significantly enhanced catalytic activities toward the catalyzed dehydrogenation of formic acid in contrast to their monometallic parents. Moreover, Au-Rh clusters are extremely stable without any segregation during the catalytic reactions. The strong abilities for alloying and stabilizing Au-Rh clusters stem from the dramatically improved electrostatic adsorption of the supports to the metal species, through heating urea at an appropriate temperature.

In conclusion, this dissertation focuses on the development of ultrafine MNPs for catalytic hydrogen generation from FA and AB. We hope that the way to the utilization of liquid chemical hydrides as the hydrogen carriers will be paved by the practical use of the presently provided catalysts.

Chapter 1

Recent Advances in Hydrogen Generation from Liquid Chemical Hydrides by Metal Nanoparticle Catalysts

1.1 Introduction

Hydrogen is considered a clean, effective and renewable energy carrier for a sustainable future.¹ In particular, hydrogen fuel cells can efficiently generate electricity to power vehicles and other devices without any emission of regulated gas pollutant.² Over the past decades, several advanced storage systems, such as cryogenic liquid cylinders, high-pressure gas cylinders and porous materials including zeolites, carbons and metal-organic frameworks (MOFs) have been developed for hydrogen storage.³ However, these systems still face practical challenges in that they are not able to meet the demands required for practical applications because of their technological limits in safety (high pressure or low temperature) and density (low volumetric/gravimetric hydrogen densities).

Recently, concepts for hydrogen production from liquid chemical hydrides, such as formic acid (HCOOH , FA) and ammonia borane (NH_3BH_3 , AB), have gained considerable interest.⁴ Since hydrogen is stored in a safe and stable manner in the form of chemical bonds, liquid chemical hydrides possessing high hydrogen contents are easy to handle. Additionally, as liquid chemical hydrides have similar characteristics to common fuels, they can be effectively employed into already existing infrastructures. Various homogeneous catalysts have been investigated and achieved very high catalytic activities for hydrogen generation from liquid chemical hydrides.⁵ Along with the ongoing progress in hydrogen generation from liquid chemical hydrides using homogeneous systems, heterogeneous catalysts have

attracted much interest due to their advantages of easy separation and recycling. Up to now, various metal nanoparticle (MNPs) have been developed and shown superior catalytic performance for catalytic hydrogen generation from liquid chemical hydrides.⁶ Herein, we detail the recent advances in the utilization of MNPs as catalysts for hydrogen generation from liquid chemical hydrides, FA and AB.

1.2 Hydrogen generation from formic acid

FA, as a promising hydrogen carrier, has several remarkable features to include: 1) nontoxicity with a high hydrogen content (4.4 wt.%); 2) high stability as a liquid at room temperature; and 3) the availability *via* various synthesis routes, *e.g.*, biomass process, CO₂ hydrogenation or methyl formate hydrolysis.⁷ Typically, suitable catalysts are used to facilitate FA decomposition *via* dehydrogenation ($\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2$, $\Delta G_{298\text{k}} = -48.8 \text{ kJ}\cdot\text{mol}^{-1}$) for practical applications, rather than dehydration ($\text{HCOOH} \rightarrow \text{H}_2\text{O} + \text{CO}$, $\Delta G_{298\text{k}} = -28.5 \text{ kJ}\cdot\text{mol}^{-1}$), which produces the CO impurity that is toxic to fuel cell catalysts.⁸

1.2.1 Monometallic catalysts

Monometallic NPs, as efficient heterogeneous catalysts for FA dehydrogenation, have received tremendous attention, owing to their high activity, easy of separation and recycling.⁹ Our group has reported amine-functionalized silica nanospheres encapsulated Au NPs as catalysts for hydrogen generation from FA.¹⁰ Unlike Au NPs encapsulated in silica nanospheres in the absence of functional amine groups, the Au NPs encapsulated in the amine-functionalized counterparts show very high activity for the dehydrogenation of FA, releasing CO-free hydrogen with fast kinetics at 90 °C (Fig. 1.1). The strong metal-molecular support interaction (*SMMSI*) between the encapsulated Au NPs and the amine-functionalized SiO₂ spheres was suggested as the

reason for the high catalytic activity. It has been demonstrated that the acid-tolerant ZrO_2 -supported Au NP (~ 1.8 nm) catalysts can facilitate the liberation of CO-free hydrogen from FA-amine mixtures with a high turnover frequency (TOF) of 1590 h^{-1} at 50°C under ambient conditions.¹¹ Zhang and co-workers developed a Schiff base-functionalized Au NPs for the catalytic dehydrogenation of high-concentration FA in the absence of additives.¹² The reactions proceeded efficiently with a high TOF of 4368 h^{-1} in 10 mol L^{-1} FA solutions at 50°C . The enhanced catalytic feature was assigned to the C-H activation between the protonated Schiff base and electronegative Au NPs at the interface.

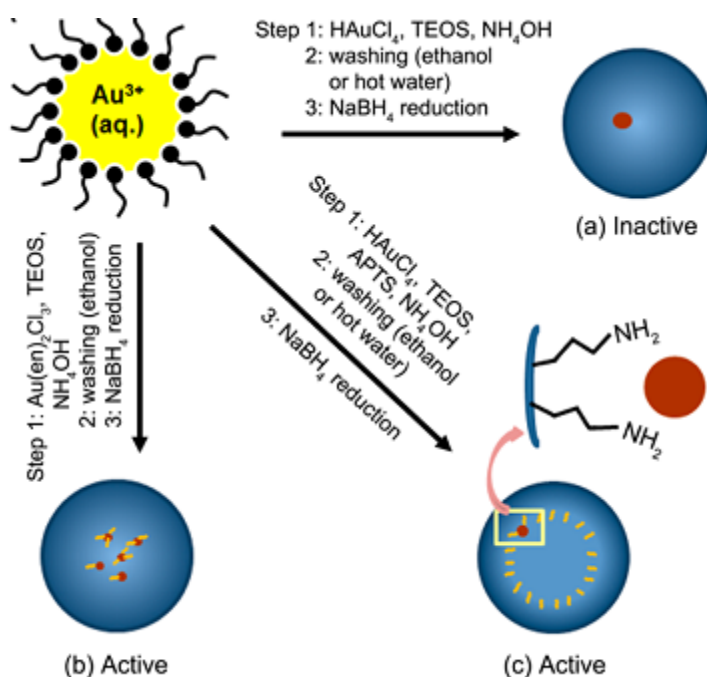


Figure 1.1. Schematic illustration for syntheses of (a) Au@SiO₂, (b) Au@SiO₂_EN, and (c) Au@SiO₂_AP. Adapted with permission from ref 10. Copyright 2012 Royal Society of Chemistry.

Compared to Au NPs, noble metal Pd NPs have received much more attention for the dehydrogenation of FA. Our group has synthesized high-performance Pd NPs

toward dehydrogenation of FA without CO under mild environment by using a sodium hydroxide-assisted reduction approach, with which the TOF reached a value as high as 2623 h^{-1} ($50\text{ }^{\circ}\text{C}$).¹³ Cai *et al.* demonstrated that boron-doped Pd NPs are efficient catalysts for hydrogen generation from FA-sodium formate system, with a high TOF of 1184 h^{-1} at $30\text{ }^{\circ}\text{C}$.¹⁴ Notably, lower coverage of CO on B-doped Pd NPs has been detected by the high-sensitivity ATR-IR instrument in comparison with the Pd/C catalyst. Our group has successfully immobilized ultrafine Pd NPs (1.4 nm) onto Vulcan XC-72R carbon using methanol as a mild reductant and a weak capping agent.¹⁵ Such Pd/XC-72R catalysts showed an excellent catalytic performance for the dehydrogenation of FA, with which an initial TOF of 7256 h^{-1} was obtained at $60\text{ }^{\circ}\text{C}$. Yu *et al.* encapsulated ultrafine Pd NPs inside the channels of nanoscale S-1 zeolite by using $[\text{Pd}(\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2]\text{Cl}_2$ as precursor under hydrothermal method.¹⁶ Remarkably, the resultant Pd/S-1-K catalysts show an high catalytic performance toward the dehydrogenation of FA with a TOF of 3027 h^{-1} at $50\text{ }^{\circ}\text{C}$, without generating CO under mild temperatures, because the ultrafine metal size and introduced basic sites. Most recently, Pd nanoclusters have been immobilized on a novel N-functionalized porous carbon prepared by a tandem nitrogen functionalization approach, with which the highest TOF of 8414 h^{-1} was obtained at $60\text{ }^{\circ}\text{C}$ for the dehydrogenation of FA.¹⁷ Notably, monometallic Au and Pd NPs have only been demonstrated as efficient catalysts for the dehydrogenation of FA until now.

1.2.2 Alloy catalysts

Metal alloy NPs are the other superior alternatives for the dehydrogenation of FA as the addition of a secondary metal phase can alter not only the electronic properties of the active sites, but also the metal dispersion/particle size. Xing and co-workers used

the carbon supported AuPd NPs with an average particle size of ~ 3.5 nm for the decomposition of FA, and achieved a high activity, although a minor trace of CO was generated.¹⁸ The catalytic performance was further improved by introducing CeO₂ as a promoter, and a maximum TOF of 832 h⁻¹ was obtained at 102 °C. Furthermore, Mullins and co-workers confirmed that bimetallic AuPd alloy NPs were excellent catalysts for the FA dehydrogenation because of appropriate synergetic effects.¹⁹ Most recently, by using an Mg²⁺-assisted low temperature reduction approach, Chen and co-workers have successfully immobilized small AuPd alloy NPs on carbon supports for hydrogen generation from FA, which achieved an initial TOF of 1120 h⁻¹ at room temperature without CO emission.²⁰

Recently, various advanced functional materials have been explored as supports to further improve the catalytic performance of metal alloy NPs. Porous metal-organic frameworks (MOFs) have proved to be unique hosts to encapsulate metal NPs with controlled particle sizes and distributions.²¹ We have employed MIL-101, one of the representative MOFs, and its ethylenediamine-grafted counterpart to support AuPd alloy NPs, which were used as highly active catalysts for the complete conversion of FA.²² The synergistic effects between Au and Pd were observed in this bimetallic AuPd NP and a high tolerance with respect to CO poisoning was obtained. This work also drew increased interest in MOF-immobilized NPs as catalysts for FA decomposition.²³ Graphene, a single-layer *sp*²-hybridized carbon sheet, has recently been considered as a promising metal NP catalyst support because of its large surface area and excellent stability.²⁴ Yan and co-workers have shown that the N-doped reduced graphene oxide (rGO) can be used as an excellent support for immobilizing ultrafine AuPd-CeO₂ nanocrystals for FA dehydrogenation.²⁵ They further prepared a bi-support consisting of ZIF-8 and rGO to immobilize AuPd-MnO_x NPs, which

showed high catalytic activity in FA dehydrogenation with an initial TOF of 382.1 h⁻¹ at 25 °C in the absence of additives.²⁶ Very recently, we reported a highly active rGO-supported AgPd alloy nanoparticle catalyst synthesized using a non-noble metal sacrificial approach (*NNMSA*) for hydrogen production from FA. As highly dispersed AgPd NPs were successfully immobilized on the rGO by the sacrifice of the co-precipitated Co₃(BO₃)₂, our catalysts exhibited the high TOF of 2739 h⁻¹ at 323 K without no trace of CO emissions.²⁷

Considering the reduction of consumption of noble metals, a trimetallic system consisting of Co, Au and Pd has been studied for the dehydrogenation of FA at room temperature.²⁸ By introducing the non-noble metal Co, the resulting surface electronic state in the alloy structure changed, which enhances the catalytic properties of noble alloy metals. The system showed a TOF of 80 h⁻¹ without the production of CO.

A core-shell structure may also improve the catalytic performance of metal alloy NPs. Xing and co-workers prepared core (PdAu)-shell (Au) NPs, which exhibited significantly enhanced catalytic activity and stability than the monometallic Au and Pd NPs for the formic acid decomposition reaction.²⁹

1.3 Hydrogen generation from ammonia borane

Ammonia borane (AB), as a potential alternative for hydrogen storage, has drawn significant attention because of several advantages: (1) low molecular weight (30.9 mg·L⁻¹) with high hydrogen content (19.6 wt.%), (2) high solubility and stability in solutions at room temperature, and (3) environmental nontoxicity.^{4,30} The hydrogen stored in AB can be released using a suitable catalyst even at low temperatures through the desirable hydrolysis and methanolysis according to the following equations: (a) $\text{NH}_3\text{BH}_3 + 2\text{H}_2\text{O} \rightarrow \text{NH}_4\text{BO}_2 + 3\text{H}_2$ and (b) $\text{NH}_3\text{BH}_3 + 4\text{CH}_3\text{OH} \rightarrow$

$\text{NH}_4\text{B}(\text{OCH}_3)_4 + 3\text{H}_2$, respectively. The hydrolysis and methanolysis of AB have been considered the safe and economical route for hydrogen supply as they lead to controlled hydrogen release under mild reaction conditions with faster rates.

1.3.1 Hydrolysis of AB

The current interest in heterogeneous catalysis for hydrogen generation from AB stems starting from our first report, which demonstrated that noble metal catalysts, such as Pt, Ru and Rh, showed high catalytic activities toward hydrolytic dehydrogenation of AB.³¹ Thereafter, significant progress has been made in the hydrolysis of AB using monometallic MNPs under mild conditions. Various solid supports, including MOFs, porous carbons, silica, polymers, metal oxides, and so on, have been applied for immobilizing noble MNPs with ultrafine size and desirable morphology. Highly dispersed Pt NPs with diameters about 1.8 nm have been encapsulated within the channels of MIL-101 by using a double solvents method (*DSM*) in our group, with which hydrogen can be released efficiently from AB, affording a high TOF of 414 min^{-1} .³² Well-dispersed Ru NPs have been immobilized on graphene, which showed high catalytic performance for the hydrolysis of AB with a TOF of 500 min^{-1} .³³ Carbon nanotubes (CNTs) treated by acid oxidation at high temperature have also been demonstrated as excellent supports for immobilizing noble MNPs.³⁴ Pt/CNTs and Ru/CNTs showed high catalytic activities in hydrolysis of AB with the TOFs of 567 min^{-1} and 706 min^{-1} , respectively. Considering the separation of MNPs from the liquid-phase catalytic reaction, ferrites have been applied as supports for supporting MNPs. Magnetic $\text{SiO}_2\text{-CoFe}_2\text{O}_4$ supported Ag, Pd and Ru NPs have exhibited excellent activities in catalytic hydrolysis of AB with the TOFs of 264, 254 and 172 min^{-1} , respectively.³⁵ In particular, such magnetic catalysts can be easily collected by using an external magnet.

On the other hand, non-noble MNPs, such as Fe, Co, Ni and Cu, are a class of promising catalysts, which may meet the low-cost demand of practical applications. In this respect, highly active dendrimer-encapsulated Co NPs, MSC-30 supported Ni NPs and graphene-supported CuCo NPs have been developed in our group for AB hydrolysis.³⁶ Fu *et al.* reported a nanostructured Ni₂P catalyst for AB hydrolysis, which showed high catalytic performance and sustainability toward hydrolysis of AB with the initial TOF of 40.4 min⁻¹ under air atmosphere and ambient temperature.³⁷ Nitrogen-doped carbon nanowires-supported Co NPs prepared by one-step carbonization of Co-MOF, where carbon shells could protect Co NPs from aggregation, exhibited high performance and low activation energy for AB hydrolysis.³⁸ Most recently, to further improve the activity of non-noble MNPs, highly dispersed Fe, Co, Ni and Cu NPs have been successfully prepared by using ZIF-8 as template, and the Ni/ZIF-8 showed the highest catalytic activity for AB hydrolysis with a TOF of 85.7 min⁻¹.³⁹ Notably, an effective “on-off” control of hydrogen generation from AB is designed inspired by the demonstration of the cleavage of an O-H bond in H₂O is the rate-determining step in AB hydrolysis.

Recently, bimetallic NPs have attracted considerable interest, in which the synergistic effects between different metals may result in enhanced catalytic performance. Conversely, for practical applications, utilizing non-noble metals may significantly reduce the catalyst cost without hindering catalytic performance. In this context, our group has used silica nanospheres to support AuNi and AuCo NPs with diameter of 3-4 nm by *in situ* reduction in an aqueous solution of NaBH₄/NH₃BH₃, which could efficiently catalyze the hydrolysis of AB.⁴⁰ Notably, these bimetallic AuNi and AuCo NPs have higher catalytic activities than their monometallic counterparts owing to a strong synergistic effect between Au and Ni (Co).

In addition to bimetallic NPs, core-shell structures have also been developed to achieve high catalytic performance for the hydrolysis of AB. We have prepared a magnetically recyclable Au@Co core-shell NP catalyst by using a one-step seeding-growth route with AB as a suitable reducing agent.⁴¹ The obtained Au@Co core-shell NPs showed excellent catalytic activity and stability for the hydrolysis of AB at room temperature. Similarly, magnetically recyclable Au/Co/Fe core-shell NPs with higher catalytic activity for AB hydrolysis have also been synthesized.⁴² Recently, Cho *et al.* reported an octahedral Au@Pt core-shell NPs synthesized *via* a polyol method using poly(diallyldimethylammonium chloride) (PDDA) as a capping agent.⁴³ When Pt coverage on the Au NPs was optimized to a Pt/Au ratio of 1, the Au@Pt catalyst displayed the highest catalytic activity with an activation energy of 44.28 kJ mol⁻¹.

The synergistic effects between metal NPs and catalyst supports can be designed to control the aggregation and dispersion of metal NPs over the surface of the catalyst support, leading to improved catalytic activities. Carbon nitrides (CNs)-supported AuCo NPs prepared by a modified wet impregnation method have been used for hydrogen production from the hydrolysis of AB.⁴⁴ Under mild conditions in the presence of photo irradiation, AuCo@CN displayed high activity for hydrogen generation with a TOF value of 2897 h⁻¹ at room temperature. The synergetic effect between Au and Co and the Mott-Schottky effect at the metal-semiconductor interface were suggested to account for the high catalytic properties. Recently, we have successfully encapsulated ultrafine AuNi NPs in the pores of MIL-101 using the double solvents method (*DSM*) in combination with a liquid-phase concentration-controlled reduction (CCR) strategy (Fig. 1.2).⁴⁵ The obtained AuNi NPs exhibit excellent catalytic activity for hydrogen generation from AB hydrolysis,

with a Ni/Au ratio of 93:7, giving a TOF value of 66.2 min^{-1} at room temperature, comparable to the most active noble-metal Pt, Rh, and Ru NPs. Additionally, the same method was also used to prepare MIL-101 encapsulated AuCo NPs with an average size of 1.8 nm, which exhibited high activity and durability for the hydrolysis of AB at room temperature.⁴⁶

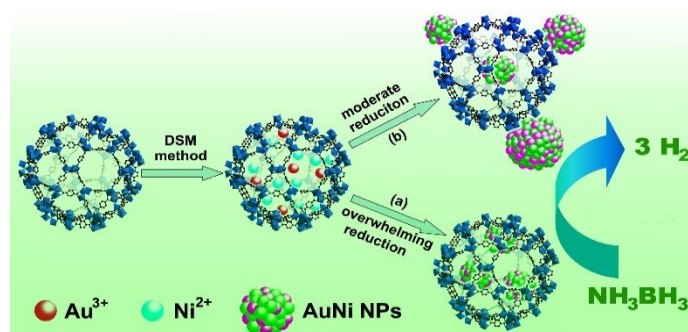


Figure 1.2. Schematic representation of immobilization of the AuNi NPs by the MIL-101 matrix using the double solvent method (DSM) combined with a liquid-phase concentration-controlled reduction (CCR) strategy. Reproduced from ref. 45 with permission. Copyright 2013 American Chemical Society.

1.3.2 Methanolysis of AB

Compared to AB hydrolysis, the methanolysis of AB has other advantages: (1) the high solubility of AB in methanol; (2) the high purity of H_2 can be produced from AB without NH_3 ; and (3) the byproduct over the methanolysis of AB is reconverted into AB by reacting with NH_4Cl at room temperature.

Through intensive efforts over the past decade, various highly active catalysts including metal salts, noble and non-noble MNPs have been investigated for hydrogen generation from the methanolysis of AB. Some representative NP catalysts have been listed in Table 1.1,⁴⁷ in which we can see the Rh- and Ru-based catalysts are the most active ones for the methanolysis of AB. Notably, the heterogeneous Rh NPs have

been homogenized by using a porous organic cage, CC3R, which exhibited the highest catalytic activities for AB methanolysis until now.^{47a}

Table 1.1 Catalytic activities of selected catalysts for the methanolysis of AB

Catalyst	Temp. (°C)	Catalyst/AB (molar ratio)	TOF (min ⁻¹)	Ref.
Rh/CC3R	25	0.0199	215	47a
Rh/SiO ₂	25	0.00245	168	47b
Ru/Graphene	25	0.003	99.4	47c
CuPd/C	25	0.072	53.2	47d
CoPd/C	25	0.027	27.7	47e
Pd/PVP	25	0.005	22.3	47f
Ni/PVP	25	0.02	12.1	47g

1.4 Conclusions

In conclusion, a number of monometallic and alloy NP catalysts with high selectivity and durability have been developed for hydrogen generation from liquid chemical hydrides, such as FA and AB, in recent years, which show promise for future applications. Catalyst activity in this area has improved over the years and in continuing the trend there are encouraging signs that future catalysts will further improve activity, especially the non-noble/noble alloy catalyst systems, in which the secondary non-noble metals play a significant role in enhancing catalytic performance, and to reduce the catalyst costs. The outlook of commercializing chemical hydrides as hydrogen sources looks promising with metal NP catalysts likely to make the breakthrough in near future.

Reference

- (a) H. Balat and E. Kirtay, *Int. J. Hydrogen Energy*, 2010, **35**, 7416; (b) A. Boddien, B. Loges, F. Gärtner, C. Torborg, K. Fumino, H. Junge, R. Ludwig and M. Beller, *J. Am. Chem. Soc.*, 2010, **132**, 8924; (c) S. E. Hosseini and M. A. Wahid, *Renew. Sustain. Energy Rev.*,

2016, **57**, 850.

2. (a) S. Ahmed and M. Krumpelt, *Int. J. Hydrogen Energy*, 2001, **26**, 291; (b) C. M. Pedersen, M. Escudero-Escribano, A. Velázquez-Palenzuela, L. H. Christensen, I. Chorkendorff and I. E. L. Stephens, *Electrochim. Acta*, 2015, **179**, 647; (c) W. Liu, C. J. Webb and E. M. Gray, *Int. J. Hydrogen Energy*, 2016, **41**, 3485.
3. (a) G. Li, H. Kobayashi, J. M. Taylor, R. Ikeda, Y. Kubota, K. Kato, M. Takata, T. Yamamoto, S. Toh, S. Matsumura and H. Kitagawa, *Nat. Mater.*, 2014, **13**, 802; (b) L. Schlapbach and A. Züttel, *Nature*, 2001, **414**, 353; (c) N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O'Keeffe and O. M. Yaghi, *Science*, 2003, **300**, 1127; (d) S. L. Li and Q. Xu, *Energy Environ. Sci.*, 2013, **6**, 1656.
4. (a) M. Yadav and Q. Xu, *Energy Environ. Sci.*, 2012, **5**, 9698; (b) Q. Zhu and Q. Xu, *Energy Environ. Sci.*, 2015, **8**, 478; (c) T. Umegaki, Q. Xu and Y. Kojima, *Materials*, 2015, **8**, 4512.
5. (a) Y. Himeda, *Green Chem.*, 2009, **11**, 2018; (b) A. Staubitz, A. P. M. Robertson and I. Manners, *Chem. Rev.*, 2010, **110**, 4079; (c) A. Guerriero, H. Bricout, K. Sordakis, M. Peruzzini, E. Monflier, F. Hapiot, G. Laurenczy and L. Gonsalvi, *ACS Catal.*, 2014, **4**, 3002.
6. (a) M. Yurderi, A. Bulut, M. Zahmakiran and K. Kaya, *Appl. Catal. B*, 2014, **160-161**, 514; (b) P. Z. Li, A. Aijariz and Q. Xu, *Angew. Chem. Int. Ed.*, 2012, **51**, 6753.
7. (a) J. Li, Q. L. Zhu and Q. Xu, *Chimia*, 2015, **69**, 348; (b) A. Boddien, D. Mellmann, F. Gärtner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig and M. Beller, *Science*, 2011, **333**, 1733; (c) P. Sponholz, D. Mellmann, H. Junge and M. Beller, *ChemSusChem.*, 2013, **6**, 1172; (d) M. Grasemann and G. Laurenczy, *Energy Environ. Sci.*, 2012, **5**, 8171.
8. (a) S. Fukuzumi, T. Kobayashi and T. Suenobu, *J. Am. Chem. Soc.*, 2010, **132**, 1496; (b) Z. L. Wang, J. M. Yan, H. L. Wang, Y. Ping and Q. Jiang, *J. Mater. Chem. A*, 2013, **1**, 12721.

9. M. Ojeda and E. Lglesia, *Angew. Chem. Int. Ed.*, 2009, **121**, 4894.
10. M. Yadav, T. Akita, N. Tsumori and Q. Xu, *J. Mater. Chem.*, 2012, **22**, 12582.
11. Q. Y. Bi, X. L. Du, Y. M. Liu, Y. Cao, H. Y. He and K. N. Fan, *J. Am. Chem. Soc.*, 2012, **134**, 8926.
12. Q. Q. Liu, X. F. Yang, Y. Q. Huang, S. T. Xu, X. L. Su, X. Pan, J. M. Xu, A. Q. Wang, C. H. Liang, X. K. Wang and T. Zhang, *Energy Environ. Sci.*, 2015, **8**, 3204.
13. Q. L. Zhu, N. Tsumori and Q. Xu, *Chem. Sci.*, 2014, **5**, 195.
14. K. Jiang, K. Xu, S. Zou, W. B. Cai, *J. Am. Chem. Soc.*, 2014, **136**, 4861.
15. Q. L. Zhu, N. Tsumori and Q. Xu, *J. Am. Chem. Soc.*, 2015, **137**, 11743.
16. N. Wang, Q. Sun, R. Bai, X. Li, G. Guo and J. Yu, *J. Am. Chem. Soc.*, 2016, **138**, 7484.
17. Z. Li, X. Yang, N. Tsumori, Z. Liu, Y. Himeda, Y. Autrey and Q. Xu, *ACS Catal.*, 2017, **7**, 2720.
18. X. C. Zhou, Y. J. Huang, W. Xing, C. P. Liu, J. H. Liao and T. H. Lu, *Chem. Commun.*, 2008, 3540.
19. W. Y. Yu, G. M. Mullen, D. W. Flaherty and C. B. Mullins, *J. Am. Chem. Soc.*, 2014, **136**, 11070.
20. S. Wu, F. Yang, H. Wang, R. Chen, P. C. Sun and T. H. Chen, *Chem. Commun.*, 2015, **51**, 10887.
21. (a) R. Li, J. H. Hu, M. S. Deng, H. L. Wang, X. J. Wang, Y. L. Hu, H. L. Jiang, J. Jiang, Q. Zhang, Y. Xie and Y. J. Xiong, *Adv. Mater.*, 2014, **26**, 4783; (b) L. J. Murray, M. Dinca and J. R. Long, *Chem. Soc. Rev.*, 2009, **38**, 1294; (c) Y. B. Huang, M. Shen, X. S. Wang, P. C. Shi, H. F. Li and R. Cao, *J. Catal.*, 2015, **330**, 452.
22. X. J. Gu, Z. H. Lu, H. L. Jiang, T. Akita and Q. Xu, *J. Am. Chem. Soc.*, 2011, **133**, 11822.
23. (a) H. M. Dai, N. Cao, L. Yang, J. Su, W. Luo and G. Z. Cheng, *J. Mater. Chem. A*, 2014, **2**, 11060; (b) H. M. Dai, B. Q. Xia, L. Wen, C. Du, J. Su, W. Luo and G. Z. Cheng, *Appl. Catal. B*, 2015, **165**, 57; (c) F. Ke, L. H. Wang and J. F. Zhu, *Nanoscale*, 2015, **7**, 8321.

24. (a) S. Park and R. S. Ruoff, *Nat. Nanotechnol.*, 2009, **4**, 217; (b) D. R. Dreyer, S. Park, C. W. Bielawski and R. S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228; (c) F. Z. Song, Q. L. Zhu, N. Tsumori and Q. Xu, *ACS Catal.*, 2015, **5**, 5141.
25. Z. L. Wang, J. M. Yan, Y. F. Zhang, Y. Ping, H. L. Wang and Q. Jiang, *Nanoscale*, 2014, **6**, 3073.
26. J. M. Yan, Z. L. Wang, L. Gu, S. J. Li, H. L. Wang, W. T. Zheng and Q. Jiang, *Adv. Energy Mater.*, 2015, 120017.
27. Y. Chen, Q. L. Zhu, N. Tsumori and Q. Xu, *J. Am. Chem. Soc.*, 2015, **137**, 106.
28. Z. L. Wang, J. M. Yan, Y. Ping, H. L. Wang, W. T. Zheng and Q. Jiang, *Angew. Chem. Int. Ed.*, 2013, **52**, 4406.
29. Y. J. Huang, X. C. Zhou, M. Yin, C. P. Liu and W. Xing, *Chem. Mater.*, 2010, **22**, 5122.
30. M. Zahmakiran and S. Özkar, *Top. Catal.*, 2013, **56**, 1171.
31. (a) M. Chandra and Q. Xu, *J. Power Sources*, 2006, **156**, 190; (b) M. Chandra and Q. Xu, *J. Power Sources*, 2007, **168**, 135.
32. A. Aijaz, A. Karkamkar, Y. J. Choi, N. Tsumori, E. Roennebro, T. Autrey, H. Shioyama and Q. Xu, *J. Am. Chem. Soc.*, 2012, **134**, 13926.
33. C. Du, Q. Ao, N. Cao, L. Yang, W. Luo and G. Cheng, *Int. J. Hydrogen Energy*, 2015, **40**, 6180.
34. (a) W. Chen, J. Ji, X. Duan, G. Qian, P. Li, X. Zhou, D. Chen and W. Yuan, *Chem. Commun.*, 2014, **50**, 2142; (b) Q. Yao, Z. H. Lu, Y. Jia, X. Chen and X. Liu, *Int. J. Hydrogen Energy*, 2015, **40**, 2207.
35. (a) J. Chen, Z. H. Lu, Y. Wang, X. Chen and L. Zhang, *Int. J. hydrogen Energy*, 2015, **40**, 4777; (b) S. Akbayrak, M. Kaya, M. Volkan and S. Özkar, *Appl. Catal. B*, 2014, **147**, 387; (c) S. Akbayrak, M. Kaya, M. Volkan and S. Özkar, *J. Mol. Catal. A: Chem.*, 2014, **394**, 253.
36. (a) K. Aranishi, Q. L. Zhu and Q. Xu, *ChemCatChem*, 2014, **6**, 1375; (b) P. Z. Li, A. Aijaz

- and Q. Xu, *Angew. Chem. Int. Ed.*, 2012, **51**, 6753.
37. C. Y. Peng, L. Kang, S. Cao, Y. Chen, Z. S. Lin and W. F. Fu, *Angew. Chem. Int. Ed.*, 2015, **54**, 15725.
38. L. Zhou, J. Meng, P. Li, Z. Tao, L. Mai and J. Chen, *Mater. Horiz.*, 2017, **4**, 268.
39. C. Wang, J. Tuninetti, Z. Wang, C. Zhang, R. Ciganda, L. Salmon, S. Moya, J. Ruiz and D. Astruc, *J. Am. Chem. Soc.*, 2017, **139**, 11610.
40. (a) H. L. Jiang, T. Umegaki, T. Akita, X. B. Zhang, M. Haruta and Q. Xu, *Chem. Eur. J.*, 2010, **16**, 3132; (b) Z. H. Lu, H. L. Jiang, M. Yadav, K. Aranishi and Q. Xu, *J. Mater. Chem.*, 2012, **22**, 5065.
41. J. M. Yan, X. B. Zhang, T. Akita, M. Haruta and Q. Xu, *J. Am. Chem. Soc.*, 2010, **132**, 5326.
42. K. Aranishi, H. L. Jiang, T. Akita, M. Haruta and Q. Xu, *Nano Res.*, 2011, **4**, 1233.
43. J. W. Park, S. W. Lai and S. O. Cho, *Int. J. Hydrogen Energy*, 2015, **40**, 16316.
44. L. T. Guo, Y. Y. Cai, J. M. Ge, Y. N. Zhang, L. H. Gong, X. H. Li, K. X. Wang, Q. Z. Ren, J. Su and J. S. Chen, *ACS Catal.*, 2005, **5**, 388.
45. Q. L. Zhu, J. Li and Q. Xu, *J. Am. Chem. Soc.*, 2013, **135**, 10210.
46. J. Li, Q. L. Zhu and Q. Xu, *Chem. Commun.*, 2014, **50**, 5899.
47. (a) J. K. Sun, W. W. Zhan, T. Akita and Q. Xu, *J. Am. Chem. Soc.*, 2015, **137**, 7063; (b) D. Özhava and S. Özkar, *Appl. Catal. B*, 2016, **181**, 716; (c) S. Peng, J. Liu, J. Zhang and F. Wang, *Int. J. Hydrogen Energy*, 2015, **40**, 10856; (d) P. Li, Z. Xiao, Z. Liu, J. Huang, Q. Li and D. Sun, *Nanotechnol.*, 2015, **26**, 025401; (e) D. Sun, V. Mazumder, Ö. Metin and S. Sun, *ACS Catal.*, 2012, **2**, 1290; (f) H. Erdogan, Ö. Metin and S. Özkar, *Phys. Chem. Chem. Phys.*, 2009, **11**, 10519; (g) D. Özhava, N. Z. Kilicaslan and S. Özkar, *Appl. Catal. B*, 2015, **162**, 573.

Chapter 2

Immobilization of Highly Catalytically Active bimetallic AuPd NPs on Reduced Graphene Oxide for Hydrogen Generation from Formic Acid

2.1 Introduction

Hydrogen is of critical importance in clean energy applications although effective hydrogen storage technologies still need to be developed.¹ Formic acid (FA) is a promising hydrogen carrier,² which has several remarkable features such as (a) nontoxicity with high hydrogen content (4.4 wt.%), (b) high stability as a liquid at room temperature, and (c) easy synthesis via a biomass process, CO₂ reduction or methyl formate hydrolysis.³ Depending on the catalysts, however, FA can be decomposed in two ways: desirable dehydrogenation ($\text{HCOOH} \rightarrow \text{H}_2 + \text{CO}_2$) and undesirable dehydration ($\text{HCOOH} \rightarrow \text{H}_2\text{O} + \text{CO}$), which produces CO impurities that are toxic to the fuel cell catalysts.⁴

So far, homogeneous catalysts have been extensively studied for hydrogen production from FA and very high catalytic activities have been reported.⁵ Along with the ongoing progress in FA dehydrogenation using homogeneous systems, heterogeneous catalysts have attracted tremendous attention due to their advantages of easy separation and recycling. A large number of metal nanoparticle (MNP) catalysts have been studied, most of which, however, suffer from severe aggregation and limited catalytic activities.⁶

Herein, we report a highly active AuPd alloy nanoparticle catalyst prepared using a non-noble metal sacrificial approach (*NNMSA*), which exhibits one of the highest turnover frequencies (TOFs) of 4840 h⁻¹ at 323 K for hydrogen generation from the

FA/sodium formate (SF) system.⁷

2.2 Experimental details

2.2.1 Chemicals

Natural graphite (Alfa Aesar, 325 mesh, metals basis, 99.8%), sodium nitrate (Kishida Chemicals Co. Ltd., 99%), sulfuric acid (Kishida Chemicals Co. Ltd., 98%), potassium permanganate (Kishida Chemicals Co. Ltd., 99.3%), hydrogen peroxide (Kishida Chemicals Co. Ltd., 30%) and hydrochloric acid (Wako Pure Chemical Industries, Ltd., 35-37%) were used to prepare graphite oxide.

Potassium tetrachloropalladate (Wako Pure Chemical Industries, Ltd., >97%), gold chloride acid (Kishida Chemicals Co. Ltd., 99%), cobalt acetate (Kishida Chemicals Co. Ltd., 99%), sodium borohydride (Sigma-Aldrich, 99%), phosphoric acid (Tokyo Chemical Industry Co. Ltd., >89%) were used to prepare the reduced graphene oxide (rGO) supported AuPd nanoparticles.

Formic acid (Merck Millipore, 98%) and sodium formate (Sigma-Aldrich, 99.5%) were used for hydrogen release with the catalysts.

2.2.2 Characterizations

The powder X-ray diffraction (PXRD) measurements were carried out using a Rigaku Ultima IV diffractometer with Cu-K α radiation. The metal contents of the catalyst were analyzed using ICP-OES on Thermo Scientific iCAP6300. The TEM, HAADF-STEM images and EDX spectra were taken by Transmission electron microscope (TEM, TECNAI G² F20) with operating voltage at 200 kV equipped with energy-dispersive X-ray (EDX) detector. The N₂ adsorption/desorption isotherms were obtained at 77 K using automatic volumetric adsorption equipment (Belsorp-max). XPS spectra were

recorded on a Shimadzu ESCA-3400 using an Mg K α source. The generated gas from FA was analyzed by GC-8A (molecular sieve 5A, Ar as carrier gas) and GC-8A (Porapack N, He as carrier gas) analyzers (Shimadzu).

2.2.3 Synthesis of catalysts

Synthesis of (Co_x)_EAu_yPd_{1-y}/rGO catalysts. GO was synthesized by the modified Hummers' method⁸ and then sonicated in water to form a colloidal dispersion. A mixed solution (0.06 mmol) of K₂PdCl₄ and HAuCl₄ with or without Co(CH₃COO)₂ was added into the GO dispersion (0.1 wt. %, 50 mL). After adding a fresh NaBH₄ solution (3.7 M, 0.5 mL), the resulted mixture was stirred for 2 h. Then, the Co_xAu_yPd_{1-y}/rGO precipitation was separated by centrifugation. Subsequently, the precipitation was re-dispersed into 2.5 vol. % H₃PO₄ (20 mL) under stirring for another 2 h. The rGO-supported AuPd nanoparticle catalyst was obtained by washing with water and centrifugation. The obtained catalyst was named as (Co_x)_EAu_yPd_{1-y}/rGO, where (Co)_E represents the acid etching of Co, x represents the molar ratio of Co/(Au+Pd) and y is the molar ratio of Au/(Au+Pd).

Synthesis of the CO poisoned (Co₃)_EAu_{0.6}Pd_{0.4}/rGO catalyst. The obtained (Co₃)_EAu_{0.6}Pd_{0.4}/rGO catalyst was continuous stirred in a round-bottom flask (50 mL) under CO atmosphere for 1 hour. Then, the catalyst was used for the dehydrogenation of FA.

2.2.4 Catalysis activity determination

An aqueous suspension containing the as-prepared catalyst was placed in a two-neck round-bottom flask, which was placed in a water bath under ambient atmosphere. A gas burette filled with water was connected to the reaction flask to measure the volume of released gas. The reaction was started when the mixed aqueous solution of FA-SF was

injected into the sealed flask to form a 4.5 mL of suspension. The molar ratio of AuPd/FA was fixed at 0.02 for all the catalytic reactions. The volume of the evolved gas was monitored by recording the displacement of water in the gas burette.

2.2.5 The turnover frequency (TOF) calculations

The TOF reported here is an apparent TOF value based on the number of (Au+Pd) atoms in catalyst, which is calculated from the equation as follows:

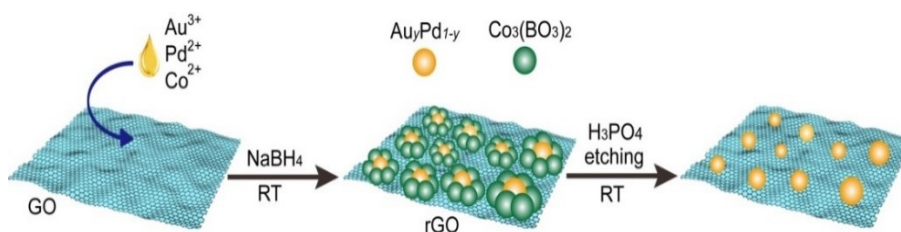
$$TOF = P_0 V / 2RT n_{AuPd} t$$

where P_0 is the atmospheric pressure (101325 Pa), V is the final generated volume of (H₂ + CO₂) gas, R is the universal gas constant (8.3145 m³ Pa mol⁻¹ K⁻¹), T is the room temperature (298 K), n_{AuPd} is the total molar number of (Au + Pd) atoms in catalyst and t is the completion time of the reaction in hour.

2.2.6 Durability test

After the catalytic reaction, the catalyst was recollected by centrifugation, washed with water and recycled for durability. In each cycle 100% FA is decomposed, corresponding to a TON value of 50 for each cycle.

2.3 Results and discussion



Scheme 2.1. Schematic illustration of the synthesis of the rGO-supported AuPd NP catalyst *via* a non-noble metal (cobalt) sacrificial approach (NNMSA).

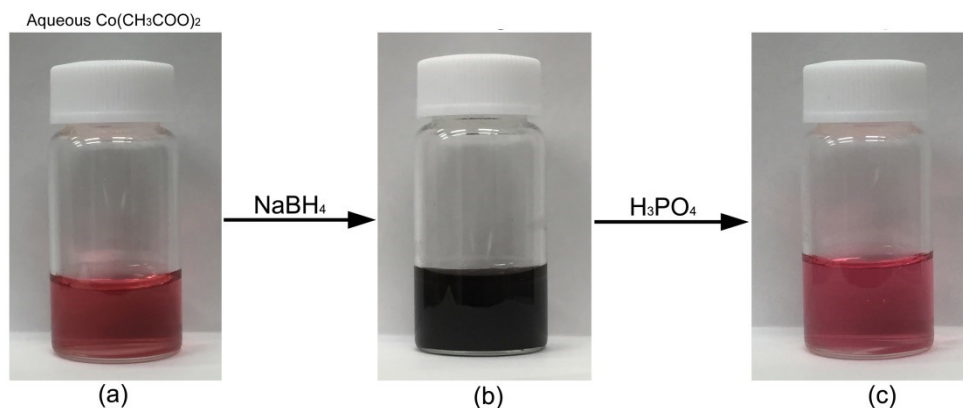


Figure 2.1. Photographs of (a) aqueous $\text{Co}(\text{CH}_3\text{COO})_2$ solution and the products from the reaction between $\text{Co}(\text{CH}_3\text{COO})_2$ and NaBH_4 at 298 K (b) before and (c) after etching with acid.

Synthesis of rGO-supported AuPd NPs. Cobalt was used as the sacrificial agent. Amorphous $\text{Co}_3(\text{BO}_3)_2$ (the black precipitation, Fig. 2.1b) was formed from the reaction between $\text{Co}(\text{CH}_3\text{COO})_2$ and NaBH_4 , which exhibits very broad powder X-ray diffraction (PXRD) peaks (Fig. 2.2a). The sample crystallizes by annealing at 823 K for 3 h (Ar atmosphere), displaying the XRD peaks (Fig. 2.2a) corresponding to $\text{Co}_3(\text{BO}_3)_2$ phase (JCPDS: 25-0102, Fig. 2.2a),⁹ which can be easily dissolved in H_3PO_4 (Fig. 2.1c). Graphite oxide (GO) was prepared from graphite using a modified Hummers' method.⁸ The rGO-supported AuPd nanoparticle (NP) catalyst was synthesized using a wet-chemical process, as illustrated in Scheme 2.1. Firstly, according to the stoichiometry, the aqueous solution containing HAuCl_4 , $\text{Co}(\text{CH}_3\text{COO})_2$ and K_2PdCl_4 was added into 50 mL of GO suspension (0.1 wt.%). Then the above mixture was reduced by a fresh aqueous solution of NaBH_4 . After continuous stirring for 2 h, the mixture was washed and re-dispersed in H_3PO_4 solution for etching (2 h). Finally, the catalyst, denoted as $(\text{Co}_x)_\text{E}\text{Au}_y\text{Pd}_{1-y}/\text{rGO}$, was obtained by centrifugation and washing with water.

Characterizations of rGO-supported AuPd NPs. Fig. 2.3a shows the PXRD pattern of the $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalyst. Except for a low and broad diffraction of rGO at 24° , the diffraction peaks, which are located between the fcc Au (JCPDS No. 65-8601) and Pd

(JCPDS No. 65-2867), indicate the formation of an AuPd alloy.¹⁰ For comparison, PXRD patterns of the non-etched counterparts $\text{Co}_3\text{Au}_{0.6}\text{Pd}_{0.4}$ and $\text{Co}_3\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ (Fig. 2.2b) show an additional broad band for $\text{Co}_3(\text{BO}_3)_2$. After etching with an acid, the characteristic peaks corresponding to AuPd are clearly visible and match well with the directly deposited counterpart of $\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ (Fig. 2.2b), confirming the successful removal of cobalt and the formation of AuPd. The N_2 sorption isotherms for $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$, $\text{Co}_3\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ and $\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ are shown in Fig. 2.3b. Generally, the restacking of rGO can be partially overcome by the direct deposition of NPs.¹¹ Hence, the $\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ and $\text{Co}_3\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ possess a type-IV N_2 sorption curve with Brunauer–Emmett–Teller (BET) surface areas of 189 and 219 $\text{m}^2 \text{g}^{-1}$, respectively. Notably, the surface area of $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ (321 $\text{m}^2 \text{g}^{-1}$) increases drastically, illustrating that the removal of cobalt by the acid etching has resulted in high porosity, which will favor the diffusion of reactants to metal NPs in catalysis.

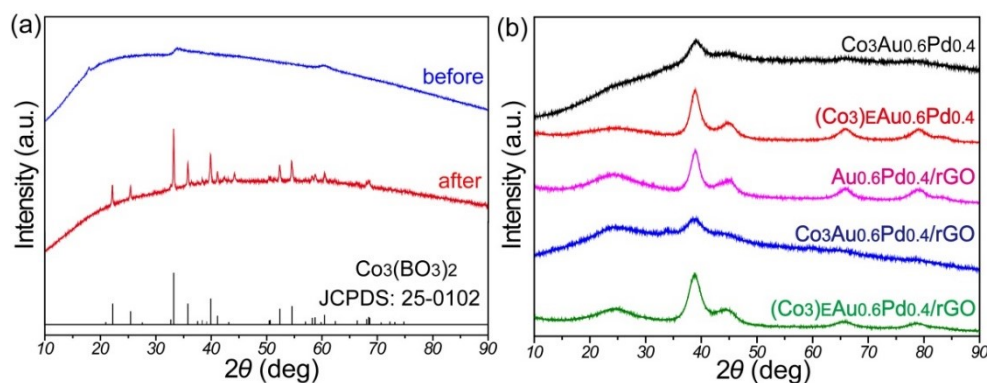


Figure 2.2. (a) XRD patterns of the products from the reaction between $\text{Co}(\text{CH}_3\text{COO})_2$ and NaBH_4 before and after annealing (823 K, 3 h, Ar), and JCPDS: 25-0102 ($\text{Co}_3(\text{BO}_3)_2$), and (b) XRD patterns of $\text{Co}_3\text{Au}_{0.6}\text{Pd}_{0.4}$, $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}$, $\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$, $\text{Co}_3\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$, and $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$.

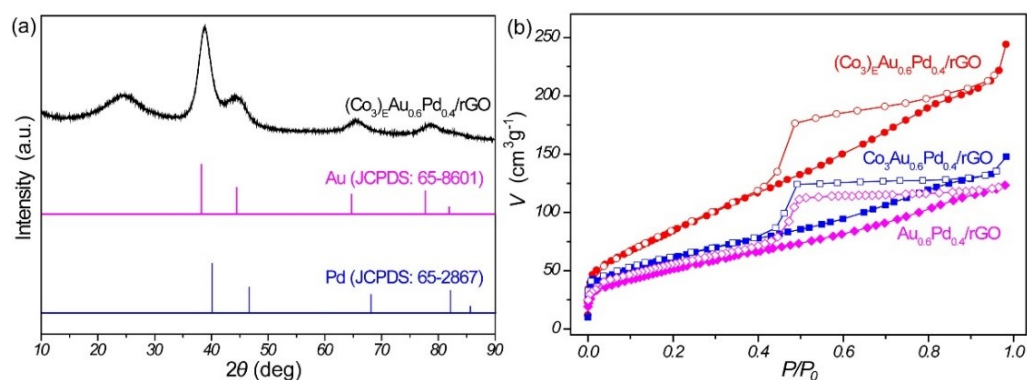


Figure 2.3. (a) PXRD pattern of $(\text{Co}_3)_E\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ and (b) N_2 sorption analyses (77 K) of $(\text{Co}_3)_E\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$, $\text{Co}_3\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ and $\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$.

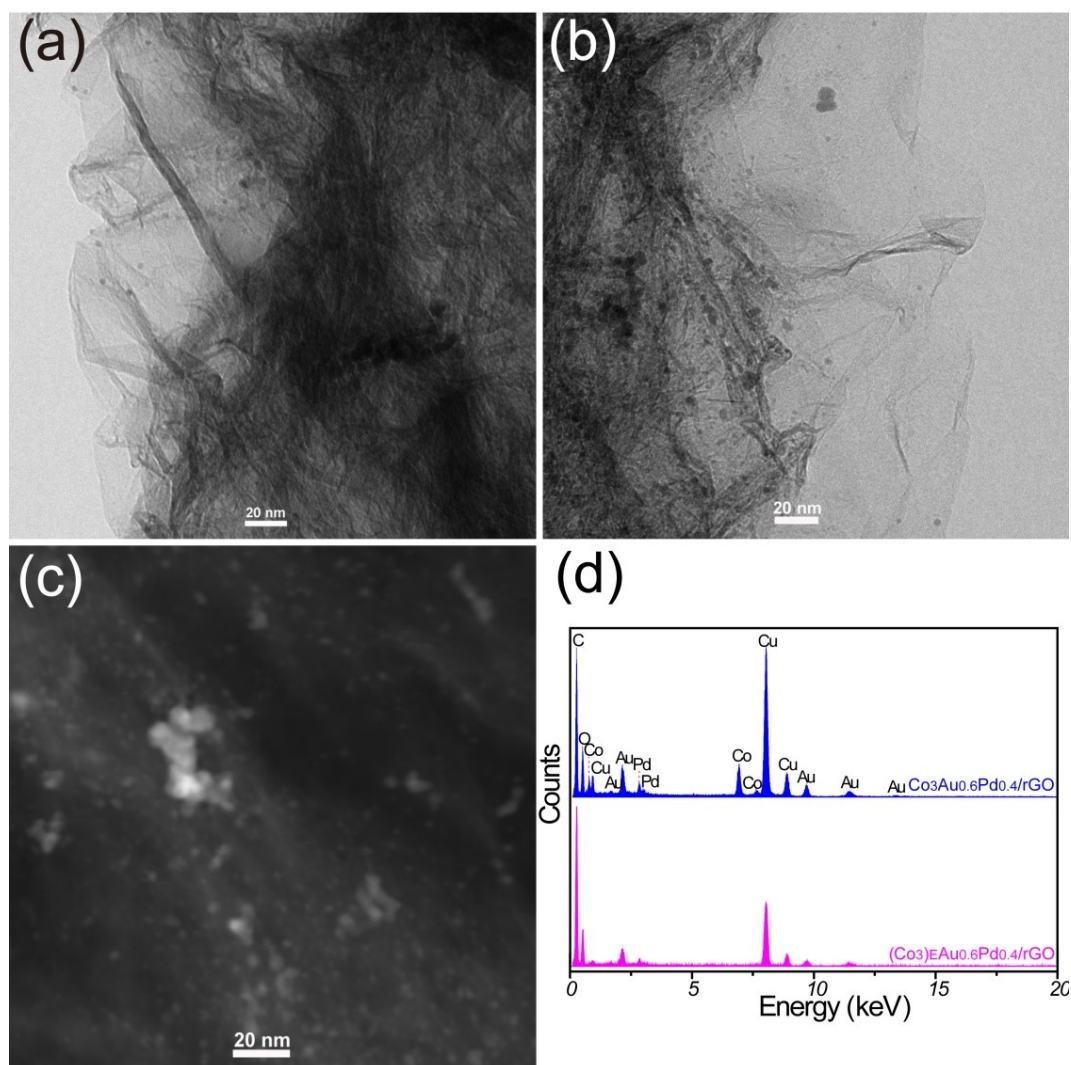


Figure 2.4. TEM image of (a) $\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ and (b) $\text{Co}_3\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$, (c) HADDF-STEM image of $\text{Co}_3\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$, (d) EDX patterns of $\text{Co}_3\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ and $(\text{Co}_3)_E\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$.

The morphologies of the $\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$, $\text{Co}_3\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ and $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalysts were analysed by transmission electron microscopy (TEM). As shown in Fig. 2.4a-c, $\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ and $\text{Co}_3\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ possess larger particles with severe aggregation. In contrast, the AuPd NPs in the $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalyst are well dispersed and immobilized on the rGO support (Fig. 2.5a-c). The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images further reveal the uniform distribution of AuPd NPs in the $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalyst with an average particle size of 3.9 ± 0.9 nm, indicating that the sacrifice of the cobalt compound can prevent the primary AuPd NPs from aggregation, which will benefit their catalytic performance. Energy dispersive X-ray (EDX) analyses (Fig. 2.4d and 2.6) show that $\text{Co}_3\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ is rich in cobalt, whereas no signals for cobalt are detected in $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$, clearly confirming that cobalt has been eliminated by the H_3PO_4 etching. The inductively coupled plasma optical emission spectroscopic analysis reveals that the molar ratio of Co : Au : Pd in $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ to be 0.04 : 0.6 : 0.4, indicating that almost all the co-precipitated $\text{Co}_3(\text{BO}_3)_2$ can be removed by H_3PO_4 . The X-ray photoelectron spectroscopic (XPS) measurements show no signals for Co of $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ before and after Ar sputtering (Fig. 2.7). The observed Au 4f and Pd 3d spectra reveals that $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ is composed of metallic Au and Pd, further confirming the successful formation of AuPd alloy NPs.

Catalytic hydrogen generation from FA. The catalytic activities of the $(\text{Co}_x)_\text{E}\text{Au}_y\text{Pd}_{1-y}/\text{rGO}$ catalysts (x is the molar ratio of $\text{Co}/(\text{Au} + \text{Pd})$ and y the molar percentage of Au in AuPd) in hydrogen generation from the FA/SF system were evaluated. As shown in Fig. 2.8a, the hydrogen generation rate increases with the increase in the sacrificial amount of $\text{Co}_3(\text{BO}_3)_2$ until x reaches to 3 when the y is fixed to 0.6. Meanwhile, Fig. 2.8b shows the excellent catalytic performance of $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ compared to $\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$.

Unquestionably, the sacrificial agent plays a dominant role, by decreasing the size of NPs, in the promotion of catalytic performance. Under our evaluation conditions, the $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalyst shows an extremely high catalytic activity for the complete dehydrogenation of FA with the release of 146 mL gas of $\text{H}_2 + \text{CO}_2$ in 0.62 min ($n_{\text{AuPd}}/n_{\text{FA}} = 0.02$ and $n_{\text{SF}}/n_{\text{FA}} = 2.5$) at 323 K, giving a TOF as high as 4840 h^{-1} (Fig. 2.8), one of the highest values reported thus far (Table 2.1).⁷ After that, the generated gas with a slow speed is attributed to the decomposition of SF.

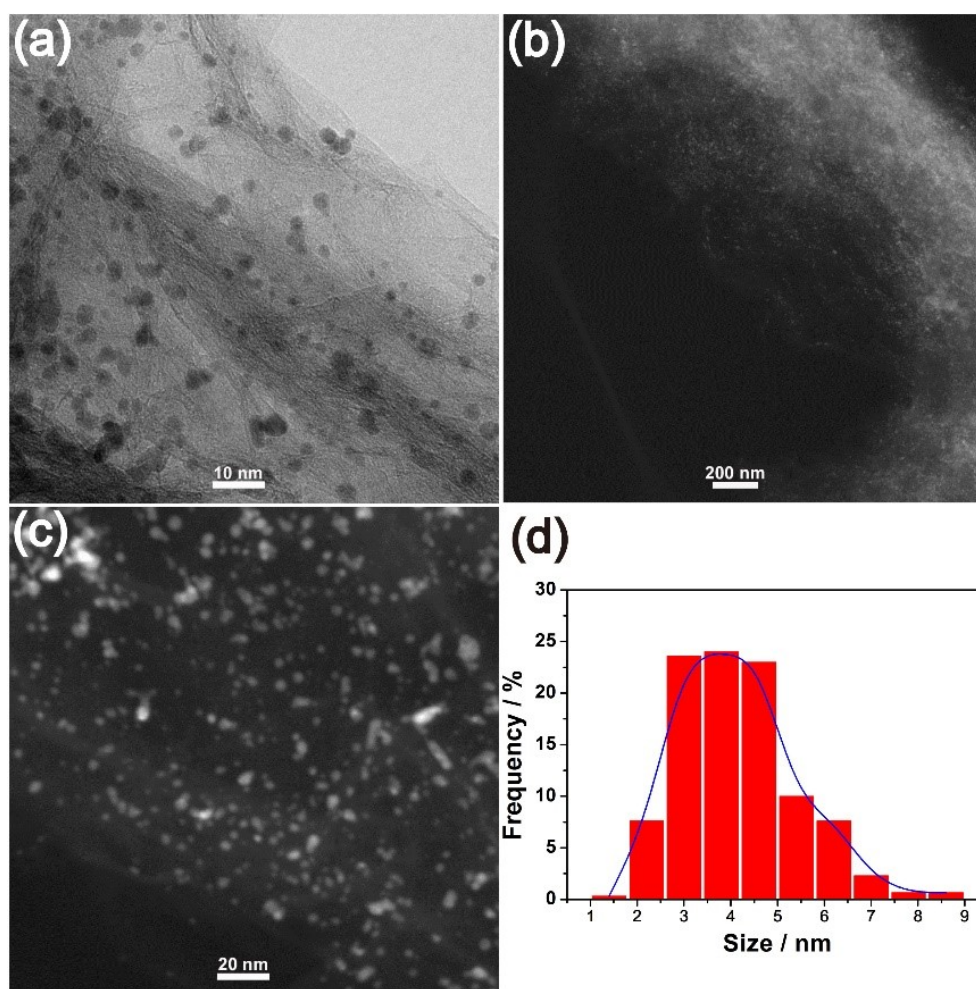


Figure 2.5. (a) TEM, (b and c) HAADF-STEM images and (d) particle size distribution histograms of AuPd NPs of $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$.

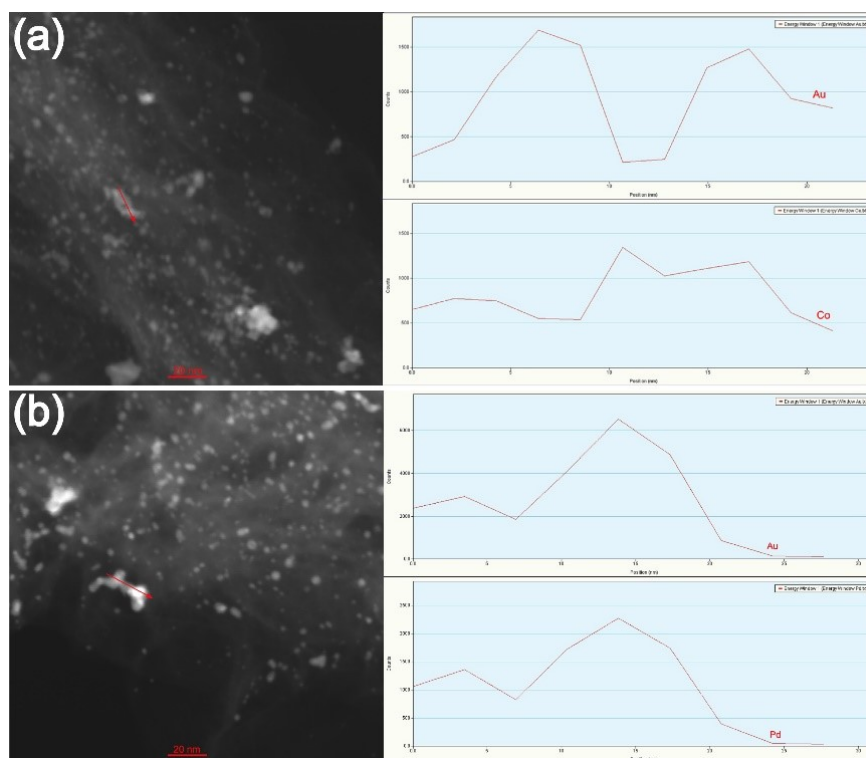


Figure 2.6. HAADF-STEM images of (a) $\text{Co}_3\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ and (b) $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$, as well as the corresponding EDX-line scan along the red line in (a) and (b).

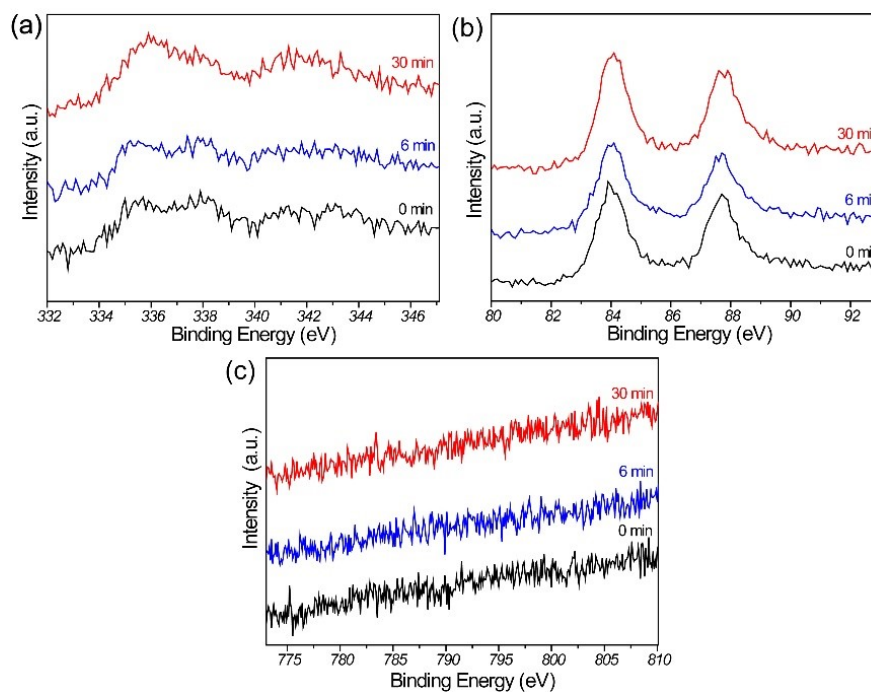


Figure 2.7. (a) Pd 3d, (a) Au 4f and (b) Co 2p XPS spectra of $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ after argon sputtering for 0, 6 and 30 min.

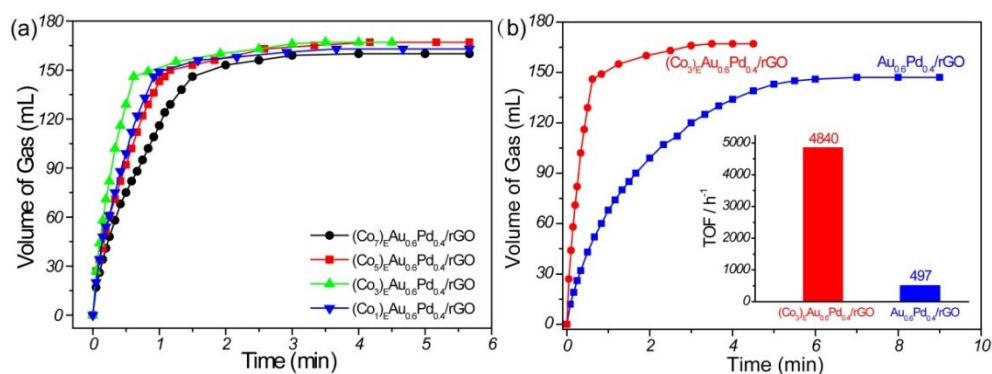


Figure 2.8. Volume of the generated gas ($\text{H}_2 + \text{CO}_2$) versus time for the dehydrogenation of FA over (a) the $(\text{Co}_x)_E\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalyst and (b) the $(\text{Co}_3)_E\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ and $\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalysts (inset: the corresponding TOF values) at 323 K ($n_{\text{AuPd}}/n_{\text{FA}}=0.02$, $n_{\text{SF}}/n_{\text{FA}}=2.5$).

Table 2.1. Catalytic activities for dehydrogenation of formic acid catalyzed by related heterogeneous catalysts.

Catalyst	Solvent/medium	Temp. (K)	CO evolution	TOF (h^{-1})	Ref.
$(\text{Co}_3)_E\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$	HCOONa	323	No	4840	This work
Pd/N-MSC30-two-175	HCOONa	323	No	5890	7(i)
Pd/C_m	HCOONa	323	No	4452 [#]	7(f)
Au@Schiff_SiO ₂	None	323	No	4368 [#]	7(d)
Pd/PDA_rGO	HCOONa	323	No	3810	7(e)
Pd/S-1-in-K	HCOONa	323	No	3027	7(g)
$(\text{Co}_6)\text{Ag}_{0.1}\text{Pd}_{0.9}/\text{rGO}$	HCOONa	323	No	2739	7(c)
Pd/MSC-30	HCOONa	323	No	2623	6(i)
Au/ZrO ₂	NEt ₃	323	No	1593 [#]	6(e)
Pd-B/C	HCOONa	303	No	1184 [#]	7(a)
Pd/CN _{0.25}	None	298	No	752 [#]	7(h)

[#]Initial TOF values calculated at the initial stages of the catalytic reactions based on total Pd atoms.

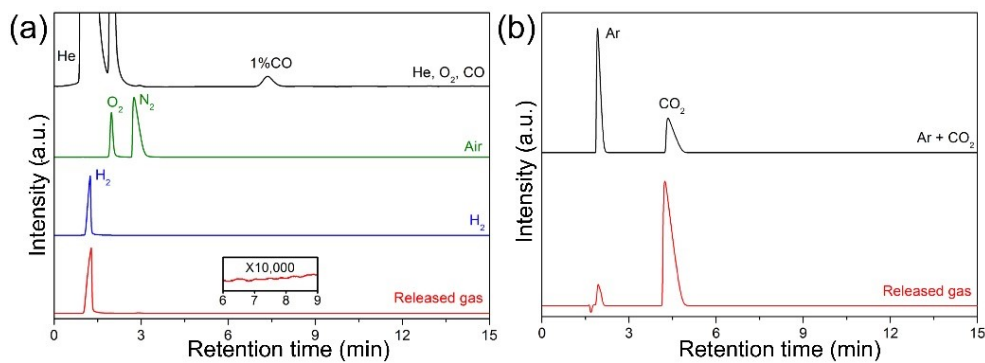


Figure 2.9. Gas chromatograms (GC) of the released gas (under Ar atmosphere) from the decomposition of FA in the FA/SF system ($n_{\text{SF}}/n_{\text{FA}}=2.5$) over the $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalyst at 323 K with (a) CO, air and H_2 and (b) CO_2 as reference gas, indicative of the absence of CO and presence of CO_2 and H_2 in the released gas.

Gas chromatography (GC) measurements demonstrate that the produced gas consists of H_2 and CO_2 without a trace of CO (below 5 ppm), implying that the as-synthesized $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalyst has a high selectivity for the dehydrogenation of FA into H_2 and CO_2 (Fig. 2.9). Such excellent catalytic performance for FA dehydrogenation can meet the requirements of practical applications. Herein, it should be noted that the molar ratio of SF/FA has an obvious influence on the gas release rate (Fig. 2.10a). The gas release rate increases rapidly until the molar ratio of SF/FA increases up to 2.5. The further increase, however, makes no actual impression on the FA decomposition. On the other hand, the catalytic performance of $(\text{Co}_3)_\text{E}\text{Au}_y\text{Pd}_{1-y}/\text{rGO}$ is affected by the molar ratio of Au/Pd (Fig. 2.10b). The mono-metallic $(\text{Co}_3)_\text{E}\text{Au}/\text{rGO}$ has no activity while $(\text{Co}_3)_\text{E}\text{Pd}/\text{rGO}$ has a low activity. However, the introduction of Au into Pd leads to a dramatically enhanced efficiency, which reaches its best value at $n_{\text{Au}}/n_{\text{Pd}} = 6/4$, indicative of the excellent synergistic effects between Au and Pd for FA decomposition.¹² Additionally, rGO is an excellent support for the catalysis, which is demonstrated by the quite low activities of their support-free counterparts (Fig. 2.11a).

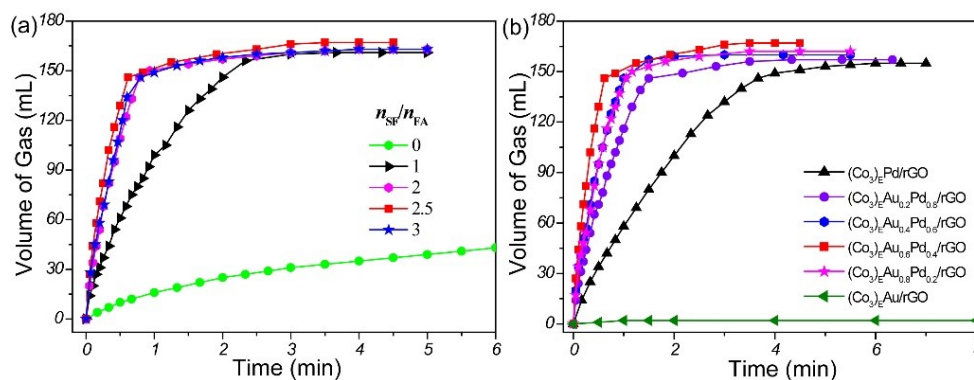


Figure 2.10. Volume of the generated gas ($\text{CO}_2 + \text{H}_2$) versus time for the decomposition of FA (a) with different $n_{\text{SF}}/n_{\text{FA}}$ molar ratios over the $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalyst at 323 K ($n_{\text{AuPd}}/n_{\text{FA}} = 0.02$), and (b) over the $(\text{Co}_3)_\text{E}\text{Au}_y\text{Pd}_{1-y}/\text{rGO}$ catalysts at 323 K ($n_{\text{AuPd}}/n_{\text{FA}} = 0.02$, $n_{\text{SF}}/n_{\text{FA}} = 2.5$).

Further, the increased hydrogen release rates from the FA/SF systems have been observed at elevated temperatures (Fig. 2.11b and c). The activation energy (E_a) in this process is calculated to be $39.77 \text{ kJ mol}^{-1}$, which is lower than most of the reported heterogeneous and homogeneous systems for FA dehydrogenation.^{5,6d,7,13} After the catalytic reaction, the catalyst was recollected by centrifugation, washed with water and recycled for further use. As shown in Fig. 2.11d and Table 2.2, no significant loss in activity was observed over five cycles. The structure and size distribution of metal NPs after the catalytic reactions have been found to be identical to those of the pristine catalyst (Fig. 2.12). The catalytic activities of the $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalysts with lower metal loadings have also not shown significant changes (Fig. 2.13a). In contrast, the CO poisoned $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$, prepared by exposing the catalyst to a CO atmosphere showed no catalytic activity (Fig. 2.13b). It is clear that the $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalyst possesses high selectivity, durability and stability during the FA dehydrogenation.

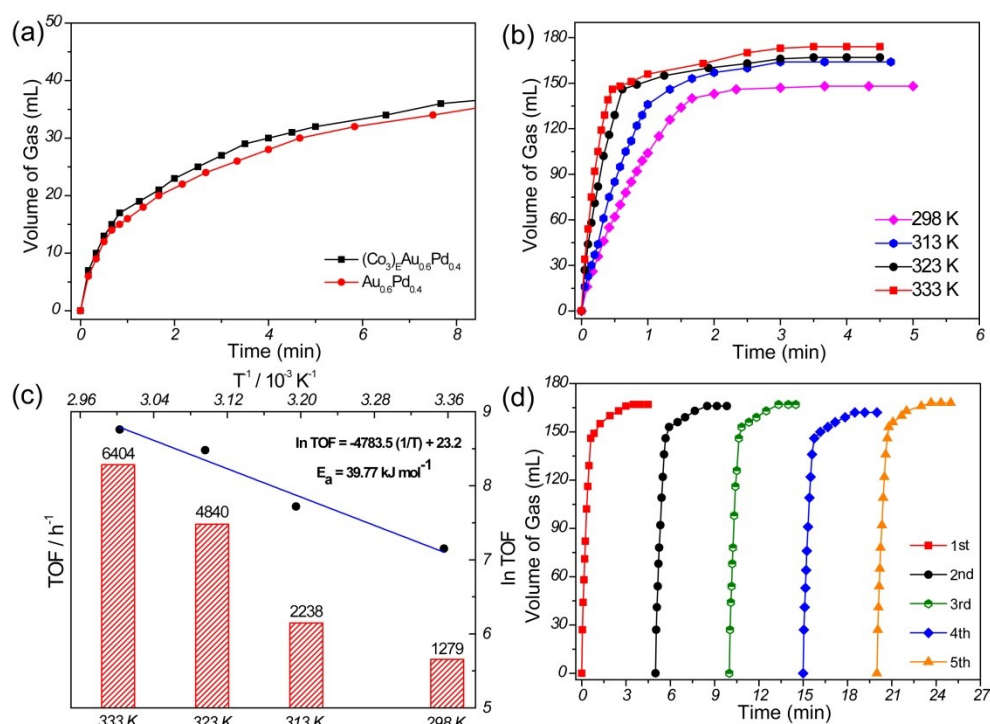


Figure 2.11. Volume of the generated gas (CO_2+H_2) versus time for the dehydrogenation of FA over (a) the support-free $(\text{Co}_3)_E\text{Au}_{0.6}\text{Pd}_{0.4}$ and $\text{Au}_{0.6}\text{Pd}_{0.4}$ catalysts ($n_{\text{AuPd}}/n_{\text{FA}} = 0.02$, $n_{\text{SF}}/n_{\text{FA}} = 2.5$, 323 K) and (b) the $(\text{Co}_3)_E\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalyst at different temperatures ($n_{\text{AuPd}}/n_{\text{FA}} = 0.02$, $n_{\text{SF}}/n_{\text{FA}} = 2.5$), (c) Arrhenius plot and TOF values for the dehydrogenation of FA over the $(\text{Co}_3)_E\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalyst at different temperatures ($n_{\text{AuPd}}/n_{\text{FA}} = 0.02$, $n_{\text{SF}}/n_{\text{FA}} = 2.5$), and (d) durability test for the dehydrogenation of FA over $(\text{Co}_3)_E\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ ($n_{\text{AuPd}}/n_{\text{FA}} = 0.02$, $n_{\text{SF}}/n_{\text{FA}} = 2.5$, 323 K).

Table 2.2. TOFs for the dehydrogenation of FA over $(\text{Co}_3)_E\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ for the cycles of durability test ($n_{\text{AuPd}}/n_{\text{FA}} = 0.02$, $n_{\text{SF}}/n_{\text{FA}} = 2.5$, 323 K)

Cycles	TOF (h^{-1})
1st	4840
2nd	4369
3rd	4592
4th	3987
5th	4265

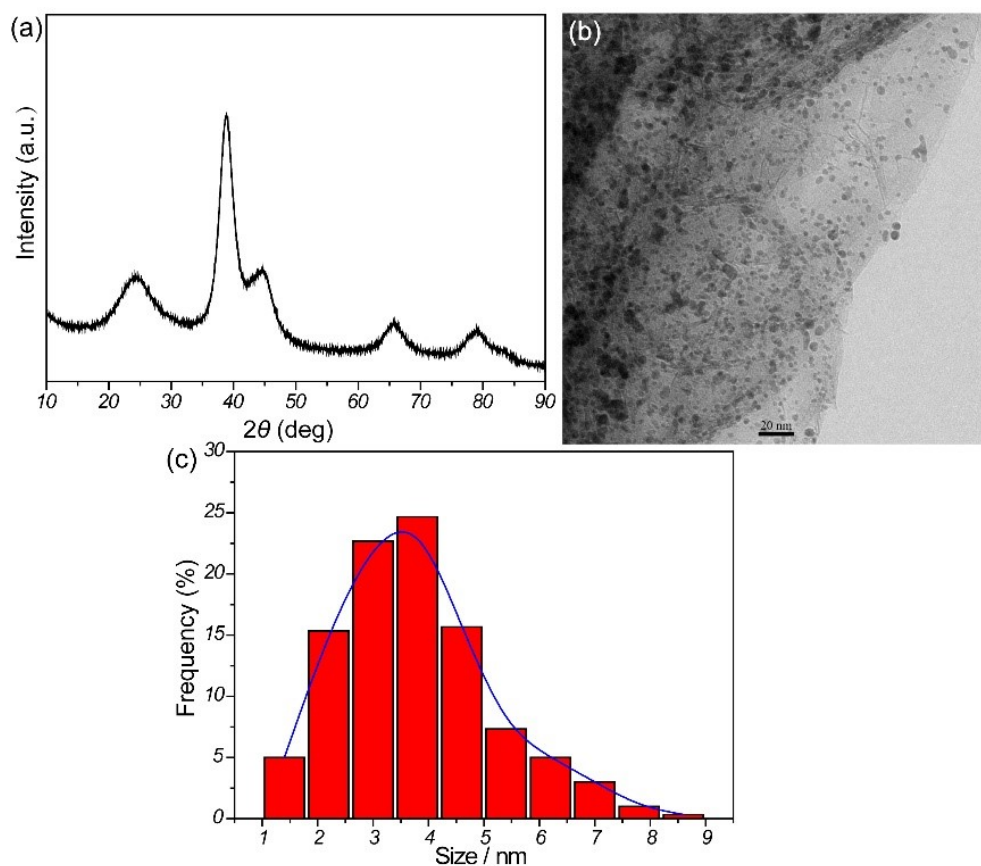


Figure 2.12. (a) XRD pattern, (b) TEM image and (c) size histogram of the $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalyst after 5 catalytic cycles ($n_{\text{AuPd}}/n_{\text{FA}} = 0.02$, $n_{\text{SF}}/n_{\text{FA}} = 2.5$, 323 K).

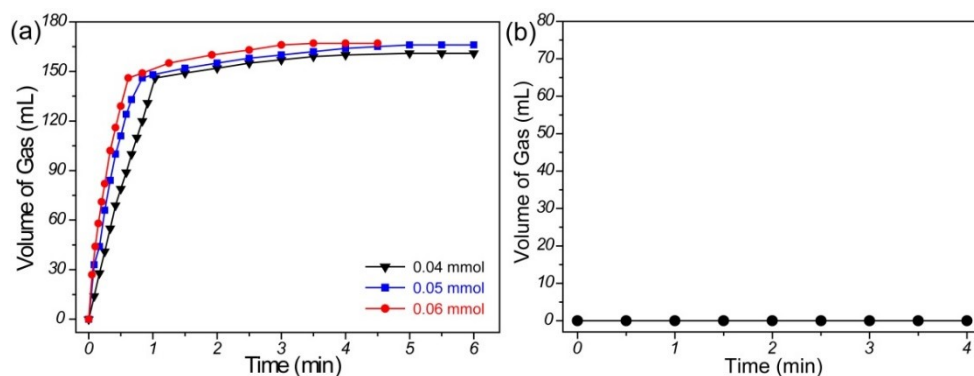


Figure 2.13. Volume of the generated gas ($\text{CO}_2 + \text{H}_2$) versus time for the dehydrogenation of FA over (a) the $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalyst with different loadings of metals (0.04, 0.05 and 0.06 mmol) and the same GO amount at 323 K ($n_{\text{SF}}/n_{\text{FA}} = 2.5$, $\text{FA} = 3$ mmol), showing TOF values of 4338, 4300, and 4840 h^{-1} , respectively, and (b) the CO poisoned $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalyst, prepared by exposing the catalyst to CO atmosphere at 323 K ($n_{\text{AuPd}}/n_{\text{FA}} = 0.02$, $n_{\text{SF}}/n_{\text{FA}} = 2.5$).

2.4 Conclusions

In conclusion, a $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalyst has been synthesized using a simple non-noble metal sacrificial method. The obtained catalyst shows efficient catalytic activity for hydrogen generation from the FA/SF system with one of the highest TOF of 4840 h^{-1} at 323 K and possesses high selectivity, durability and stability over 5 cycles. It is believed that the way to the utilization of FA as a hydrogen carrier will be paved by the practical use of the presently provided catalyst.

References

1. (a) L. Schlapbach and A. Züttel, *Nature*, 2001, **414**, 353; (b) P. E. de Jongh, *Nat. Mater.*, 2011, **10**, 265; (c) A. Boddien, C. Federsel, P. Sponholz, D. Mellmann, R. Jackstell, H. Junge, G. Laurenczy and M. Beller, *Energy Environ. Sci.*, 2012, **5**, 8907.
2. (a) M. Grasemann and G. Laurenczy, *Energy Environ. Sci.*, 2012, **5**, 8171; (b) A. F. Dalebrook, W. Gan, M. Grasemann, S. Moret and G. Laurenczy, *Chem. Commun.*, 2013, **49**, 8735.
3. (a) M. Yadav and Q. Xu, *Energy Environ. Sci.*, 2012, **5**, 9698; (b) Q. Y. Bi, J. D. Lin, Y. M. Liu, X. L. Du, J. Q. Wang, H. Y. He and Y. Cao, *Angew. Chem., Int. Ed.*, 2014, **53**, 13583.
4. (a) S. Fukuzumi, T. Kobayashi and T. Suenobu, *J. Am. Chem. Soc.*, 2010, **132**, 1496; (b) Z. L. Wang, J. M. Yan, H. L. Wang, Y. Ping and Q. Jiang, *J. Mater. Chem. A*, 2013, **1**, 12721.
5. (a) C. Fellay, P. J. Dyson and G. Laurenczy, *Angew. Chem., Int. Ed.*, 2008, **47**, 3966; (b) Y. Himeda, *Green Chem.*, 2009, **11**, 2018; (c) A. Boddien, B. Loges, F. Gärtner, C. Torborg, K. Fumino, H. Junge, R. Ludwig and M. Beller, *J. Am. Chem. Soc.*, 2010, **132**, 8924; (d) A. Boddien, D. Mellmann, F. Gärtner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig and M. Beller, *Science*, 2011, **333**, 1733; (e) Z. L. Wang, J. M. Yan, Y. Ping, H. L. Wang, W. T. Zheng and Q. Jiang, *Angew. Chem., Int. Ed.*, 2013, **52**, 4406; (f) D. Mellmann, E. Barsch, M. Bauer, K. Grabow, A. Boddien, A. Kammer, P. Sponholz, U. Bentrup, R. Jackstell, H. Junge, G. Laurenczy, R. Ludwig and M. Beller, *Chem. Eur. J.*, 2014, **20**, 13589; (g) S. J. Li,

- Y. Ping, J. M. Yan, H. L. Wang, M. Wu and Q. Jiang, *J. Mater. Chem. A*, 2015, **3**, 14535.
6. (a) D. A. Bulushev, S. Beloshapkin and J. R. H. Ross, *Catal. Today*, 2010, **154**, 7; (b) D. R. Dreyer, S. J. Park, C. W. Bielawski and R. S. Ruoff, *Chem. Soc. Rev.*, 2010, **39**, 228; (c) K. Tedsree, T. Li, S. Jones, C. W. A. Chan, K. M. K. Yu, P. A. J. Bagot, E. A. Marquis, G. D. W. Smith and S. C. E. Tsang, *Nat. Nanotechnol.*, 2011, **6**, 302; (d) X. J. Gu, Z. H. Lu, H. L. Jiang, T. Akita and Q. Xu, *J. Am. Chem. Soc.*, 2011, **133**, 11822; (e) Q. Y. Bi, X. L. Du, Y. M. Liu, Y. Cao, H. Y. He and K. N. Fan, *J. Am. Chem. Soc.*, 2012, **134**, 8926; (f) N. Yi, H. Saltsburg and M. Flytzani-Stephanopoulos, *ChemSusChem*, 2013, **6**, 816; (g) K. Mori, M. Dojo and H. Yamashita, *ACS Catal.*, 2013, **3**, 1114; (h) Z. L. Wang, Y. Ping, J. M. Yan, H. L. Wang and Q. Jiang, *Int. J. Hydrogen Energy*, 2014, **39**, 4850; (i) Q. L. Zhu, N. Tsumori and Q. Xu, *Chem. Sci.*, 2014, **5**, 195; (j) Q. L. Zhu and Q. Xu, *Energy Environ. Sci.*, 2015, **8**, 478; (k) K. Mandal, D. Bhattacharjee and S. Dasgupta, *Int. J. Hydrogen Energy*, 2015, **40**, 4786; (l) S. Wu, F. Yang, H. Wang, R. Chen, P. C. Sun and T. H. Chen, *Chem. Commun.*, 2015, **51**, 10887; (m) M. Hattori, H. Einaga, T. Daioc and M. Tsuji, *J. Mater. Chem. A*, 2015, **3**, 4453; (n) A. Bulut, M. Yurderi, Y. Karatas, M. Zahmakiran, H. Kivrak, M. Gulcan and M. Kaya, *Appl. Catal., B*, 2015, **164**, 324.
7. (a) K. Jiang, K. Xu, S. Zou and W. B. Cai, *J. Am. Chem. Soc.*, 2014, **136**, 4861; (b) J. M. Yan, Z. L. Wang, L. Gu, S. J. Li, H. L. Wang, W. T. Zheng and Q. Jiang, *Adv. Energy Mater.*, 2015, **5**, 1500107; (c) Y. Chen, Q. L. Zhu, N. Tsumori and Q. Xu, *J. Am. Chem. Soc.*, 2015, **137**, 106; (d) Q. G. Liu, X. F. Yang, Y. Q. Huang, S. T. Xu, X. Su, X. L. Pan, J. M. Xu, A. Q. Wang, C. H. Liang, X. K. Wang and T. Zhang, *Energy Environ. Sci.*, 2015, **8**, 3207; (e) F. Z. Song, Q. L. Zhu, N. Tsumori and Q. Xu, *ACS Catal.*, 2015, **5**, 5141; (f) Q. L. Zhu, N. Tsumori and Q. Xu, *J. Am. Chem. Soc.*, 2015, **137**, 11743; (g) N. Wang, Q. Sun, R. Bai, X. Li, G. Guo and J. Yu, *J. Am. Chem. Soc.*, 2016, **138**, 7484; (h) Q. Bi, J. Lin, Y. Liu, H. He, F. Huang and Y. Cao, *Angew. Chem., Int. Ed.*, 2016, **55**, 11849; (i) Z. Li, X. Yang, N. Tsumori, Z. Liu, Y. Himeda, T. Autrey and Q. Xu, *ACS Catal.*, 2017, **7**, 2720.

8. (a) W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339; (b) Y. Chen, X. Zhang, P. Xu and Y. Ma, *Chem. Commun.*, 2009, 4527.
9. G. N. Glavee, K. J. Klabunde, C. M. Sorensen and G. C. Hadjapnayis, *Langmuir*, 1992, **8**, 771.
10. (a) T. García, S. Agouram, A. Dejoz, J. F. Sánchez-Royo, L. TorrenteMurciano and B. Solsona, *Catal. Today*, 2015, **248**, 48; (b) C. C. Han, L. N. Wu, L. Ge, Y. J. Li and Z. Zhao, *Carbon*, 2015, **92**, 32.
11. (a) F. Ye, X. Cao, L. Yu, S. Chen and W. Lin, *Int. J. Electrochem. Sci.*, 2012, **7**, 1251; (b) Z. Huang, S. Wang, J. Wang, Y. Yu, J. Wen and R. Li, *Electrochim. Acta*, 2015, **152**, 117.
12. (a) B. Pawelec, E. Cano-Serrano, J. M. Campos-Martin, R. M. Navarro, S. Thomas and J. L. G. Fierro, *Appl. Catal., A*, 2004, **275**, 127; (b) T. Déronzier, F. Morfin, M. Lomello and J. L. Rousset, *J. Catal.*, 2014, **311**, 221.
13. (a) X. Zhou, Y. Huang, W. Xing, C. Liu, J. Liao and T. Lu, *Chem. Commun.*, 2008, 3540; (b) D. A. Bulushev, L. Jia, S. Beloshapkin and J. R. H. Ross, *Chem. Commun.*, 2012, **48**, 4184.

Chapter 3

Encapsulation of Highly Catalytically Active Pd Nanoclusters inside Porous Organic Cages for Hydrogen Generation from Ammonia Borane

3.1 Introduction

The creation of ultrafine metal nanostructured materials with uniform distribution as advanced heterogeneous catalysts has attracted great attention owing to their remarkable catalytic capabilities and essential applications in industries and environments.¹ To date, highly dispersed metal nanostructured materials are usually synthesized either by using high surface area materials as supports for MNPs nucleation and growth,² or by protecting the outer surfaces of prefabricated MNPs using stabilizers.³ In the former case, the disadvantages such as NP aggregation, constant leaching, irregular distribution and regrowth, and weak affinities of MNPs to supports are often encountered in catalysts synthesis. In the latter, the techniques for synthesizing MNPs involve the use of extensive surface capping agents, which may block the diffusion of reactants to metal active sites, leading to reduced catalytic activities.

Emerging as a new type of microporous materials consisting of discrete molecules with intrinsic and guest accessible cavities, porous organic cages (POCs) have drawn considerable attention since the reports from Cooper's group.⁴ Very recently, our group firstly demonstrated that POCs can serve as good stabilizers and homogenizers for Rh NPs while it was difficult to encapsulate Rh NPs inside the cavities of POCs.⁵ Considering the current research impetus of MNPs, as well as the unique

characteristics of POCs such as high inner surface areas, high porosities, uniform but flexible pores and, in particular, the excellent solubility,⁶ the encapsulation of ultrafine MNPs inside POCs is conceived as a promising strategy for developing advanced catalysts. Understandably, the construction of MNP@POC hybrids by encapsulation of MNPs within soluble cages allows the generation of soluble MNPs with merits of controlling particle growth to a narrow size distribution by confinement of MNPs in cage cavities, diminishing particle aggregation and enhancing particle stability. Moreover, since being stabilized inside the open cavities of discrete molecular cages, such soluble MNPs can achieve extremely high dispersibility in solution with more accessible metal active sites for liquid-phase catalytic reactions, and thus an enhanced catalytic activity than their insoluble counterparts can be highly expected.

Herein, for the first time, we demonstrate a reverse double solvents approach (*RDSA*) for facile encapsulation of ultrafine Pd NCs inside the cavity of POC. As encapsulated by soluble and discrete POC shells, the Pd NC cores show excellent solubility, resulting in extremely high dispersibility in solution. Furthermore, the short and open channels of POC shells provide excellent accessibility of Pd NC cores to reactants, and thus could exhibit significantly enhanced catalytic activities in various liquid-phase catalytic reactions for practical applications.

3.2 Experimental details

3.2.1 Chemicals

All chemicals were from commercial and used without further purification. Methanol (Kishida Chemicals Co., Ltd.), dichloromethane (Kishida Chemicals Co., Ltd.), (*R,R*)-1,2-diaminocyclohexane (Sigma-Aldrich Co. LLC.), 1,3,5-triformylbenzene (Beijing Yisiyan Technology Development Center), trifluoroacetic acid (Tokyo

Chemical Industry Co., Ltd.), sodium borohydride (Tokyo Chemical Industry Co., Ltd.), palladium(II) acetate (Wako Pure Chemical Industries, Ltd., >98%), cetyltrimethyl ammonium bromide (CTAB, Sigma-Aldrich Co. LLC.), polyvinylpyrrolidone K40 (PVP, Viscosity Average Molecular Wt. 40000, Tokyo Chemical Industry Co., Ltd.), Pd/C (Nacalai Tesque. Inc.), Pd metal powder (Nacalai Tesque. Inc.), Pd black (Mitsuwa Chemicals Co., Ltd.), bis(triphenylphosphine)-palladium (II) dichloride (Tokyo Chemical Industry Co., Ltd.), tetrakis(triphenylphosphine) palladium (0) (Tokyo Chemical Industry Co., Ltd.) and ammonia borane (JSC Aviator, purity 97%) were used as received.

3.2.2 Characterizations

The powder X-ray diffraction measurements were carried out using a Rigaku Ultima IV diffractometer with Cu-K α radiation. The N₂ sorption isotherm measurements were performed at liquid nitrogen temperature (77 K) using automatic volumetric adsorption equipment (Belsorp-max). The UV-vis absorption measurements were recorded using a UV-2550 spectrophotometer (SHIMADZU). X-ray photoelectron spectrometry (XPS) analyses were carried out on a Shimadzu ESCA-3400 X-ray photoelectron spectrometer using an Mg K α source (10 kV, 10 mA). Scanning electron microscopy (SEM) analyses were performed using a JEOL JSM-IT100 microscope. Fourier transform infrared (FTIR) spectra were collected on a TRTracer-100 spectrometer (SHIMADZU). Scanning transmission electron microscopy (STEM) images and energy-dispersive X-ray spectroscopy (EDS) mapping analyses were recorded on Titan3 G2 60-300 (FEI) with Super-X EDS system (Bruker) under operating voltages of 300 kV. Solution ¹H, ¹³C, 2D DOSY and NOESY NMR spectra were recorded at 500.13 MHz using a Bruker-biospin Avance III 500 NMR spectrometer.

3.2.3 Synthesis of organic cages

Synthesis of CC3-R. The synthesis of CC3-R is according to the previous method.^{7a} A typical procedure is as follows: CH₂Cl₂ (10 mL) was added slowly to solid 1,3,5-triformylbenzene (0.5 g) at room temperature. Trifluoroacetic acid (10 µL) was added directly to this solution as a catalyst for imine bond formation. Finally, a solution of (*R,R*)-1,2-diaminocyclohexane (0.5 g, 4.464 mmol) in CH₂Cl₂ (10 mL) was added. The vessel of the mixture solution was capped and left to stand for one week. The crystals grew on the sides of the vessel. The crystalline product was removed by centrifugation and washed with CH₂Cl₂/CH₃OH mixture (v/v, 5/95) for 5 times, and further dried at 100 °C under vacuum overnight.

Synthesis of RCC3. The synthesis of RCC3 is according to the previous method.^{7b} The imine cage CC3-R (463 mg) was dissolved in a CH₂Cl₂/CH₃OH mixture (v/v, 1/1, 25 mL) by stirring. When this solution became clear, NaBH₄ (0.5 g) was added and the reaction was stirred for 15 h at room temperature. Water (1 mL) was then added, and the solution was continuously stirred for 9 h. The solvent was then removed under vacuum. The resulted solid was washed by water and collected by centrifugation, and the obtained solid was dried at 70 °C under vacuum overnight. Finally, 458 mg of RCC3 was obtained in a yield close to 100 %.

Purification of RCC3 cages. The RCC3 cage was purified according to the previous method.^{7b} In a 30 mL flask, 100 mg of crude RCC3 was dissolved in 10 mL of acetone. The solution was covered and left to stand. Crystals started appearing on the wall of the flask after 30 mins. The crystals were collected after 24 h by centrifugation and then dissolved in 10 mL of CH₂Cl₂/CH₃OH mixture (v/v, 1/1) by continuous stirring. 0.1 mL of distilled water was added to the solution and the mixture was

stirred for another 48 h. After removal of the solvents, pure RCC3 (60 mg, 60%) was recovered.

3.2.4 Synthesis of catalysts

Synthesis of the Pd@RCC3 catalyst by the RDSA. In a typical synthesis, 85 mg of dehydrated RCC3 powder was soaked in 20 mL of water and stirred for 20 min. After constant vigorous stirring for a while, 0.02 mL of Pd(OAc)₂/CH₂Cl₂ solution containing 0.01 mmol of Pd(OAc)₂ as the hydrophobic solution was added dropwise into the cage/water dispersion, and the resulted mixture was continuously stirred for 3 h. Finally, 0.5 mL of freshly prepared aqueous NaBH₄ (50 mg) solution was added quickly and then kept under stirring for 3 h. The synthesized samples were gathered by centrifugation and washed by water. The obtained solid samples were dried in air at 70 °C for 2.5 h, and used for the catalytic reactions.

Synthesis of the Pd/RCC3 catalyst by conventional impregnation method. In a typical synthesis, 85 mg of RCC3 powder was ultrasonically dissolved in 9 mL of CH₂Cl₂/CH₃OH mixture (v/v, 2/1) and aged for additional 20 min, to which palladium acetate (0.01 mmol) in 0.02 mL CH₂Cl₂ was subsequently added. The resulted mixture was further sonicated and aged for additional 20 min. Then, 30 mg of NaBH₄ was added into the above solution with vigorous shaking, resulting in the generation of Pd/RCC3 catalyst.

Synthesis of the Pd-SP-Free catalyst. In a typical synthesis, 0.01 mmol of palladium acetate was ultrasonically dissolved in 9 mL of CH₂Cl₂/CH₃OH mixture (v/v, 2/1). The resulted mixture was further sonicated and aged for additional 20 min. Then, 0.50 mL of CH₃OH solution containing 30 mg of NaBH₄ was added into the above solution with vigorous shaking, resulting in the generation of Pd-SP-Free catalyst.

Synthesis of the Pd/CTAB and Pd/PVP catalyst. In a typical synthesis, 85 mg of CTAB (PVP) powder was ultrasonically dissolved in 9 mL of CH₂Cl₂/CH₃OH mixture (v/v, 2/1), to which palladium acetate (0.01 mmol) was subsequently added. The resulted mixture was further sonicated for 1 min and then aged for additional 20 min. Then, 0.50 mL of CH₃OH solution containing 20 mg of NaBH₄ was added into the above solution with vigorous shaking, resulting in the generation of Pd/CTAB (PVP) catalyst.

Synthesis of the Pd/(*R,R*)-1,2-diaminocyclohexane Pd/1,3,5-triformylbenzene catalyst.

In a typical synthesis, 85 mg of (*R,R*)-1,2-diaminocyclohexane (1,3,5-triformylbenzene) powder was ultrasonically dissolved in 9 mL of CH₂Cl₂/CH₃OH mixture (v/v, 2/1), to which palladium acetate (0.01 mmol) was subsequently added. The resulted mixture was further sonicated for 1 min and then aged for additional 20 min. Then, 0.50 mL of CH₃OH solution containing 20 mg of NaBH₄ was added into the above solution with vigorous shaking, resulting in the generation of Pd/(*R,R*)-1,2-diaminocyclohexane (1,3,5-triformylbenzene) catalyst.

Recrystallization of RCC3 and Pd@RCC3 cages. The RCC3 and Pd@RCC3 were recrystallized according to the previous method.^{7b} 85 mg of RCC3 or Pd@RCC3 was dissolved in 10 mL of CH₂Cl₂. After slow evaporation for 3 days, the crystals of RCC3 or Pd@RCC3 were obtained.

3.2.5 Procedures for catalysis

Procedures for the methanolysis of AB. Method for evaluating the hydrogen evolution from the methanolysis of AB is as previously reported.⁵ In general, the as-synthesized catalyst with 9 mL of CH₂Cl₂/CH₃OH mixture (v/v, 2/1) was carefully poured into a two-necked flask, which was placed in a water bath under ambient atmosphere. A gas

burette filled with water was connected to the two-necked flask to collect the generated gas. After 1 mL of AB (1 mmol) contained CH₃OH solution was added into the flask, the catalytic reaction started, and the yield of generated H₂ was recorded by reading the volume of the displacement of water in the gas burette. The AB methanolysis was finished when no gas was generated. Generally, the AB methanolysis can be expressed as: $\text{NH}_3\text{BH}_3 + 4\text{CH}_3\text{OH} \rightarrow \text{NH}_4\text{B}(\text{CH}_3\text{O})_4 + 3\text{H}_2$.

Procedures for the catalytic hydrogenation of 4-NPh. Typically, the catalytic process proceeded under ambient conditions. Firstly, 10 mg of NaBH₄ (0.264 mmol) and 4 mL of 4-NPh (0.165 mmol/L) in CH₂Cl₂/CH₃OH mixture (v/v, 2/1) was mixed in a quartz cell. Then a mixture of 10 μL of catalyst (0.000011 mmol Pd) was added in this solution. Initially, the molar ratio of Pd/4-NPh/NaBH₄ was adjusted to 1/60/24000. After adding the as-prepared catalyst, the color of 4-NPh solution gradually faded from bright yellow to colorless as the reaction continued. The conversion of 4-NPh to 4-Aph was monitored by recording the UV-Vis spectra at short intervals in a range of 250-550 nm. On the basis of the change of the intensity at $\lambda = 400$ nm as a function of time, the rate constants of the catalytic hydrogenation of 4-NPh were determined. The procedures for the catalytic hydrogenation of 2-NPh, 2-NAn, 3-NAn and 4-NAn were similar to that of 4-NPh except using λ of 420, 400, 368 and 368 nm.

Procedures for the catalytic decomposition of organic dyes. Typically, methanol solutions (4 mL, 0.05 mmol/L) of Congo red or Methyl orange were mixed with 6 mg of NaBH₄ at room temperature in a quartz cell, respectively. Then a mixture of 10 μL of catalyst (0.000011 mmol Pd) was added in this solution, and the catalytic reactions were monitored using a UV-vis spectrophotometer.

3.3 Results and discussion

The design of reverse double solvents approach (RDSA). Recently, the double solvents approach (*DSA*), which involves the use of tiny amount of water solution of metal precursor with plenty of a hydrophobic organic liquid, has been successfully used to encapsulate MNPs inside hydrophilic pores of metal-organic frameworks (MOFs).⁸ As the POC cavities are hydrophobic, here, we apply a *RDSA* (Fig. 3.1a), which involves a hydrophobic and a hydrophilic solvent, the former (CH_2Cl_2), in a small amount, containing the metal precursor which can be absorbed, driven by the strong interaction between hydrophobic molecules and hydrophobic cavities, within the hydrophobic cavities of the organic cage, and the latter (H_2O), being provided with a large quantity for dispersing the organic cages and facilitating the molecular diffusion of the small amount of palladium acetate-containing CH_2Cl_2 into the hydrophobic cage cavities. Finally, a highly concentrated aqueous solution of NaBH_4 is introduced to reduce metal precursors rapidly and completely, resulting in the formation of ultrafine Pd NCs inside the cage cavities.

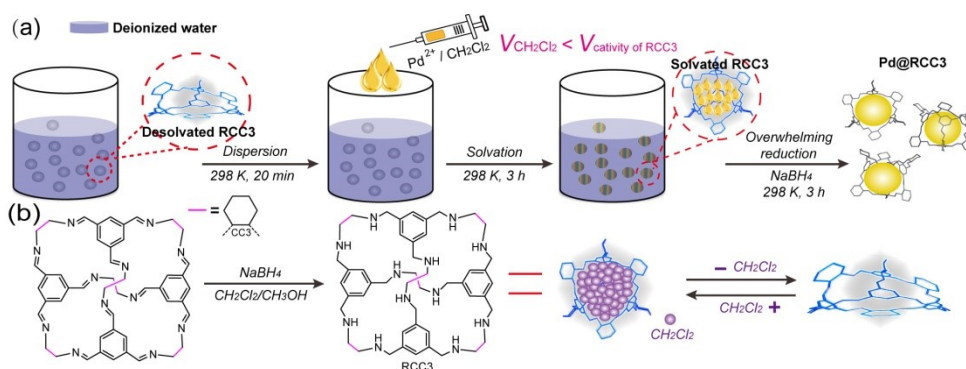


Figure 3.1. (a) Schematic illustration of the encapsulation of Pd NCs inside the RCC3 matrix by using *RDSA*, and (b) the reduction of CC3-R to RCC3 by NaBH_4 , desolvated RCC3 shows a significant loss of porosity due to the collapse of flexible cage cavities, desolvated RCC3 can be recovered immediately to its original crystalline state after adding a few drops of CH_2Cl_2 .

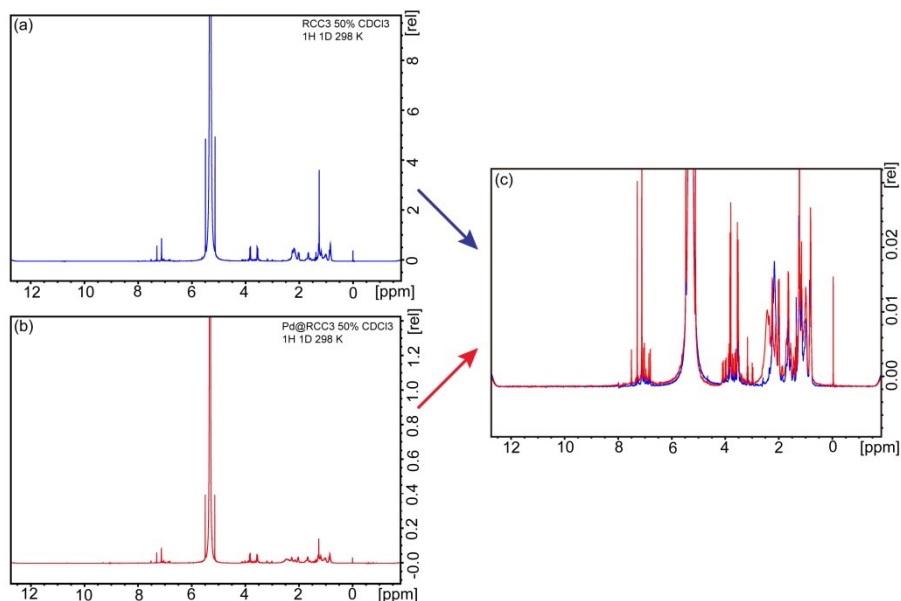


Figure 3.2. ^1H NMR spectra of (a) RCC3, (b) Pd@RCC3 and (c) the comparison between RCC3 and Pd@RCC3.

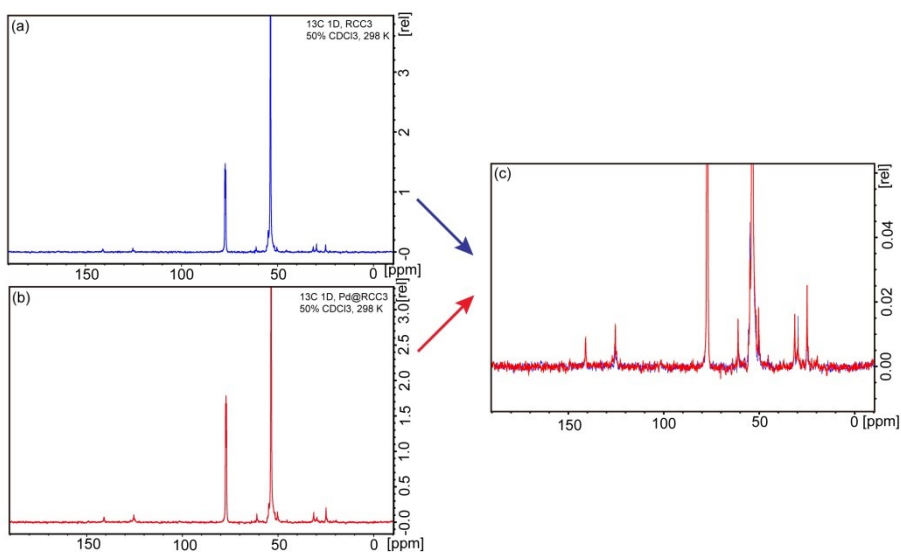


Figure 3.3. ^{13}C NMR spectra of (a) RCC3, (b) Pd@RCC3 and (c) the comparison between RCC3 and Pd@RCC3.

The reduced amine cage, RCC3, is selected as a good platform for the *RDSA* owing to its several unique features such as a) high stability in water and air, b) highly hydrophobic, flexible and ultrafine cavities with pore windows large enough for metal precursors diffusion, and c) excellent solubility in certain solvents with well-kept

prefabricated open skeletons.^{6a,b} RCC3 can be readily synthesized by reduction of prefabricated chiral imine cage CC3-*R* according to the previous method using NaBH₄ in CH₂Cl₂/CH₃OH solvent in close to 100 % yield (Fig. 3.1b).⁷ ¹H and ¹³C nuclear magnetic resonances (NMR) (Fig. 3.2a and 3.3a), elemental analysis (Table 3.1) and fourier transform infrared spectroscopy (FTIR) (Fig. 3.4a) of the product, are all consistent with those previously reported,^{7b} confirming the successful formation of RCC3 and its isolation. It is noteworthy that RCC3 has a significantly stable and flexible structure (Fig. 3.1b). As illustrated by powder X-ray diffraction (PXRD) measurements (Fig. 3.4b), desolvated RCC3 shows a broad band in a range of 10-30° owing to the collapse of the cavities upon solvent removal. Interestingly, the diffraction peaks of crystalline RCC3 recover immediately after addition of a few drops of CH₂Cl₂ to desolvated RCC3. However, by addition of water on desolvated RCC3, such phenomenon cannot be observed, clearly indicating that those collapsed cavities of RCC3 are “thirsty” to hydrophobic molecules for the restoration of original crystalline state. The molecules of CH₂Cl₂ are easily encapsulated within RCC3 cages by *RDSA* as confirmed by PXRD measurement (Fig. 3.4c). This feature benefits the incorporation of metal precursors into cage cavities by using the *RDSA*.

Table 3.1. Atomic mass ratios of C, H and N in RCC3

Run details		Results		
Run	Weight (mg)	C (wt.%)	H (wt.%)	N (wt.%)
1	1.679	73.60	9.59	14.05
2	1.717	73.51	9.55	14.09
3	1.660	73.76	9.51	14.23

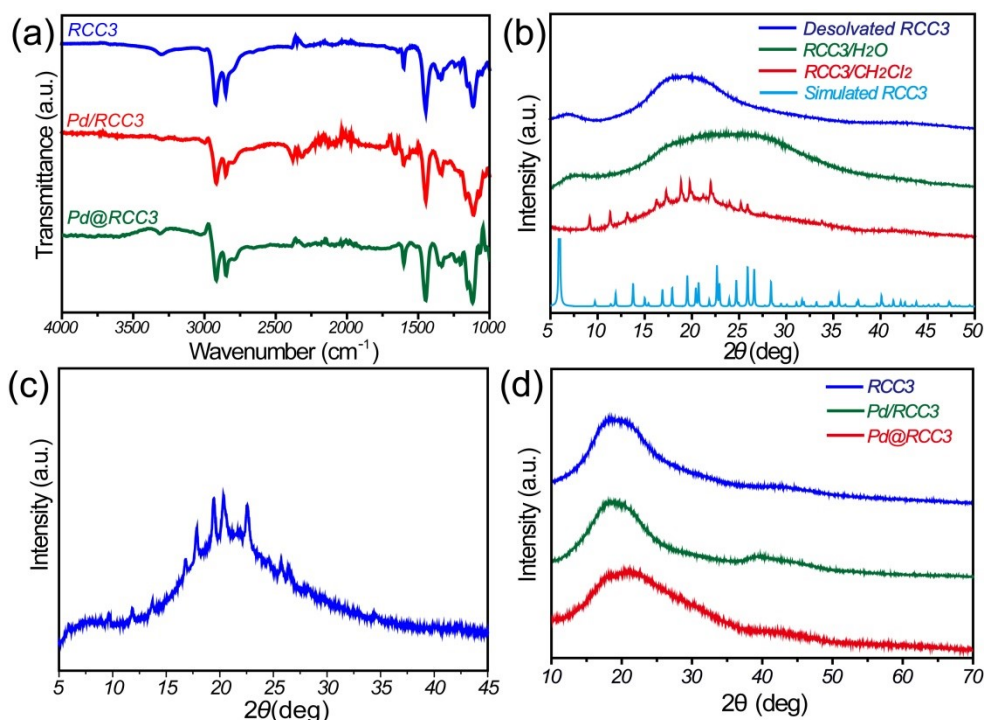


Figure 3.4. (a) FTIR spectra of RCC3, Pd/RCC3 and Pd@RCC3, (b) XRD patterns of desolvated RCC3, RCC3/H₂O and RCC3/CH₂Cl₂, (c) XRD pattern of RCC3 cage with CH₂Cl₂ (without metal salts) introduced by *RDSA*, and (d) XRD patterns of RCC3, Pd/RCC3 and Pd@RCC3.

Synthesis and characterization of the organic molecular cage-encapsulated Pd NCs.

For encapsulating Pd NCs within the cavities of RCC3, the desolvated RCC3 powders (85 mg) are firstly dispersed in 20 mL of water, to which a CH₂Cl₂ solution (20 μL) containing Pd(OAc)₂ (0.01 mmol) is added dropwise under vigorous stirring. After continuous stirring for 3 h, the as-prepared mixture is reduced by adding a highly concentrated aqueous solution of NaBH₄ (2.7 M, 0.5 mL) to yield Pd@RCC3. Similar to the desolvated RCC3 cages, the PXRD pattern of the as-prepared Pd@RCC3 shows a broad band in the range of 10-30° (Fig. 3.4d), suggesting the RCC3 cage is maintained. Meanwhile, no diffraction peaks of Pd NCs have been observed, indicating the successful formation of well-dispersed ultrasmall Pd NCs. No changes have been found in the FTIR spectra (Fig. 3.4a) and scanning electron microscopy

(SEM) images (Fig. 3.5a and 3.6a) of Pd@RCC3, further suggesting the covalent bonding of RCC3 is intact after the encapsulation of Pd NCs. As observed in the N₂ sorption isotherms (Fig. 3.5b), desolvated RCC3 exhibits no porosity to N₂ as having a collapsed structure, whereas the obtained Pd@RCC3 possesses an increased porosity to N₂, illustrating that the involvement of Pd NCs inside the pores of RCC3 has contributed to an increased porosity of RCC3. The PXRD pattern of re-crystallized Pd@RCC3 (Fig. 3.5c) shows the similar crystal lattice to that of re-crystallized RCC3, suggesting that most of the Pd NCs are encapsulated inside the RCC3 cages. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) of Pd@RCC3 suggests that Pd NCs are uniformly dispersive, possessing an ultrafine average diameter of 0.72 nm (Fig. 3.6b-d). Considering the significantly flexible cage structure as well as the *RDSA* employed here for introducing metal precursors,⁶ we believe that most of Pd NCs (~70 %) are encapsulated within the cages, in agreement with the estimated pore size of cage (~0.7 nm).^{7b} Compared to HAADF-STEM, it is difficult to detect Pd NCs by transmission electron microscopy (TEM) because of their ultrafine size (Fig. 3.7). Energy-dispersive X-ray spectroscopy (EDS) elemental mapping (Fig. 3.6e-j) of Pd@RCC3 further confirms that the obtained ultrafine Pd NCs are highly distributed inside the cage cavities of RCC3. Additionally, X-ray photoelectron spectroscopy (XPS) analysis is performed for identifying the chemical states of N and Pd elements of the as-prepared Pd@RCC3 (Fig. 3.5d). The peak at 399 eV is ascribed to the sum of N atoms of primary and secondary amines. Successful formation of metallic Pd NCs is confirmed by the peaks at 335.9 and 341.1 eV, corresponding to two distinct spin-orbit pairs of Pd 3d_{5/2} and Pd 3d_{3/2}, respectively.⁹

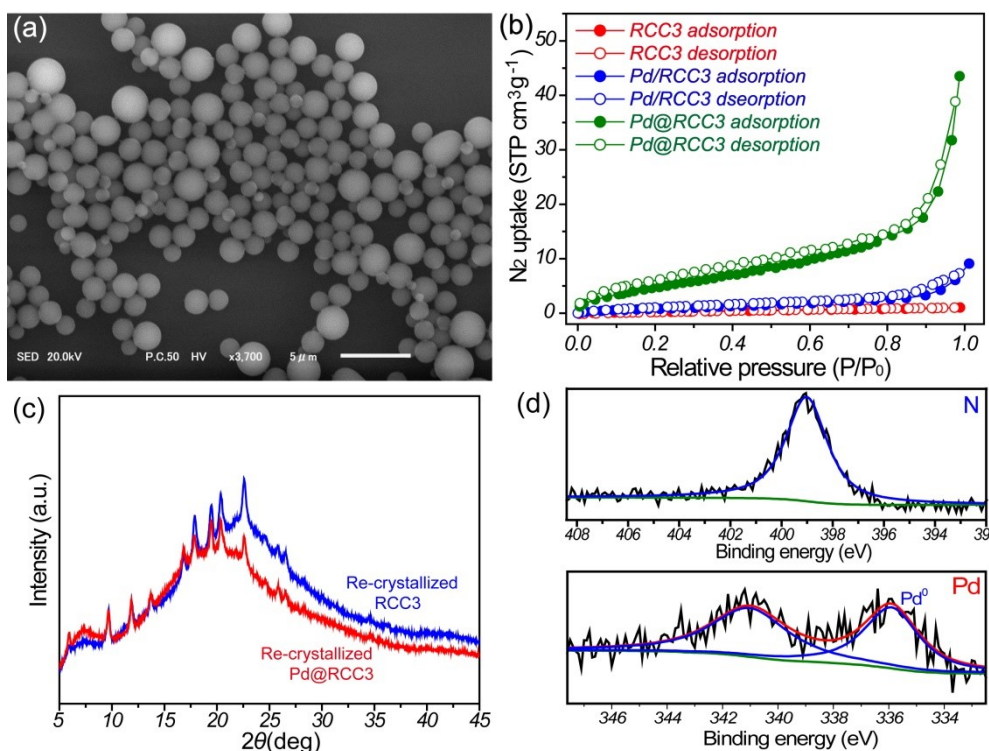


Figure 3.5. (a) SEM image of RCC3, (b) N₂ sorption isotherms of RCC3, Pd/RCC3 and Pd@RCC3, (c) XRD patterns of the re-crystallized RCC3 and Pd@RCC3, and (d) N 1s and Pd 3d XPS spectra of the as-prepared Pd@RCC3.

NMR has been applied to better analyze the structure of Pd@RCC3 and, specifically, the spatial relationship between the cage host and the encapsulated Pd NC guest. The ¹³C NMR spectrum of Pd@RCC3 (Fig. 3.3b) is very similar to that of RCC3 (Fig. 3.3a), suggesting that the RCC3 cage is in approximately the same configuration with or without the encapsulated NCs. Interestingly, compared to RCC3 (Fig. 3.2a), the broadening in the widths of all peaks in the ¹H NMR spectrum of Pd@RCC3 (Fig. 3.2b) are observed, which can be attributed to the local restricted motion and heterogeneity due to encapsulation of the Pd NCs.^{10a} Additionally, 2D DOSY (Fig. 3.8) shows very similar diffusion coefficients for Pd@RCC3 and RCC3, which confirms the similar size and shape of free RCC3 cage and Pd@RCC3. In particular, this offers important evidence to support that Pd NC is encapsulated in the

cage rather than stabilized by two or more cages, or the functional groups of cages.¹⁰ We have also tried but failed in getting mass spectra for the Pd NCs because of the low intensities of expected large amount of isotope peaks due to the broad and continuous particle size distribution from 0.2 nm to 0.7 nm as observed by HAADF-STEM.

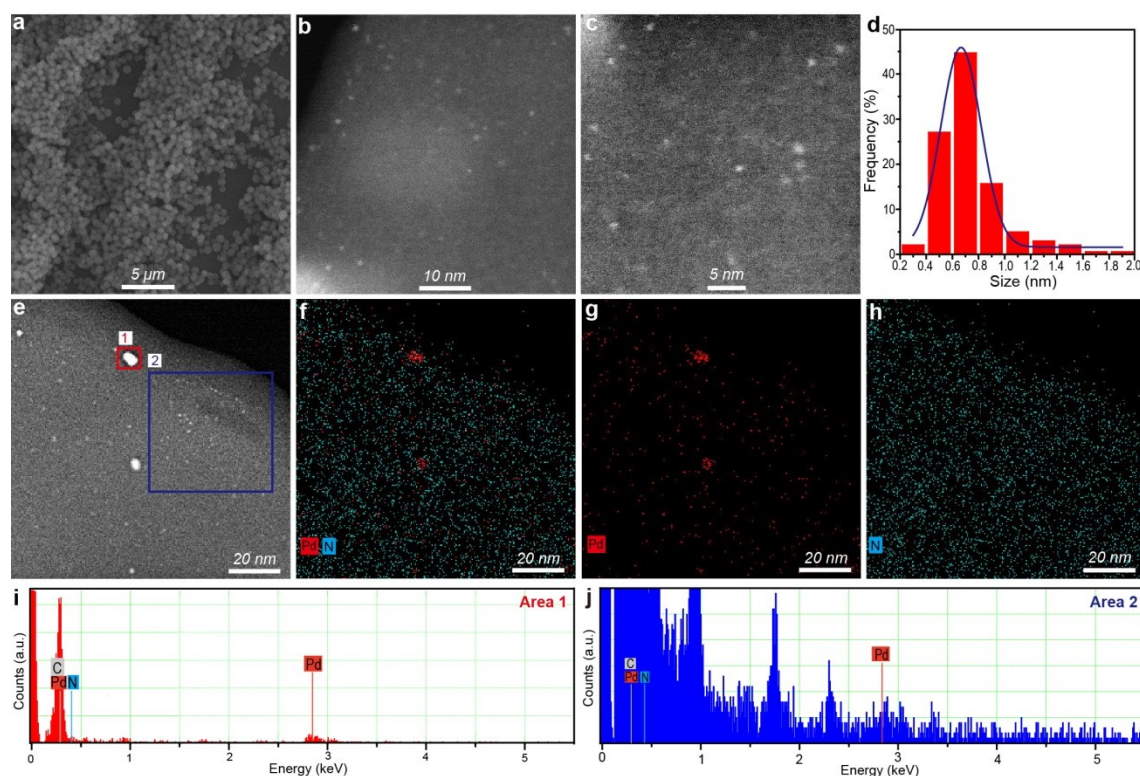


Figure 3.6. (a) SEM image, (b, c) HAADF-STEM images, (d) particle size distribution histograms, (e) HAADF-STEM image, (f-h) the corresponding EDS mapping images, and (i, j) the EDS patterns of the selected area in (e) of Pd@RCC3.

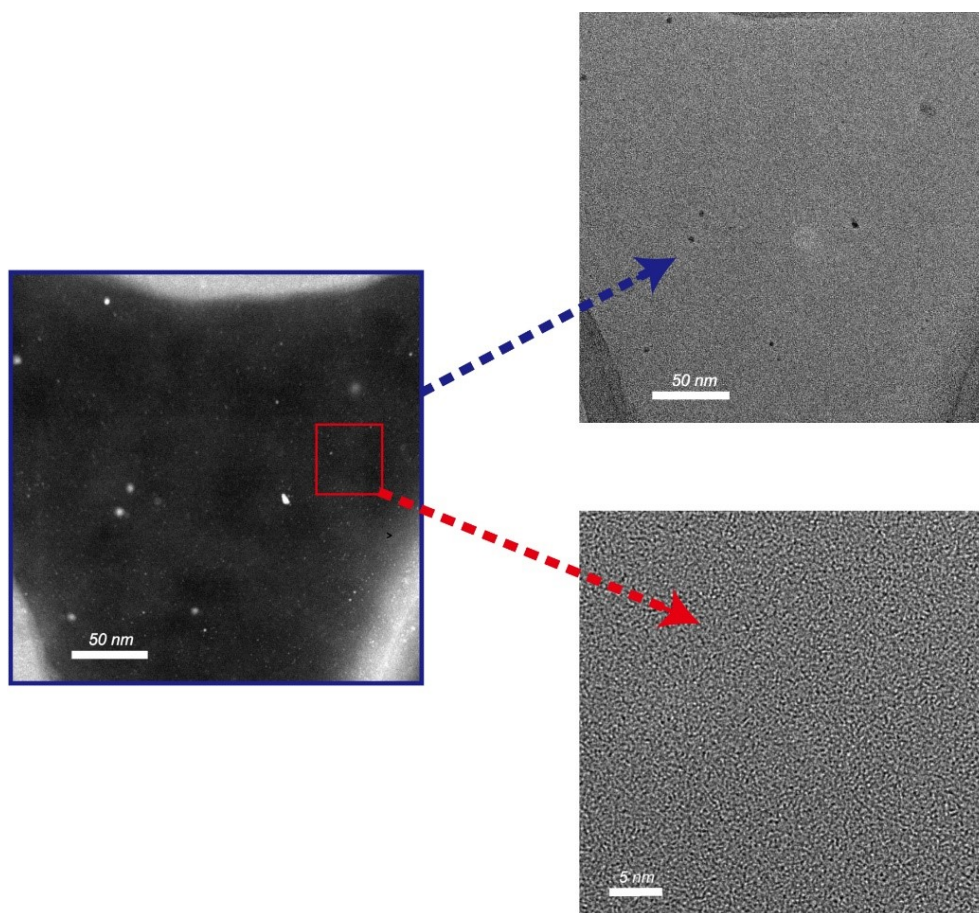


Figure 3.7. HAADF-STEM image and the corresponding TEM images of Pd@RCC3.

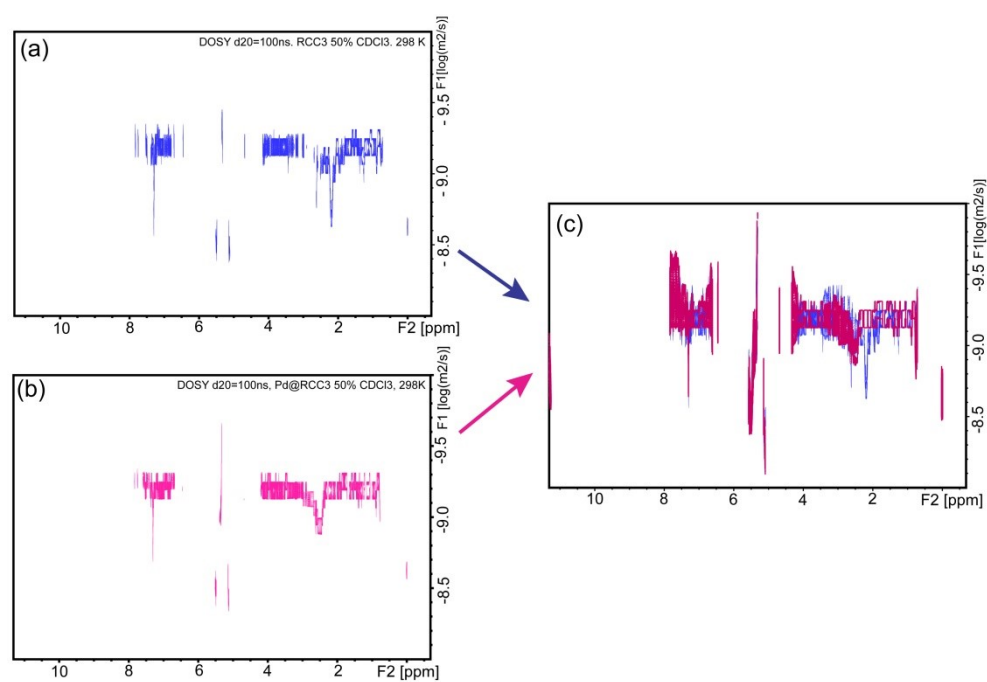


Figure 3.8. 2D-DOSY NMR spectra of (a) RCC3, (b) Pd@RCC3, and (c) the comparison between RCC3 and Pd@RCC3.

In order to understand the roles of the *RDSA*, a control experiment has been performed using the conventional impregnation method to produce Pd/RCC3. Unlike Pd@RCC3, PXRD pattern of Pd/RCC3 retains low and broad band of desolvated RCC3 with a characteristic peak of Pd NPs at 39.5° (Fig. 3.4d). N₂ sorption isotherms indicate a very low N₂ uptake, almost the same as the desolvated RCC3 (Fig. 3.5b). HAADF-STEM analysis shows severely aggregated and non-uniformly dispersed Pd NPs with a 2.2 nm average diameter (Fig. 3.9), much larger than the pore size of RCC3. These observations illustrate that the Pd NPs in Pd/RCC3 are supported on the outer surfaces of RCC3, suggesting that the *RDSA* is effective for controlling the growth of Pd NCs inside POCs.

The solubility and dispersibility of Pd@RCC3 and Pd/RCC3 in different solvents have been investigated. Interestingly, Pd@RCC3 can be dissolved in CH₃OH, CH₂Cl₂ and their mixture, giving clear solutions, which show no change even after several days (Fig. 3.10). In contrast, the as-prepared Pd/RCC3 catalyst is insoluble in CH₃OH, CH₂Cl₂ and their mixture, giving a dark dispersion (Fig. 3.11). Presumably, the RCC3 cage shell serves as an effective protector for Pd NCs, preventing them from aggregations as well as endowing them a good solubility.

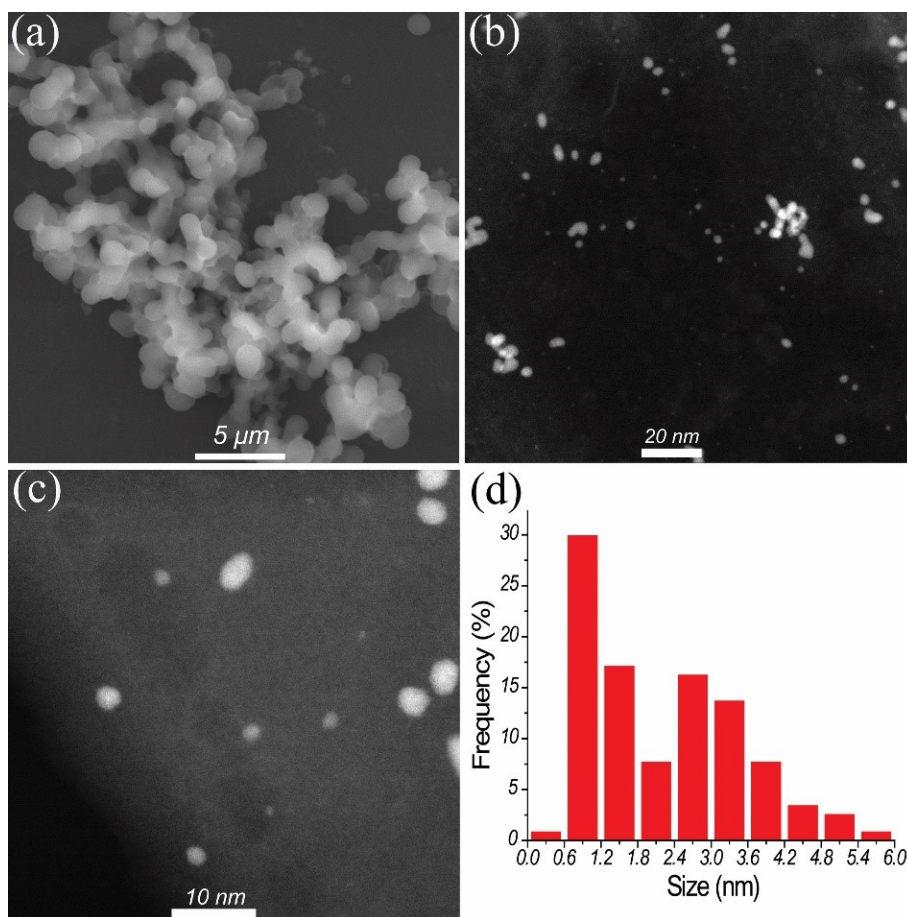


Figure 3.9. (a) SEM image, (b, c) HAADF-STEM images and (d) particle size distribution histograms of Pd/RCC3.

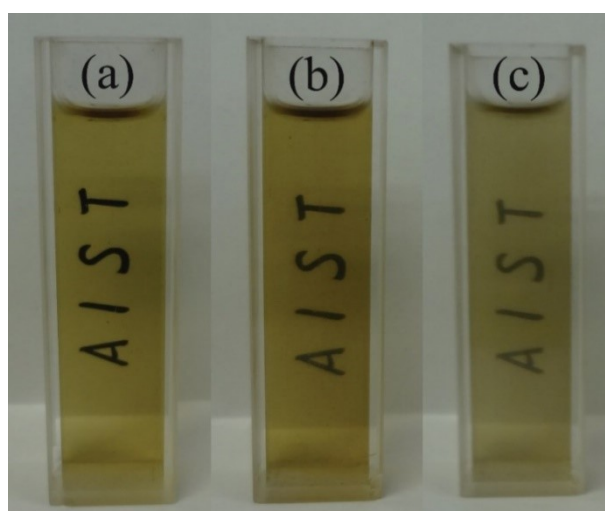


Figure 3.10. Photographs of the Pd@RCC3 catalysts in (a) CH₂Cl₂, (b) CH₂Cl₂/CH₃OH (v/v, 2/1) and (c) CH₃OH (C_{Pd} = 0.0017 M).

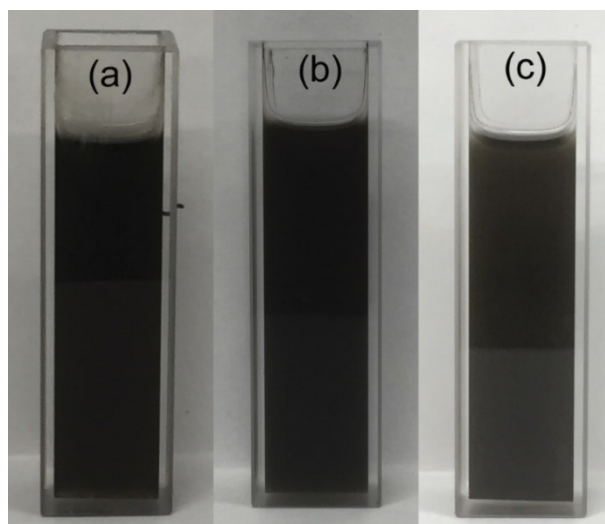


Figure 3.11. Photographs of the Pd/RCC3 catalysts in (a) CH_2Cl_2 , (b) $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (v/v, 2/1) and (c) CH_3OH ($C_{\text{Pd}} = 0.0017 \text{ M}$).

Catalytic hydrogen generation from ammonia borane (AB). As a promising and environmentally-friendly hydrogen supply chemical compound, AB (NH_3BH_3) has obtained broad attention, from which hydrogen can be released through catalytic thermolysis, hydrolysis and methanolysis.¹¹ In this work, for assessing the catalytic activities of the as-prepared Pd@RCC3 catalysts, the methanolysis of AB to generate H_2 has been selected as the test reaction. The catalytic methanolysis is initiated by adding AB into a reaction flask containing the as-synthesized soluble Pd@RCC3 catalyst with vigorous shaking at 303 K. The amount of produced hydrogen is monitored by using a buret. Under our evaluation conditions, the Pd@RCC3 catalyst with Pd loading of 1.23 wt.% exhibits an extraordinary catalytic performance for the methanolysis of AB (Fig. 3.12a), with which the reaction has been finished ($n[\text{H}_2]/n[\text{AB}] = 3$) in 1.67 min ($n[\text{Pd}]/n[\text{AB}] = 0.01$) at 303 K, giving a TOF value up to 176 mol of H_2 per mol of Pd per min, among the highest values for the methanolysis of AB reported thus far.^{5, 12} Notably, Pd-based catalysts usually show low catalytic performance in the AB methanolysis, but here we first demonstrate that the Pd NCs with sub-1 nm size inside soluble POC possess extremely high catalytic

activity. Such outstanding catalytic ability indicates that the strategy of encapsulating metal NPs within the organic cages is effective for developing high performance heterogeneous catalysts.

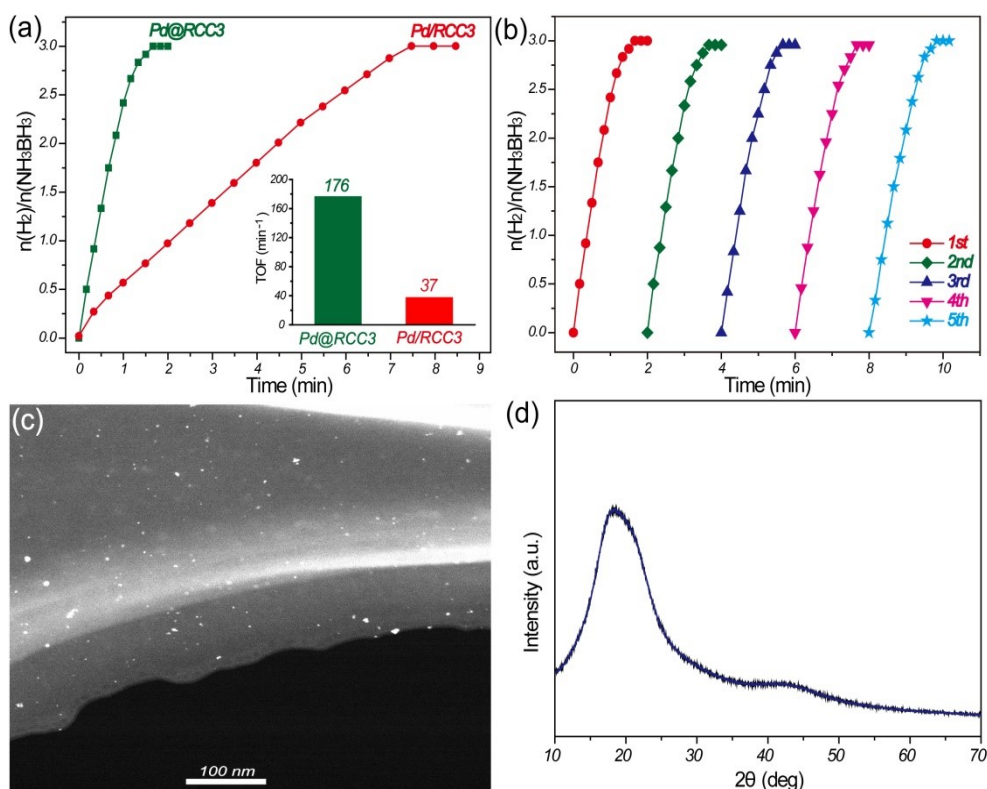


Figure 3.12. (a) Time course plots for the methanolysis of AB over the Pd@RCC3 and Pd/RCC3 catalysts at 303 K ($n_{\text{Pd}}/n_{\text{AB}} = 0.01$, $V_{\text{CH}_2\text{Cl}_2}/V_{\text{CH}_3\text{OH}} = 2/1$); Inset: the corresponding TOF values of the catalysts, (b) durability test for the methanolysis of AB over the Pd@RCC3 catalyst at 303 K ($n_{\text{Pd}}/n_{\text{AB}} = 0.01$, $V_{\text{CH}_2\text{Cl}_2}/V_{\text{CH}_3\text{OH}} = 2/1$), (c) HAADF-STEM and (d) PXRD pattern of the Pd@RCC3 catalyst after AB methanolysis reactions ($n_{\text{Pd}}/n_{\text{AB}} = 0.01$, $V_{\text{CH}_2\text{Cl}_2}/V_{\text{CH}_3\text{OH}} = 2/1$).

Catalytic hydrogenation of nitroarenes. To further confirm the use of the current Pd@RCC3 catalyst for boosting the activity in liquid-phase catalytic reactions, the catalytic hydrogenation of 4-nitrophenol (4-NPh) by NaBH_4 to produce 4-aminophenol (4-APh) has been investigated as another test reaction. The variation

of 4-NPh is constantly monitored by using UV-Vis measurements after adding the Pd@RCC3 catalyst into the alkaline solution. With the reaction proceeds, the characteristic peaks of 4-NPh at 400 nm decreases along with the growth of the characteristic absorbance of 4-APh at 300 nm. The use of catalysts gives no influence on the UV-vis observation of the change of characteristic absorption at $\lambda = 400$ nm for the 4-NPh reduction (Fig. 3.13). As shown in Fig. 3.15a and c, the complete hydrogenation of 4-NPh to 4-APh in the presence of Pd@RCC3 only needs 4 min ($n[\text{Pd}]/n[4\text{-NPh}] = 1/60$). For a comparison, the insoluble Pd/RCC3 counterpart gives a lower catalytic performance with the complete conversion in 10 min ($n[\text{Pd}]/n[4\text{-NPh}] = 1/60$) (Fig. 3.15b and c). By applying the pseudo-first-order kinetic model, the related linear correlations of $\ln(A_t/A_0)$ versus time (A_t and A_0 stand for the absorbance at the intervals and the initial stage of 4-nitrophenolate ion, respectively) have been obtained to evaluate the reaction rates of the reduction of 4-NPh. The Pd@RCC3 catalyst has an extremely high rate constant (k) of 1.25 min^{-1} , which is superior to those of the reported catalysts under ambient conditions.¹³ In contrast, the estimated rate constant k value of the insoluble Pd/RCC3 catalyst is only 0.49 min^{-1} , demonstrating that Pd@RCC3 has an enhanced catalytic activity.

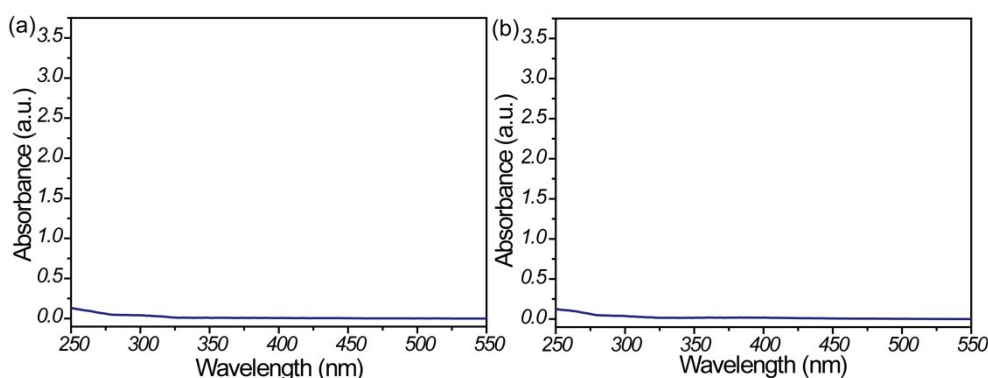


Figure 3.13. UV-vis absorption spectrum of the (a) Pd@RCC3 and (cb) Pd/RCC3 catalyst ($n_{\text{Pd}} = 0.000011 \text{ mmol}$) in 4 mL of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ mixture (v/v, 2/1), showing no peak at the range of 250-550 nm.

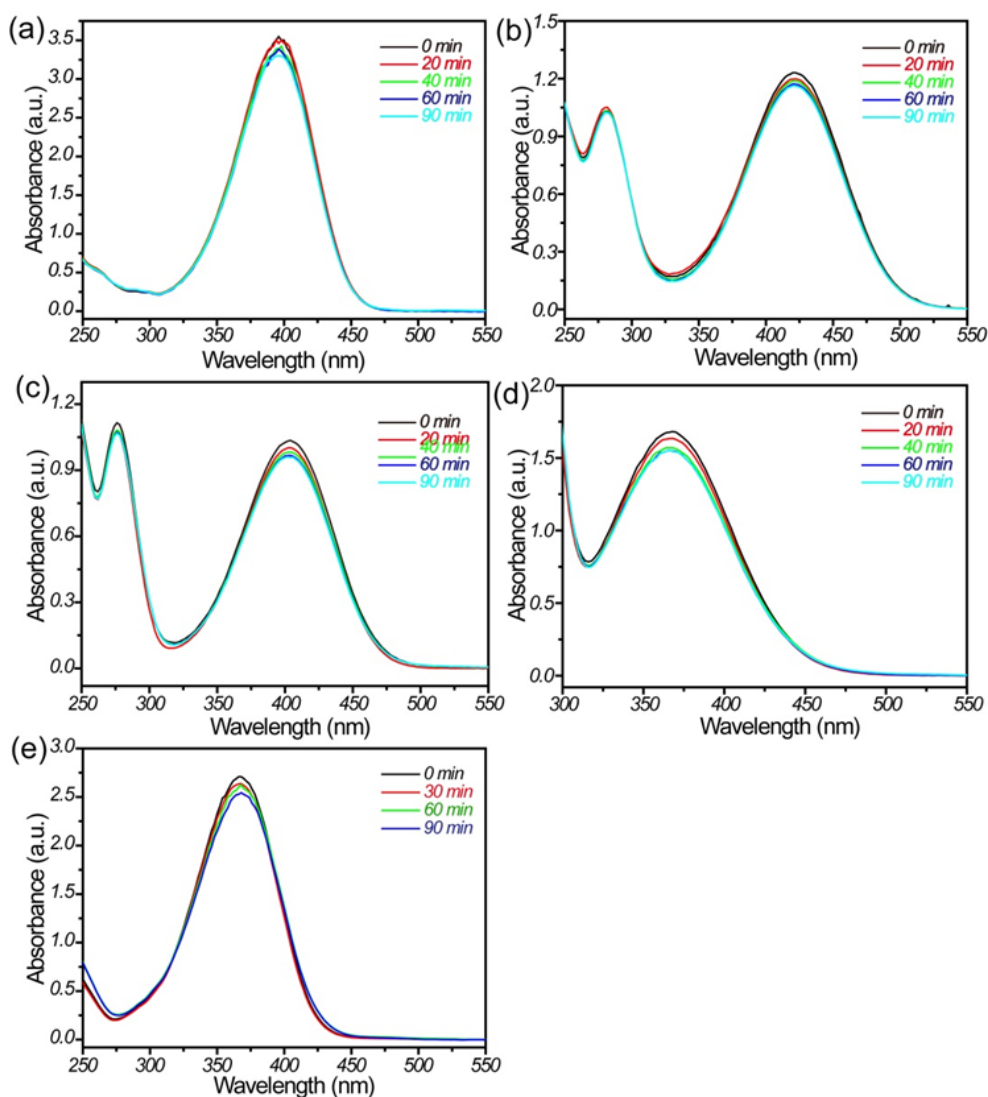


Figure 3.14. UV-vis absorption spectra of (a) 4-NPh, (b) 2-NPh, (c) 2-NAn, (d) 3-NAn and (e) 4-NAn in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$ (v/v, 2/1) in the presence of NaBH_4 without catalyst. The absorption spectra show no significant changes in 90 min.

Furthermore, $\text{Pd}@\text{RCC3}$ has been used for the hydrogenation of other nitroarene derivatives including 2-nitrophenol (2-NPh), 2-nitroaniline (2-NAn), 3-nitroaniline (3-NAn) and 4-nitroaniline (4-NAn) (Fig. 3.16-3.19). Regardless of which the types and where the positions the substituents have, the $\text{Pd}@\text{RCC3}$ catalyst exhibits significantly enhanced catalytic performance and constant k values toward these catalytic hydrogenation of nitroarenes compared to the $\text{Pd}/\text{RCC3}$ counterpart.

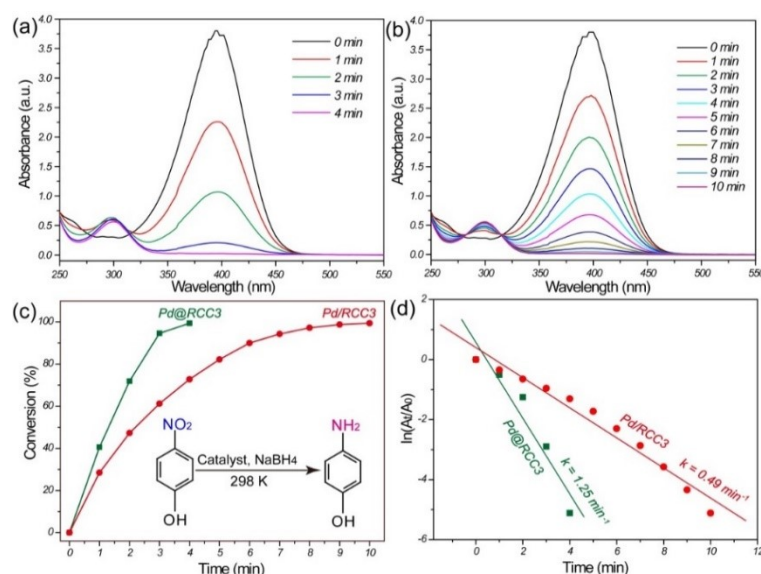


Figure 3.15. UV-vis spectra showing hydrogenation of 4-NPh over the (a) Pd@RCC3 and (b) Pd/RCC3 catalysts at 298 K, (c) comparative catalytic conversion of 4-NPh over the Pd@RCC3 and Pd/RCC3 catalysts at 298 K, (d) plots of $\ln(A_t/A_0)$ of absorbance of 4-NPh at 400 nm obtained from the spectra in (a) and (b) versus time for the hydrogenation of 4-NPh catalyzed by the Pd@RCC3 and Pd/RCC3 catalyst.

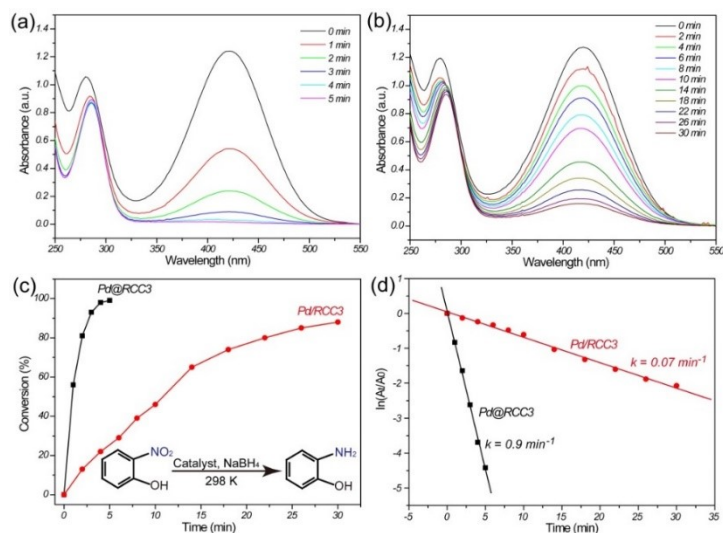


Figure 3.16. UV-vis spectra showing hydrogenation of 2-NPh over the (a) Pd@RCC3 and (b) Pd/RCC3 catalysts at 298 K, (c) comparative catalytic conversion of 2-NPh over the Pd@RCC3 and Pd/RCC3 catalysts at 298 K, (d) plots of $\ln(A_t/A_0)$ of absorbance of 2-NPh at 420 nm obtained from the spectra in (a) and (b) versus time for the hydrogenation of 2-NPh catalyzed by the Pd@RCC3 and Pd/RCC3 catalyst.

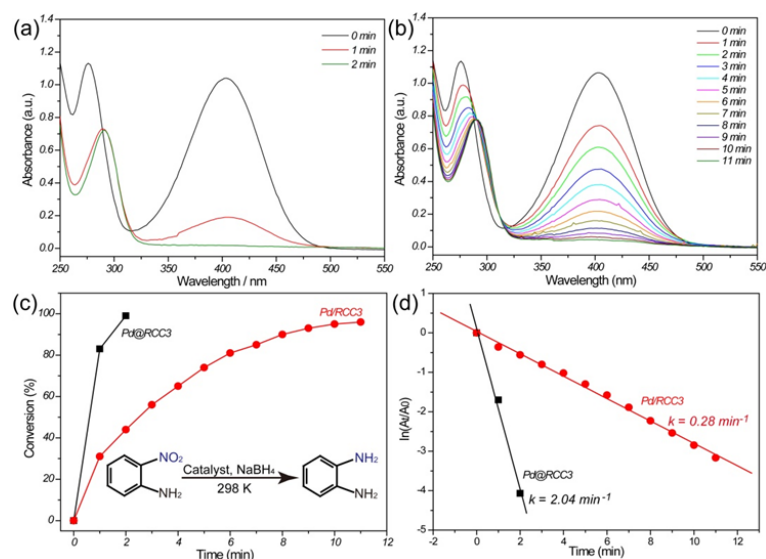


Figure 3.17. UV-vis spectra showing hydrogenation of 2-NAN over the (a) Pd@RCC3 and (b) Pd/RCC3 catalysts at 298 K, (c) comparative catalytic conversion of 2-NAN over the Pd@RCC3 and Pd/RCC3 catalysts at 298 K, (d) plots of $\ln(A_t/A_0)$ of absorbance of 2-NAN at 400 nm obtained from the spectra in (a) and (b) versus time for the hydrogenation of 2-NAN catalyzed by the Pd@RCC3 and Pd/RCC3 catalyst.

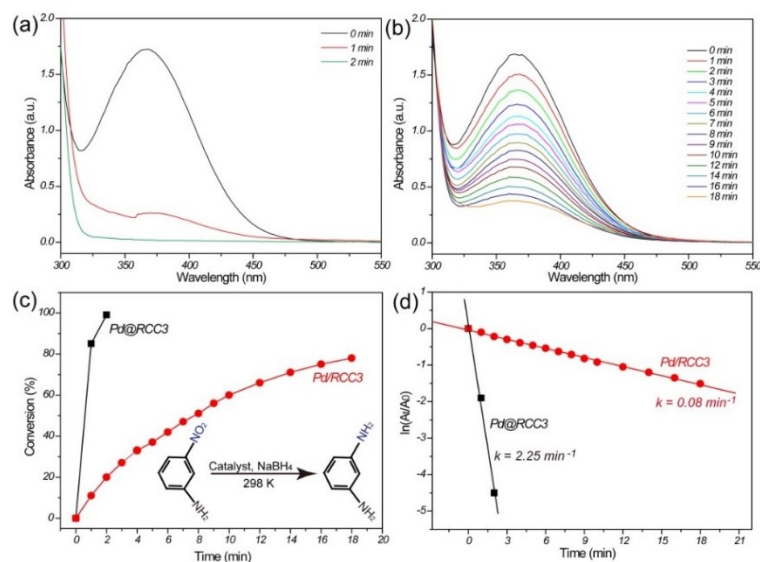


Figure 3.18. UV-vis spectra showing hydrogenation of 3-NAN over the (a) Pd@RCC3 and (b) Pd/RCC3 catalysts at 298 K, (c) comparative catalytic conversion of 3-NAN over the Pd@RCC3 and Pd/RCC3 catalysts at 298 K, (d) plots of $\ln(A_t/A_0)$ of absorbance of 3-NAN at 368 nm obtained from the spectra in (a) and (b) versus time for the hydrogenation of 3-NAN catalyzed by the Pd@RCC3 and Pd/RCC3 catalyst.

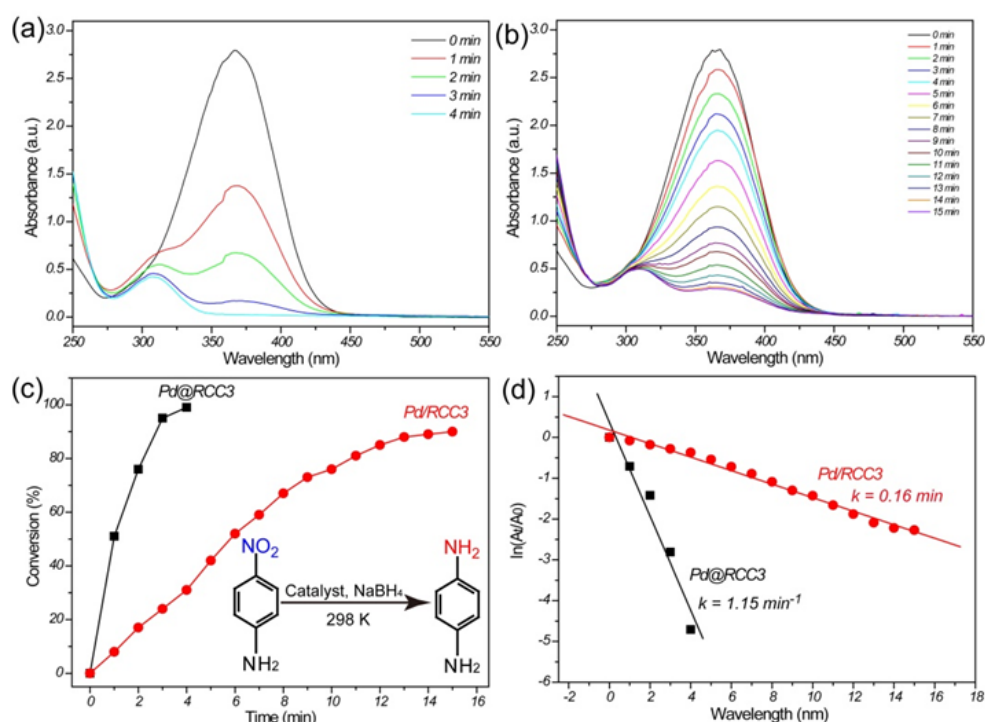


Figure 3.19. UV-vis spectra showing hydrogenation of 4-NAN over the (a) Pd@RCC3 and (b) Pd/RCC3 catalysts at 298 K, (c) comparative catalytic conversion of 4-NAN over the Pd@RCC3 and Pd/RCC3 catalysts at 298 K, (d) plots of $\ln(A_t/A_0)$ of absorbance of 4-NAN at 368 nm obtained from the spectra in (a) and (b) versus time for the hydrogenation of 4-NAN catalyzed by the Pd@RCC3 and Pd/RCC3 catalyst.

Catalytic reduction of organic dyes. Organic dyes are well-known toxic pollutants to human health. Herein, as a promising catalyst, Pd@RCC3 has been applied for the catalytic reduction of organic dyes such as Congo red (CR) and methyl orange (MO) by NaBH₄. The absorption peaks of CR at 500 nm and MO at 420 nm successively decrease with reaction time after the addition of catalyst, respectively, and the dyes are completely reduced to colorless leuco-forms within seconds, showing that Pd@RCC3 possesses fast rate constants for these reactions (Fig. 3.20 and 3.21). In contrast, its Pd/RCC3 counterpart shows lower catalytic activities for these reactions (Fig. 3.20 and 3.21). Undoubtedly, Pd@RCC3 is promising for a series of liquid-phase catalytic reactions.

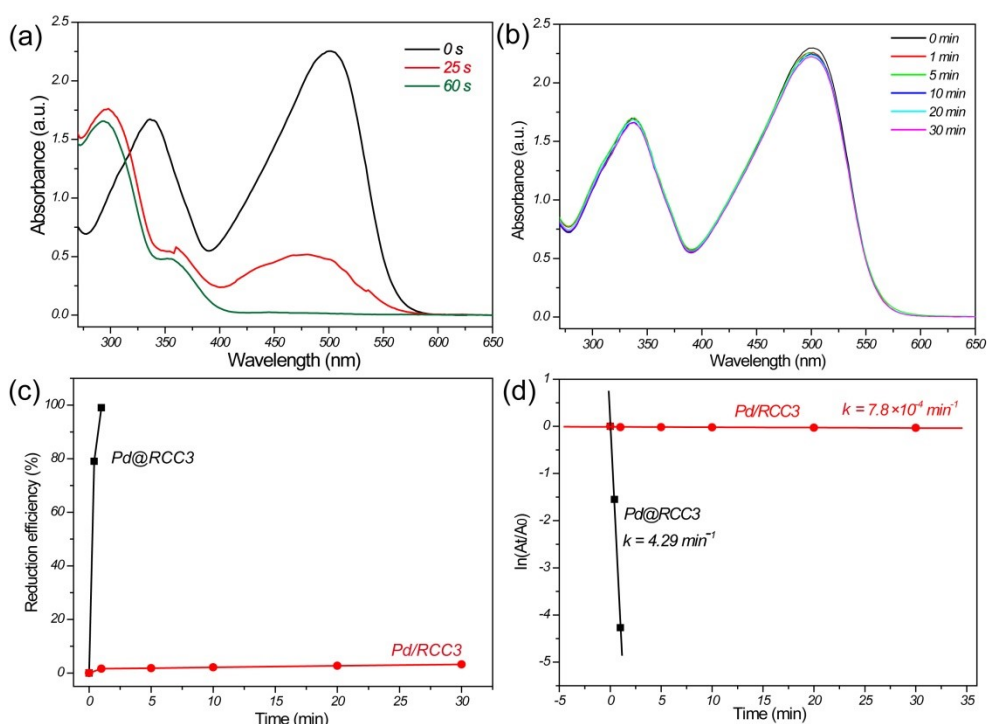


Figure 3.20. UV-vis spectra showing reduction of CR over the (a) Pd@RCC3 and (b) Pd/RCC3 catalysts at 298 K, (c) comparative catalytic conversion of CR over the Pd@RCC3 and Pd/RCC3 catalysts at 298 K, and (d) plots of $\ln(A/A_0)$ of absorbance of CR at 500 nm obtained from the spectra in (a) and (b) versus time for the reduction of CR catalyzed by the Pd@RCC3 and Pd/RCC3 catalyst, respectively.

Durability test. Durability and stability are the other crucial indicator for evaluating the heterogeneous catalysts. Here, the durability and stability of Pd@RCC3 have been tested by the methanolysis of AB. The high catalytic performance of Pd@RCC3 maintains after five cycles (Fig. 3.12b). HAADF-STEM and PXRD measurements (Fig. 3.12c and d) show that the size, structure and morphology of encapsulated Pd NCs remain the same after catalytic reaction. It is clear that the Pd@RCC3 catalyst has merits of excellent activity, durability and stability toward various liquid-phase catalytic reactions.

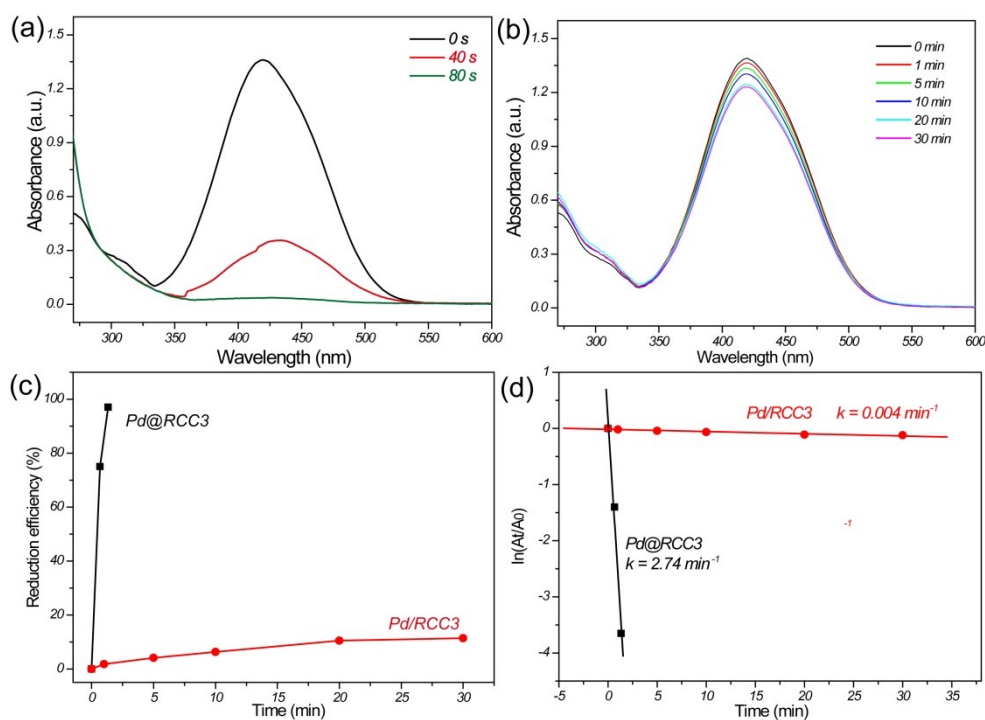


Figure 3.21. UV-vis spectra showing reduction of MO over the (a) Pd@RCC3 and (b) Pd/RCC3 catalysts at 298 K, (c) comparative catalytic conversion of MO over the Pd@RCC3 and Pd/RCC3 catalysts at 298 K, and (d) plots of $\ln(A/A_0)$ of absorbance of MO at 420 nm obtained from the spectra in (a) and (b) versus time for the reduction of MO catalyzed by the Pd@RCC3 and Pd/RCC3 catalyst, respectively.

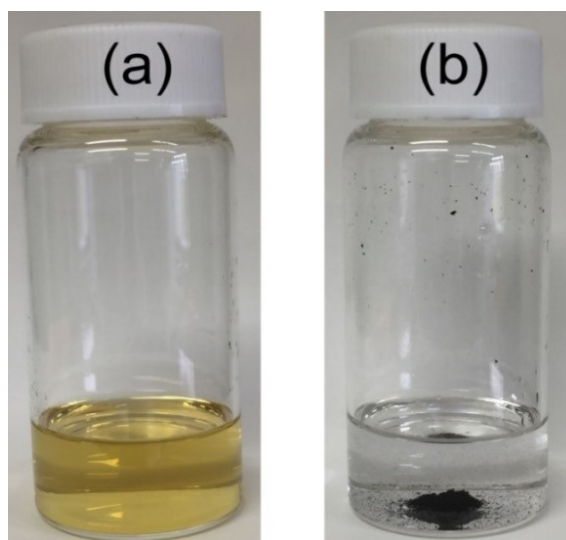


Figure 3.22. Photographs of (a) Pd(OAc)₂ in CH₂Cl₂/CH₃OH mixture (v/v, 2/1), and (b) the SP-free-Pd catalyst obtained by reduction of Pd(OAc)₂.

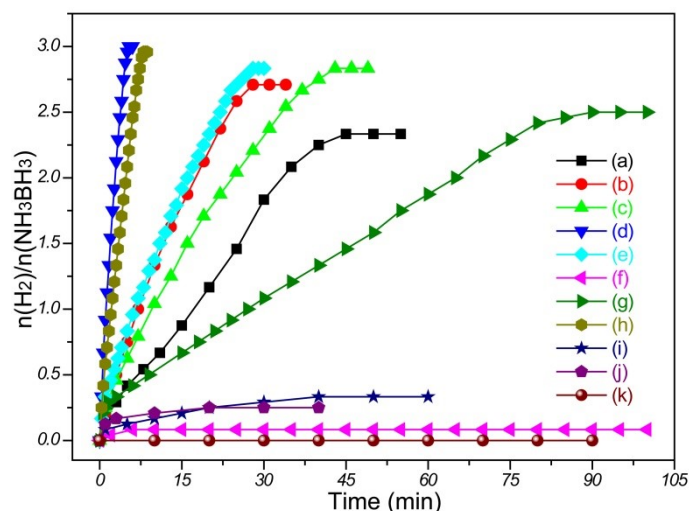


Figure 3.23. Time course plots for the methanolysis of AB over the (a) SP-free-Pd, (b) Pd/PVP, (c) Pd/CTAB, (d) Pd/(*R,R*)-1,2-diaminocyclohexane, (e) Pd/1,3,5-triformylbenzene, (f) Pd metal powder, (g) Pd black, (h) Pd/C, (i) bis(triphenylphosphine)-palladium (II) dichloride, (j) tetrakis(triphenylphosphine) palladium (0) and (k) RCC3 catalyst at 303 K ($n_{\text{Pd}}/n_{\text{AB}} = 0.01$, $V_{\text{CH}_2\text{Cl}_2}/V_{\text{CH}_3\text{OH}} = 2/1$).

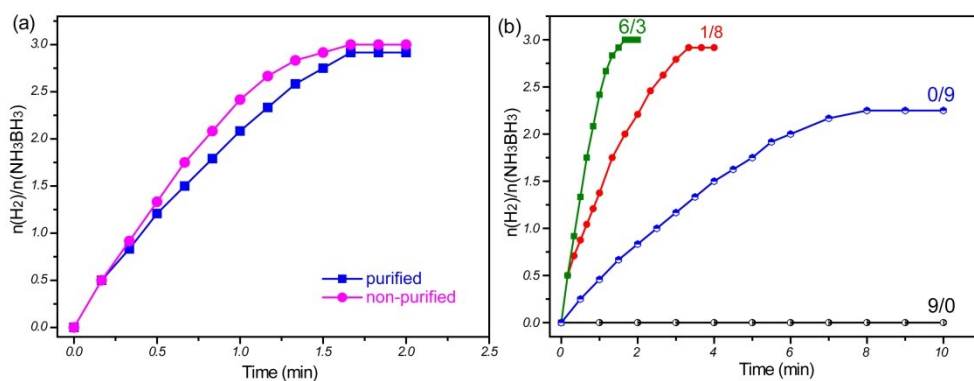


Figure 3.24. Time course plots for the methanolysis of AB over (a) Pd NCs encapsulated in purified and non-purified RCC3 cages ($n_{\text{Pd}}/n_{\text{AB}} = 0.01$, $V_{\text{CH}_2\text{Cl}_2}/V_{\text{CH}_3\text{OH}} = 2/1$, 303 K), and (b) the Pd@RCC3 catalyst at 303 K with different volume ratios of $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{OH}$: (a) 9/0, (b) 6/3, (c) 1/8 and (d) 0/9 ($n_{\text{Pd}}/n_{\text{AB}} = 0.01$).

Discussion. It is reasonable that such enhanced catalytic feature of Pd@RCC3 can be assigned to the ultrasmall Pd NCs confined inside the cavities of discrete organic molecular cages with uniform distribution. In particular, the open skeletons as well as

the excellent solubility of discrete molecular cages endow extremely high dispersibility of Pd NCs in solution with more accessible active sites for catalytic reactions. To prove this hypothesis, the Pd/RCC3 counterpart prepared by the conventional impregnation method has been used for the methanolysis of AB. As insoluble in the CH₂Cl₂/CH₃OH mixture and most of the Pd NPs are supported on the outer surfaces of cages, this Pd/RCC3 catalyst has a low dispersibility of Pd NPs. As shown in Fig. 3.12a, the Pd/RCC3 shows fairly poor catalytic activities, with which the methanolysis of AB is completed ($n[\text{H}_2]/n[\text{AB}] = 3$) within 7.5 min ($n[\text{Pd}]/n[\text{AB}] = 0.01$), giving a TOF value of 37 mol of H₂ per mol of Pd per min. Such a H₂ release rate is much lower than that of Pd@RCC3 catalyst. To further investigate the essential roles of discrete cage supports in liquid-phase catalysis, a control experiment by using support-free catalyst (SP-free-Pd) for the methanolysis of AB under the similar conditions is performed. As expected, the obtained SP-free-Pd catalyst shows serious aggregation (Fig. 3.22) and low catalytic activity (Fig. 3.23a), giving a TOF of 5.1 mol of H₂ per mol of Pd per min, which is only 1/34.5 of the Pd@RCC3 catalyst. Cetyltrimethyl ammonium bromide (CTAB), polyvinylpyrrolidone (PVP), and the starting chemicals for cage synthesis, (*R,R*)-1,2,-diaminocyclohexane and 1,3,5-triformylbenzene, have been used as surface capping agents to stabilize Pd NPs, which offer very poor catalytic kinetics because a large part of Pd active sites may be blocked by the capping agents (Fig. 3.23b-e). Commercially available Pd sources, including Pd metal powder, Pd black and Pd/carbon, show low catalytic activities (Fig. 3.23f-h). Meanwhile, commercially available homogeneous catalysts such as bis(triphenylphosphine)-palladium (II) dichloride and tetrakis(triphenylphosphine) palladium (0) also exhibit poor catalytic performance for AB methanolysis in comparison with the Pd@RCC3 catalyst (Fig. 3.23i and j). No significant difference in the catalytic methanolysis of AB has been observed for Pd NCs encapsulated in

purified and non-purified RCC3 cages (Fig. 3.24a). Notably, without MNPs, RCC3 displays no catalytic activity for the AB methanolysis (Fig. 3.23k). The observations reveal that the soluble cage shells with open and flexible skeletons can promote catalytic reactions by downsizing the nanoparticles, providing more accessible active sites, and enhancing the dispersibility of Pd NCs in solutions. In addition, it is worth noting that the H₂ generation rates of the methanolysis of AB over the Pd@RCC3 catalyst are obviously influenced by the volume ratios of reaction solvents of CH₂Cl₂/CH₃OH (Fig. 3.24b). No H₂ generation is observed with pure CH₂Cl₂ solution and a low H₂ generation rate is observed with pure CH₃OH solution. The introduction of mixed solvents consisting of CH₂Cl₂ and CH₃OH leads to dramatically increased efficiencies. The main reason is the collapsed skeletons of RCC3 could be fully braced by a certain amount of CH₂Cl₂ molecules, forming unhindered channels for favoring the mass transfer.^{6a, 6d, 7b} Interestingly, these mixed solvents can serve as the potential controller to adjust the hydrogen generation rates from methanolysis of AB for practical applications.

3.4 Conclusions

In conclusion, a facile, scalable and effective reverse double solvents approach (*RDSA*) has been developed for synthesizing Pd@RCC3 hybrids with Pd NCs encapsulated inside the cavities of RCC3 cages for the first time. The excellent solubility of RCC3 with open skeletons has resulted in extremely high dispersion of soluble Pd NCs in solutions and favored mass transfer, and thus is beneficial for various liquid-phase catalytic reactions. Moreover, the as-prepared catalysts possess excellent stability and durability owing to the good confinement of Pd NCs within the discrete POC matrix. The present results provide a new perspective to the catalysis field in terms of the exploration of advanced catalysts through the use of flexible functionalized cavities of

soluble microporous materials as matrix for highly dispersed ultrafine MNPs.

References

1. (a) A. Dhakshinamoorthy and H. Garcia, *Chem. Soc. Rev.*, 2012, **41**, 5262; (b) L. Borchardt, C. Hoffmann, M. Oschartz, L. Mammitzsch, U. Petasch, M. Herrmann and S. Kaskel, *Chem. Soc. Rev.*, 2012, **41**, 5053; (c) P. Buchwalter, J. Rosé and P. Braunstein, *Chem. Rev.*, 2015, **115**, 28; (d) B. Li, H. M. Wen, Y. Cui, W. Zhou, G. Qian and B. Chen, *Adv. Mater.*, 2016, **28**, 8819; (e) L. He, F. Weniger, H. Neumann and M. Beller, *Angew. Chem. Int. Ed.*, 2016, **55**, 12582; (f) C. -D. Wu and M. Zhao, *Adv. Mater.*, 2017, **29**, 1605446.
2. (a) S. Ding, J. Gao, Q. Wang, Y. Zhang, W. Song, C. Su and W. Wang, *J. Am. Chem. Soc.*, 2011, **133**, 19816; (b) S. B. Kalidindi, O. Hyunchul, M. Hirscher, D. Esken, C. Wiktor, S. Turner, G. V. Tendeloo and R. A. Fisher, *Chem. Eur. J.*, 2012, **18**, 10848; (c) C. M. Doherty, D. Buso, A. J. Hill, S. Furukawa, S. Kitagawa and P. Falcaro, *Acc. Chem. Res.*, 2014, **47**, 396; (d) L. -B. Sun, X. -Q. Liu and H. -C. Zhou, *Chem. Soc. Rev.* 2015, **44**, 5092; (e) X. Yang, P. Pachfule, Y. Chen, N. Tsumori and Q. Xu, *Chem. Commun.*, 2016, **52**, 4171; (f) C. Meng, T. Ling, T. Y. Ma, H. Wang, Z. Hu, Y. Zhao, J. Mao, X. Du, M. Jaroniec and S. Qiao, *Adv. Mater.*, 2017, **29**, 1604607; (g) H. Tabassum, W. Guo, W. Meng, A. Mamood, R. Zhao, Q. Wang and R. Zou, *Adv. Energy Mater.* 2017, **7**, 1601671.
3. (a) D. J. M. Snelders, W. Gan, N. Yan, G. Laurenczy and P. J. Dyson, *ACS Catal.*, 2012, **2**, 201; (b) G. Lu, S. Li, Z. Guo, O. K. Farha, B. G. Hauser, X. Qi, X. Wang, S. Han, X. Liu, J. S. DuChene, H. Zhang, Q. Zhang, X. Chen, J. Ma, S. C. J. Loo, W. D. Wei, Y. Yang, J. T. Hupp and F. Huo, *Nat. Chem.*, 2012, **4**, 310; (c) Z. Niu and Y. Li, *Chem. Mater.*, 2014, **26**, 72; (d) N. Huang, Y. Xu and D. Jiang, *Sci. Rep.*, 2014, **4**, 7728.
4. (a) T. Tozawa, J. T. A. Jones, S. I. Swamy, S. Jiang, D. J. Adams, S. Shakespeare, R. Clowes, D. B. Shaw, T. Hasell, S. Y. Chong, C. Tang, S. Thompson, J. Parker, A. Trewin, J.

- Bacsa, A. M. Z. Slawin, A. Steiner and A. I. Cooper, *Nat. Mater.*, 2009, **8**, 973; (b) T. Hasell, M. Schmidtman and A. I. Cooper, *J. Am. Chem. Soc.*, 2011, **133**, 14920; (c) A. Avellaneda, P. Valente, A. Burgun, J. D. Evans, A. W. Markwell-Heys, D. Rankine, D. Nielsen, M.R. Hill, C. J. Sumby and C. J. Doonan, *Angew. Chem. Int. Ed.*, 2013, **52**, 3746; (d) G. Zhang, O. Presly, F. White, I. M. Oppel and M. Mastalerz, *Angew. Chem. Int. Ed.*, 2014, **53**, 1516; (e) A. G. Slater and A. I. Cooper, *Science*, 2015, **348**, aaa8075; (f) T. Hasell and A. I. Cooper, *Nat. Rev. Mater.*, 2016, **1**, 16053.
5. J. -K. Sun, W. -W. Zhan, T. Akita and Q. Xu, *J. Am. Chem. Soc.*, 2015, **137**, 7063.
 6. (a) J. R. Holst, A. Trewin and A. I. Cooper, *Nat. Chem.*, 2010, **2**, 915; (b) K. E. Jelfs, X. Wu, M. Schmidtman, J. T. A. Jones, J. E. Warren, D. J. Adams and A. I. Cooper, *Angew. Chem. Int. Ed.*, 2011, **50**, 10653; (c) T. Hasell, S. Y. Chong, K. E. Jelfs, D. J. Adams and A. I. Cooper, *J. Am. Chem. Soc.*, 2012, **134**, 588; (d) M. A. Little, S. Y. Chong, M. Schmidtman, T. Hasell and A. I. Cooper, *Chem. Commun.*, 2014, **50**, 9465.
 7. (a) T. Hasell, H. Zhang and A. I. Cooper, *Adv. Mater.*, 2012, **24**, 5732; (b) M. Liu, M. A. Little, K. E. Jelfs, J. T. A. Jones, M. Schmidtman, S. Y. Chong, T. Hasell, A. I. Cooper, *J. Am. Chem. Soc.*, 2014, **136**, 7583.
 8. (a) A. Aijaz, A. Karkamkar, Y. J. Choi, N. Tsumori, E. Rönnebro, T. Autrey, H. Shioyama and Q. Xu, *J. Am. Chem. Soc.*, 2012, **134**, 13926; (b) Q. -L. Zhu, J. Li and Q. Xu, *J. Am. Chem. Soc.*, 2013, **135**, 10210; (c) Y. Z. Chen, Y. X. Zhou, H. Wang, J. Lu, T. Uchida, Q. Xu, S. H. Yu and H. L. Jiang, *ACS Catal.*, 2015, **5**, 2062.
 9. Z. Li, X. Yang, N. Tsumori, Z. Liu, Y. Himeda, T. Autrey and Q. Xu, *ACS Catal.*, 2017, **7**, 2720.
 10. (a) M. Victoria Gomez, J. Guerra, A. H. Velders and R. M. Crooks, *J. Am. Chem. Soc.*, 2009, **131**, 341; (b) V. Sue Myers, M. G. Weir, E. V. Carino, D. F. Yancey, S. Pande and R. M. Crooks, *Chem. Sci.*, 2011, **2**, 1632.
 11. (a) A. Gutowska, L. Li, Y. Shin, C. M. Wang, X. S. Li, J. C. Linehan, R. S. Smith, B. D. Kay,

- B. Schmid, W. Shaw, M. Gutowski and T. Autrey, *Angew. Chem. Int. Ed.*, 2005, **44**, 3578; (b) R. J. Keaton, J. M. Blacquiere and R. T. Baker, *J. Am. Chem. Soc.*, 2007, **129**, 1844; (c) S. K. Kim, W. S. Han, T. J. Kim, T. Y. Kim, S. W. Nam, M. Mitoraj, L. Piekos, A. Michalak, S. J. Hwang and S. O. Kang, *J. Am. Chem. Soc.*, 2010, **132**, 9954; (d) U. B. Demirci and P. Miele, *Energy Environ. Sci.*, 2011, **4**, 3334; (e) Z. Huang and T. Autrey, *Energy Environ. Sci.* 2012, **5**, 9257; (f) C. Y. Peng, L. Kang, S. Cao, Y. Chen, Z. S. Lin and W. F. Fu, *Angew. Chem. Int. Ed.*, 2015, **54**, 15725; (g) H. A. Kalviri, F. Gärtner, G. Ye, I. Korobkov and R. T. Baker, *Chem. Sci.*, 2015, **6**, 618; (h) Z. Li, T. He, L. Liu, W. Chen, M. Zhang, G. Wu and P. Chen, *Chem. Sci.*, 2017, **8**, 781.
12. (a) P. V. Ramachandran and P. D. Gagare, *Inorg. Chem.*, 2007, **46**, 7810; (b) S. D. Kalidindi, A. S. Vernekar and B. R. Jadirgar, *Phys. Chem. Chem. Phys.*, 2009, **11**, 770; (c) M. Yadav and Q. Xu, *Energy Environ. Sci.*, 2012, **5**, 9698; (d) Q. Yao, M. Huang, Z.-H. Lu, Y. Yang, Y. Zhang, X. Cheng and Z. Yang, *Dalton Trans.*, 2015, **44**, 1070. (e) W. -W. Zhan, Q. -L. Zhu and Q. Xu, *ACS Catal.*, 2016, **6**, 6892.
13. (a) H. -L. Jiang, T. Akita, T. Ishida, M. Haruta and Q. Xu, *J. Am. Chem. Soc.*, 2011, **133**, 1304; (b) W. Zhang, G. Lu, C. Cui, Y. Liu, S. Li, W. Yang, C. Xing, Y. R. Chi, Y. Yang and F. Huo, *Adv. Mater.*, 2014, **26**, 4056, (c) G. Huang, Q. Yang, Q. Xu, S. -H. Yu and H. -L. Jiang, *Angew. Chem. Int. Ed.*, 2016, **55**, 7379; (d) P. Zhao, X. Feng, D. Huang, G. Yang, and D. Astruc, *Coordin. Chem. Rev.*, 2015, **287**, 114.

Chapter 4

Solid Solution Alloying of Classically Immiscible Au and Rh for Highly Efficient Catalytic Hydrogen Generation from Formic Acid

4.1 Introduction

Solid-solution alloying opens enormous possibilities for a variety of applications,¹ especially the industrial catalysis, through tuning the size, shape and composition of the component metals. Fascinatingly more, the synergistic effect occurred from the random and homogeneous integration of different metals at atomic-level enable, in most cases, the alloys with enhanced intrinsic properties or even a new property.² Great advances have been made in synthesizing well-defined solid-solution alloys consisting of miscible metals at ambient temperatures,³ however, a great many metals are found to be immiscible with each other even above their melting points, according to the related phase diagrams. Considering the fascinating but unpredictable features, as well as the ever-increasing demands come from human society, solid-solution alloying of the entirely immiscible metals is particularly desirable, although there are considerable challenges in mixing such immiscible metals at atomic-level while maintaining a stable alloy structure, actually, these alloys are easy to segregate due to their metastable structures, making them almost the same as their monometallic parents.

Downscaling of bulk metals to a few nanometers has attracted significant attention in recent years,⁴ because it not only serves to reduce the consumption of nonrenewable metals but also provides tremendously enhanced fundamental

properties, for instance, at free surfaces the high percentage of exposed atoms can highly improve the conductivity and catalytic activity. More excitingly, assuming the use of recently developed nanofabrication techniques, a series of alloys containing non-equilibrium metals that can only be mixed at high temperatures, such as Au-Co⁵, Au-Ni⁶ and Au-Pt⁷, have been easily synthesized at ambient temperatures. It thus seems very promising for obtaining high-performance nanoscale alloys composed of the entirely immiscible metals.

Au and Rh are two representative noble metals for various catalytic reactions.⁸ Au is more abundant in nature, whereas Rh is scarce and expensive. It is reasonable to presume that Au-Rh alloys possess super catalytic capability with a reduced cost if such two elements can be homogeneously mixed at atomic-level. Unfortunately, a large immiscibility gap is predicted by the phase diagram for Au-Rh alloys, even in the liquid phase at around 2273 K. Here, we demonstrate a relatively simple, effective and general approach that, through downsizing enabled by dramatically enhancing the electrostatic adsorption from the designed supports to metal species, can effectively alloy the entirely immiscible Au and Rh at room temperature. Interestingly, applying the as-synthesized ultrafine (~ 1.65 nm), highly dispersed and well-alloyed Au-Rh clusters for catalytic dehydrogenation of formic acid (FA) shows that solid-solution alloys are more active than their monometallic parents: Au becomes more active when diluted in alloys with Rh, although the latter is catalytically inactive. The optimized Au_{0.5}Rh_{0.5} clusters afford one of the highest turnover frequencies (TOFs) of 10877 h⁻¹ at 80 °C for heterogeneous catalyzed FA dehydrogenation. Moreover, Au-Rh clusters are extremely stable without any segregation during the catalytic reactions. Notably, there are rare reports on Au and no reports on Rh for catalyzed FA dehydrogenation so far. Alloys containing the entirely immiscible metals hold out great potentials for our

common future.

4.2 Experimental details

4.2.1 Chemicals

All chemicals were commercially available and used without further purification. Maxsorb MSC-30 (Nanoporous Carbon, Kansai Coke and Chemicals Co. Ltd.), urea (TCI), HAuCl_4 and RhCl_3 (Wako Pure Chemical Industries, Ltd., >97%), sodium borohydride (NaBH_4 , Tokyo Chemical Industry Co. Ltd., >95%), sodium hydroxide (NaOH , Wako Pure Chemical Industries, Ltd., >93%), formic acid (FA, HCOOH , Merck Chemicals, >98%), sodium formate (SF, HCOONa , Chameleon Reagent, >98%) were used as received. De-ionized (DI) water with a specific resistance of $>18.0 \text{ M}\Omega\cdot\text{cm}$ was used in all experiments.

4.2.2 Synthesis of catalysts

Synthesis of the functionalized carbon. Urea has been select for introducing functional groups onto the surfaces of carbons. Briefly, 0.5 g of commercial carbon (MSC-30) and 1.0 g of urea are mixed nicely, and then heat at 423 K for 1 hour, followed at 548 K for 3 hours under the heating rate of 3 K/min. After cooling to room temperature, the resulted functionalized carbon, denoted as $\mu\text{C-548}$, are obtained by centrifugation followed by washing with water and ethanol, and drying at 343 K in an oven. For comparison, the control functionalized carbons yielded using the similar method at different temperatures are denoted as $\mu\text{C-T}$ ($T = 498, 548, 573, 598$ and 1075 K).

Alloying of Au and Rh. A simple wet-chemical process has been applied to alloy the entirely immiscible Au and Rh. Typically, a black dispersion of $\mu\text{C-548}$ powders

(100 mg) in 6 mL of ultrapure water is firstly synthesized, to which an aqueous solution (0.6 mL) of HAuCl_4 and RhCl_3 according to the stoichiometry is added dropwise under vigorous stirring. After being continuously stirred for another 3 hours, the above mixture is reduced by addition of a fresh sodium hydroxide aqueous solution (0.5 M, 1 mL) containing 40 mg of sodium borohydride to yield well-alloyed Au-Rh NCs. Finally, the functionalized carbon stabilized alloy clusters, named as $\text{Au}_x\text{Rh}_{1-x}/\text{uC-548}$, are collected by centrifugation followed with water washing.

4.2.3 Catalytic activity characterization

An aqueous suspension containing the as-prepared catalyst is placed in a two-neck round-bottom flask, which was placed in a water bath under ambient atmosphere. A gas burette filled with water is connected to the reaction flask to measure the volume of released gas. The reaction is started when the mixed aqueous solution of FA-SF was injected into the sealed flask. The molar ratio of total metal/FA was fixed at 0.02 for all the catalytic reactions. The volume of the evolved gas was monitored by recording the displacement of water in the gas burette.

4.3 Results and discussion

The design of functionalized carbons. As a class of emerging, but powerful, members of the carbon superfamily, functionalized carbons, synthesized from direct carbonization of organic precursors or post-synthetic modification of carbon surfaces with functional groups, exhibit a broad scope of properties and applications owing to their high surface area, porosity, conductivity and thermal stability.⁹ Notably, functionalized carbons have been extended to design metal nanoparticles (MNPs) recently,¹⁰ on the surfaces of which the incorporated groups or sites serve as coordination sites for binding/adsorbing metal species, as well as controlling their

nucleation. Furthermore, such functionalized carbon stabilized MNPs possess clean surfaces with high percentage of exposed atoms in comparison with those stabilized by the excess organic ligands, which is beneficial for the catalytic performance. We here propose an unusual perspective of designing the appropriate functionalized carbon to facilitate the solid-solution alloying of the entirely immiscible Au and Rh at room temperature.

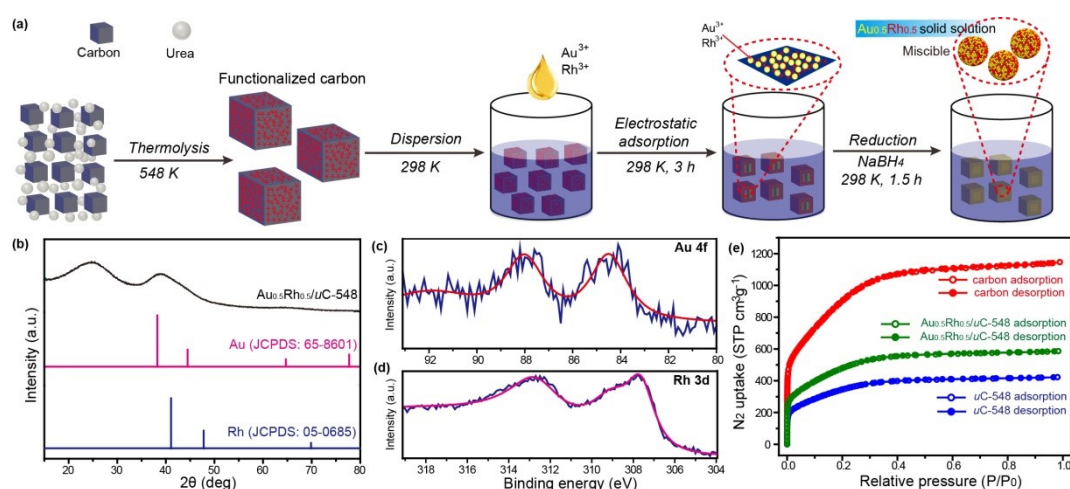


Figure 4.1. (a) Schematic illustration of the synthesis of functionalized carbon and the solid-solution alloying of the immiscible Au and Rh, (b) PXRD pattern of Au_{0.5}Rh_{0.5}/uC-548, (c) Au 4f and Rh 3d XPS spectra of Au_{0.5}Rh_{0.5} in Au_{0.5}Rh_{0.5}/uC-548 and N₂ sorption isotherms of non-treated carbon, uC-548 and Au_{0.5}Rh_{0.5}/uC-548.

In a first step, urea, a traditional nitrogen (N) source, is chose to synthesize the ideal functionalized carbon (Fig. 4.1a). Briefly, 1.0 of urea and 0.5 g of commercial carbon (MSC-30) are mixed nicely, and then this mixture is heated at 423 K for 1 h, followed at 548 K for 3 h. After cooling to room temperature, the resulted mixture is washed by hot water and ethanol to yield the functionalized carbon, denoted as uC-548. Using Raman measurements (Fig. 4.2), we first confirm that the electronic structures are maintained in the as-synthesized uC-548, as all peaks are similar to those of non-treated carbon. Meanwhile, the specific surface area of uC-548 decreases

drastically compared to that of non-treated carbon, illustrating that a great deal of functional groups produced from the pyrolysis of urea are incorporated into/onto the carbon surfaces (Fig. 4.1e). X-ray photoelectron spectroscopy (XPS) further suggests that *uC*-548 is rich of amine, amide and hydroxyl groups (Fig. 4.3).¹¹

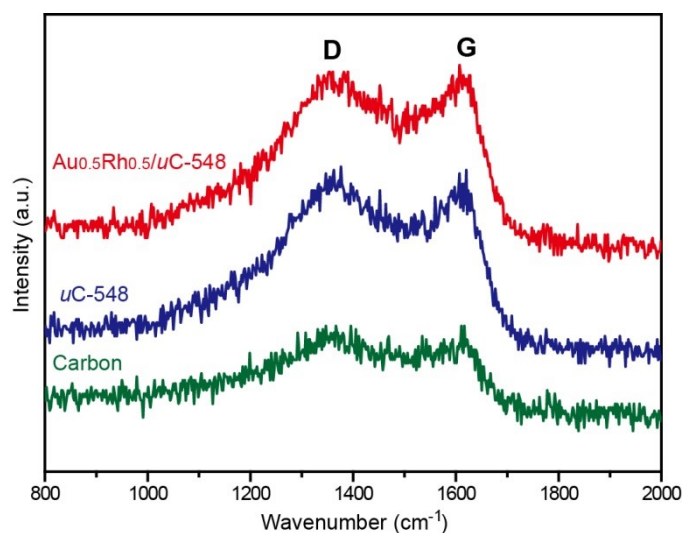


Figure 4.2. Raman spectra of Au_{0.5}Rh_{0.5}/*uC*-548, *uC*-548 and non-treated carbon.

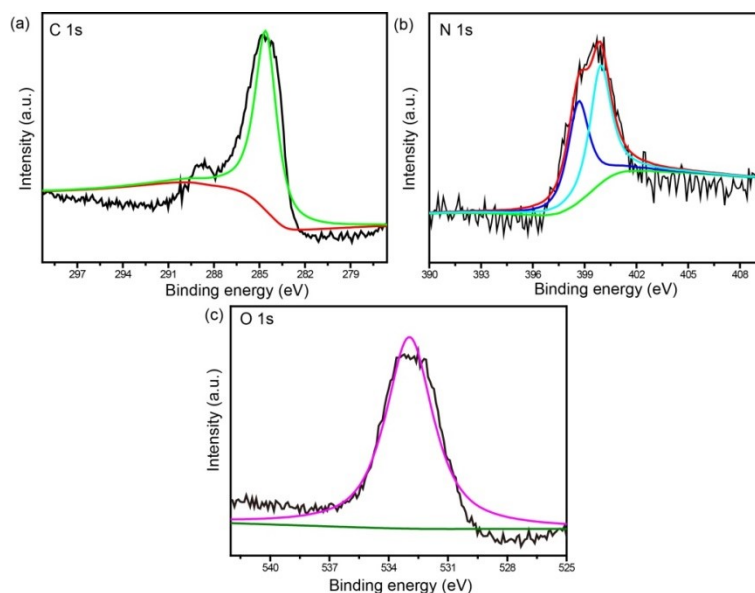


Figure 4.3. (a) C 1s, (b) N 1s and (c) O 1s XPS spectra of the as-prepared *uC*-548.

Synthesis and characterization of Au-Rh alloys. Au-Rh alloy clusters supported on *uC*-548, namely Au_{*x*}Rh_{1-*x*}/*uC*-548, are fabricated using a simple wet-chemistry

process. Briefly, $\text{Au}_x\text{Rh}_{1-x}/\text{uC-548}$ is synthesized by mixing of an aqueous solution containing HAuCl_4 and RhCl_3 and a black aqueous dispersion containing uC-548 powders, followed by a reduction of the metal precursors with a fresh sodium hydroxide/sodium borohydride aqueous solution. As indicated by PXRD patterns (Fig. 4.1b), the successful formation of a solid-solution alloy is confirmed by the weak and broad diffraction peaks located in between the characteristic peaks of the individual Au (JCPDS File No. 65-8601) and Rh (JCPDS File No. 05-0685), with a ultrafine size and uniform distribution. By further examination with the transmission electron microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM), $\text{Au}_{0.5}\text{Rh}_{0.5}$ clusters are found to be well-alloyed and highly dispersed with an ultrasmall size of ~ 1.65 nm (Fig. 4.4). Energy dispersive X-ray (EDX) spectra of several $\text{Au}_{0.5}\text{Rh}_{0.5}$ clusters suggest that the Au and Rh atoms are distributed randomly and homogeneously in the alloy structures (Fig. 4.4). XPS analysis identifies the metallic Au and Rh in formed $\text{Au}_{0.5}\text{Rh}_{0.5}$ clusters (Fig. 4.1c). Definitely, Au and Rh are well-alloyed in the $\text{Au}_{0.5}\text{Rh}_{0.5}$ clusters at the atomic-level by the designed uC-548 .

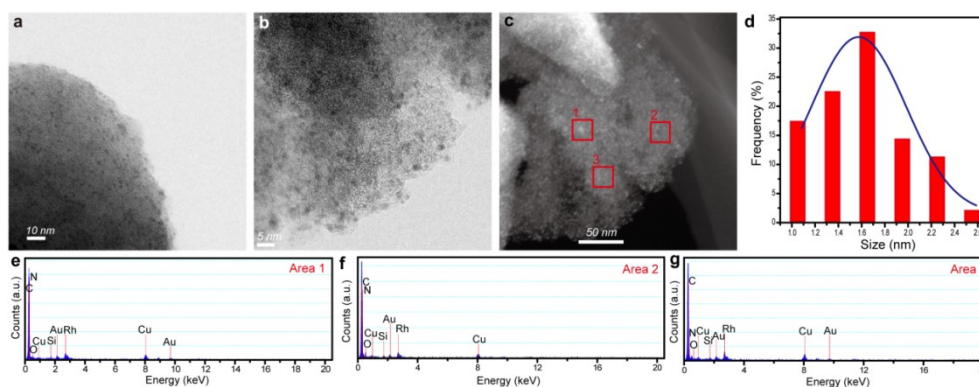


Figure 4.4. (a, b) TEM images, (c) HAADF-STEM image, (d) particle size distribution histograms, and (e-g) the corresponding EDS patterns of the selected area in (c) of $\text{Au}_{0.5}\text{Rh}_{0.5}/\text{uC-548}$.

In contrast, non-treated carbons are used to produce $\text{Au}_{0.5}\text{Rh}_{0.5}$ NPs. As expected,

the strong characteristic peaks are observed in PXRD pattern (Fig. 4.5) for unalloyed Au, indicating the aggregated and segregated NPs with large size.

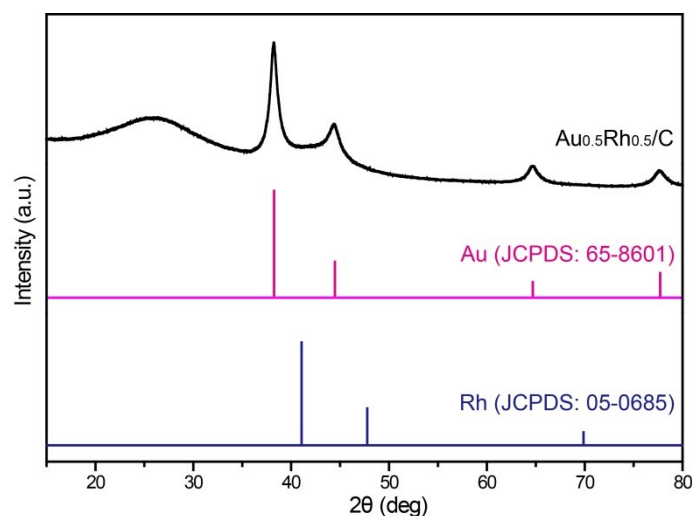


Figure 4.5. PXRD pattern of Au_{0.5}Rh_{0.5}/C.

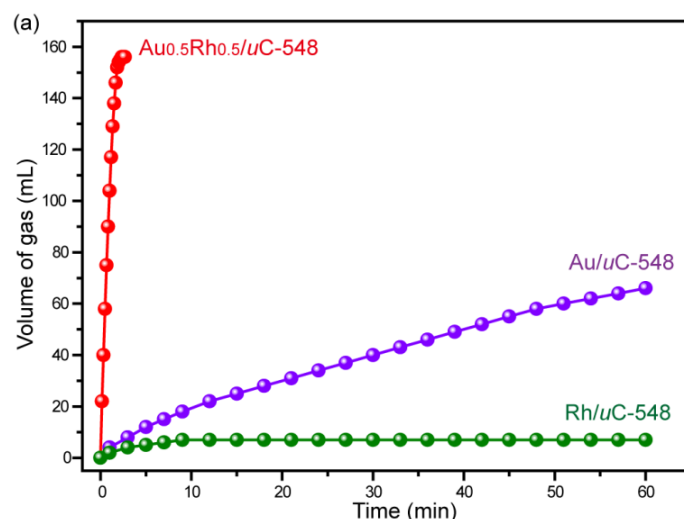


Figure 4.6. Volume of the Generated gas versus time for the dehydrogenation of FA over the Au_{0.5}Rh_{0.5}/uC-548, Au/uC-548, and Rh/uC-548.

Catalytic dehydrogenation of formic acid (FA) in aqueous solution. As a safe, nontoxic, easily accessible and highly stable hydrogen carrier, FA (HCOOH) has won great attention worldwide, from which hydrogen can be released through an atom economical dehydrogenation ($\text{HCOOH} \rightarrow \text{CO}_2 + \text{H}_2$).¹² Herein, as an effective probe reaction, the FA dehydrogenation is selected for investigating the potential catalytic

performances of the as-synthesized $\text{Au}_x\text{Rh}_{1-x}$ clusters. Hydrogen in FA can be released by addition of $\text{Au}_x\text{Rh}_{1-x}/\text{uC-548}$ catalysts into a reaction flask containing FA aqueous solution with sodium formate (SF) as an additive. As shown in Figure 4.6, in contrast to the poor activity of monometallic $\text{Au}/\text{uC-548}$ and the no activity of monometallic $\text{Rh}/\text{uC-548}$, the catalytic activities of $\text{Au}_{0.5}\text{Rh}_{0.5}/\text{uC-548}$ for FA dehydrogenation are dramatically enhanced by the solution alloying of Au and Rh at atomic-level. Moreover, $\text{Au}_{0.5}\text{Rh}_{0.5}/\text{uC-548}$ is found to be highly active by tuning the molar ratios of Au and Rh (Fig. 4.7), with which FA can be completely dehydrogenated within 1.67 min ($n_{\text{Au}}/n_{\text{FA}} = 0.01$ and $n_{\text{SF}}/n_{\text{FA}} = 2.5$) at 333 K with the release of 146 mL of H_2 and CO_2 , giving a TOF as high as 3582 h^{-1} , one of the highest values among all heterogeneous catalysts reported thus far. As expected, the carbon-supported $\text{Au}_{0.5}\text{Rh}_{0.5}$ clusters exhibit a poor catalytic activity (Fig. 4.8). The purity of generated gas is confirmed by gas chromatography (GC) analysis (Fig. 4.9), and the generated gas is entirely composed of H_2 and CO_2 without a wee bit of CO (below 5 ppm), implying the high selectivity of the as-synthesized Au-Rh alloy catalysts, which is of critical importance in H_2 powered fuel cell applications. Moreover, the increased catalytic rates for FA dehydrogenation are observed at elevated temperatures, and the TOFs reach up to 3582, 7083, and 10877 h^{-1} at 333, 342 and 353 K, respectively. The activation energy (E_a) is calculated to be $57.23 \text{ kJ mol}^{-1}$, which is comparable to the most reported results under similar conditions of the catalyzed FA dehydrogenation (Fig. 4.10). Notably, to date, no Au-Rh catalyst has been reported for the catalytic dehydrogenation of FA, and the Pd-based catalysts have been demonstrated as the excellent catalysts.

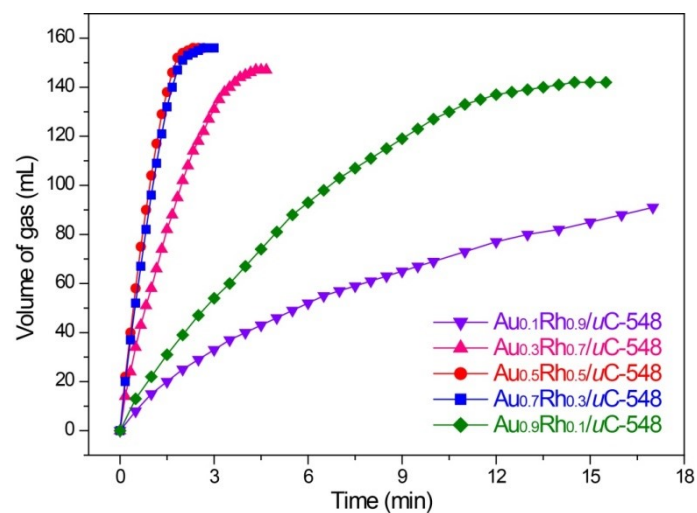


Figure 4.7. Volume of the generated gas ($\text{CO}_2 + \text{H}_2$) versus time for the dehydrogenation of FA over the $\text{Au}_x\text{Rh}_{1-x}/\text{uC-548}$ catalysts at 333 K ($n_{\text{metal}}/n_{\text{FA}} = 0.02$, $n_{\text{SF}}/n_{\text{FA}} = 2.5$).

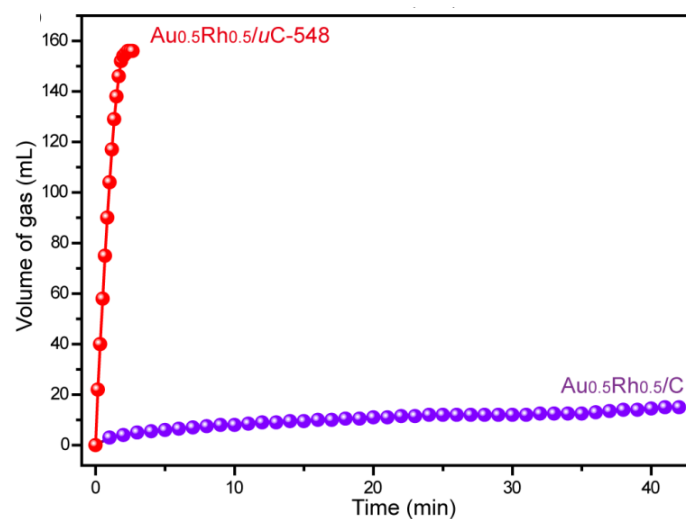


Figure 4.8. Volume of the Generated gas versus time for the dehydrogenation of FA over the $\text{Au}_{0.5}\text{Rh}_{0.5}/\text{uC-548}$ and $\text{Au}_{0.5}\text{Rh}_{0.5}/\text{C}$.

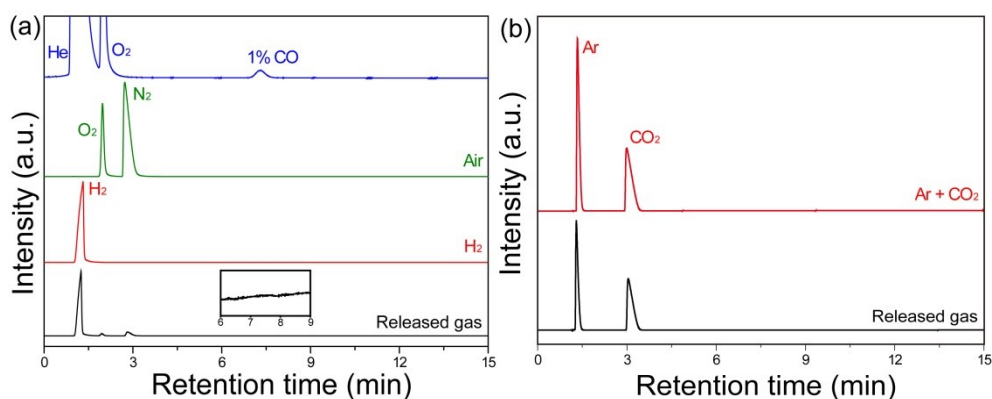


Figure 4.9. GC of the released gas (under Ar atmosphere) from the dehydrogenation of FA in the FA/SF system ($n_{\text{SF}}/n_{\text{FA}} = 2.5$) over the $\text{Au}_{0.5}\text{Rh}_{0.5}/\text{uC-548}$ catalyst at 333 K with (a) CO, air and H₂ and (b) CO₂ as reference gas, indicative of the absence of CO and presence of CO₂ and H₂ in the released gas.

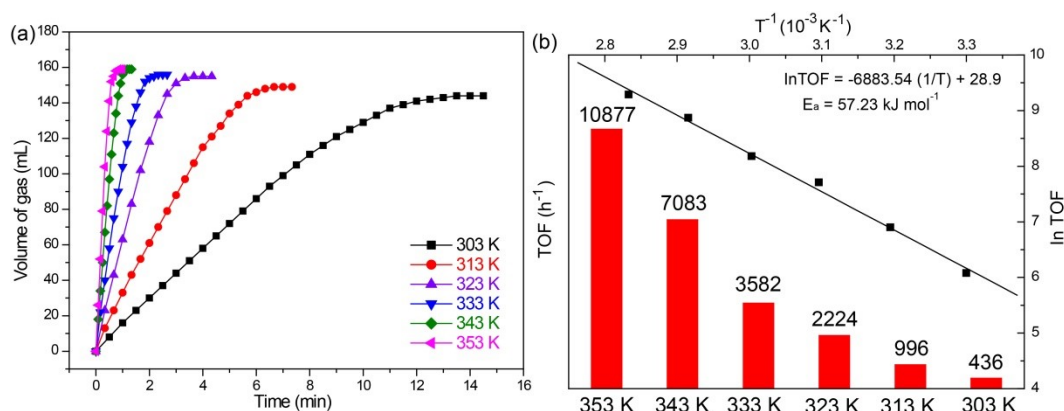


Figure 4.10. (a) Volume of the generated gas (CO₂ + H₂) versus time, (b) Arrhenius plot and TOF values for the dehydrogenation of FA over the $\text{Au}_{0.5}\text{Rh}_{0.5}/\text{uC-548}$ catalysts at different temperatures ($n_{\text{metal}}/n_{\text{FA}} = 0.02$, $n_{\text{SF}}/n_{\text{FA}} = 2.5$).

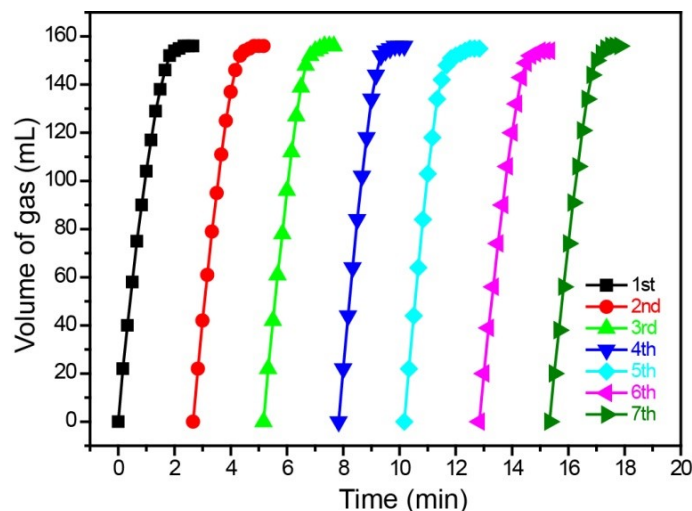


Figure 4.11. Durability test for the dehydrogenation of FA over the $\text{Au}_{0.5}\text{Rh}_{0.5}/\text{uC-548}$ catalysts at 323 K ($n_{\text{metal}}/n_{\text{FA}} = 0.02$, $n_{\text{SF}}/n_{\text{FA}} = 2.5$).

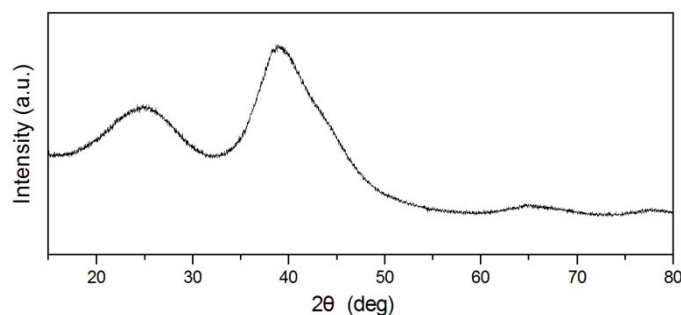


Figure 4.12. XRD pattern of the $\text{Au}_{0.5}\text{Rh}_{0.5}/\text{uC-548}$ catalyst after 7 catalytic cycles ($n_{\text{metal}}/n_{\text{FA}} = 0.02$, $n_{\text{SF}}/n_{\text{FA}} = 2.5$, 323 K).

The stability and durability are two critical indicators for heterogeneous catalysts. Alloys consisting of the immiscible metal are easy to segregate as the metastable structures, which may strongly reduce their stability and durability. Here, the recycled ability of $\text{Au}_{0.5}\text{Rh}_{0.5}/\text{uC-548}$ is also evaluated. As indicated in Figure 4.11, no significant loss in catalytic activities is observed even over seven cycles. PXRD pattern of the recycled $\text{Au}_{0.5}\text{Rh}_{0.5}$ clusters is same to that of the fresh catalysts. Undoubtedly, the Au-Rh alloy clusters stabilized by the ideal support uC-548 are highly stable without any segregation toward the dehydrogenation of FA.

4.4 Conclusions

In conclusion, we have demonstrated a relatively simple, effective and general method for solid-solution alloying of the entirely immiscible Au and Rh at room temperature. The obtained Au-Rh are ultrafine, high-dispersed and well-alloyed, showing significantly enhanced catalytic activity, selectivity, stability and durability for the dehydrogenation of FA in comparison with their monometallic parents. Our success relies on the design of ideal functionalized carbon through heating urea at an appropriate temperature, and more importantly, the simple *in situ* formation of discrete metal species from the strong electrostatic adsorption during the solid-solution alloying process.

References

1. (a) C.-H. Cui and S. -H. Yu, *Acc. Chem. Res.*, 2013, **46**, 1427; (b) H. Kobayashi, K. Kusada and H. Kitagawa, *Acc. Chem. Res.*, 2015, **48**, 1551; (c) L. Chen, R. Luque and Y. Li, *Chem. Soc. Rev.*, 2017, **46**, 4614;
2. (a) H. L. Jiang, T. Akita, T. Ishida, M. Haruta and Q. Xu, *J. Am. Chem. Soc.*, 2011, **133**, 1304; (b) X. Gu, Z.-H. Lu, H.-L. Jiang, T. Akita and Q. Xu, *J. Am. Chem. Soc.* 2011, **133**, 11822; (c) P. Buchwalter, J. Rosé and P. Braunstein, *Chem. Rev.*, 2015, **115**, 28; (d) S. -Y. Ma, H.- H. Li, B. -C. Hu, X. Cheng, Q. -Q. Fu and S. -H. Yu, *J. Am. Chem. Soc.*, 2017, **139**, 5890.

3. (a) Y. Chen, Q. -L. Zhu, N. Tsumori and Q. Xu, *J. Am. Chem. Soc.*, 2015, **137**, 106; (b) L. Chen, B. Huang, X. Qiu, X. Wang, R. Luque and Y. Li, *Chem. Sci.*, 2016, **7**, 228; (c) X. Yang, P. Pachfule, Y. Chen, N. Tsumori and Q. Xu, *Chem. Commun.*, 2016, **52**, 4171.
4. (a) A. Gutowska, L. Li, Y. Shin, C. M. Wang, X. S. Li, J. C. Linean, R. S. Smith, B. D. Kay, B. Schmid, W. Shaw, M. Gutowski and T. Autrey, *Angew. Chem. Int. Ed.*, 2005, **44**, 3578; (b) G. Lu, S. Li, Z. Guo, O. K. Farha, B. G. Hauser, X. Qi, X. Wang, S. Han, X. Liu, J. S. DuChene, H. Zhang, Q. Zhang, X. Chen, J. Ma, S. C. J. Loo, W. D. Wei, Y. Yang, J. T. Hupp and F. Huo, *Nat. Chem.*, 2012, **4**, 310; (c) C. Y. Peng, L. Kang, S. Cao, Y. Chen, Z. S. Lin and W. F. Fu, *Angew. Chem. Int. Ed.*, 2015, **54**, 15725; (d) L. -B. Sun, X. -Q. Liu and H. -C. Zhou, *Chem. Soc. Rev.*, 2015, **44**, 5092; (e) Y. Cui, B. Li, H. He, W. Zhou, B. Chen and G. Qian, *Acc. Chem. Res.*, 2016, **49**, 483; (f) Z. Li, T. He, L. Liu, W. Chen, M. Zhang, G. Wu and P. Chen, *Chem. Sci.*, 2017, **8**, 781; (g) R.V. Jagadeesh, K. Murugesan, A. S. Alshammari, H. Neumann, M. M. Pohl, J. Radnik and M. Beller, *Science*, 2017, **358**, 326.
5. D. Wang and Y. Li, *J. Am. Chem. Soc.*, 2010, **132**, 6280.
6. Q. -L. Zhu, J. Li and Q. Xu, *J. Am. Chem. Soc.*, 2013, **135**, 10210.
7. L. Luo, Z. Duan, T. Li, J. Kim, G. Henkelman and R. M. Crooks, *J. Am. Chem. Soc.*, 2017, **139**, 5538.
8. (a) P. Zhao, X. Feng, D. Huang, G. Yang and D. Astruc, *Coordin. Chem. Rev.*, 2015, **287**, 114; (b) J. -K. Sun, W. -W. Zhan, T. Akita and Q. Xu, *J. Am. Chem. Soc.*, 2015, **137**, 7063.
9. (a) Y. Zheng, Y. Jiao, Y. Zhu, L. H. Li, Y. Han, Y. Chen, A. Du, M. Jaroniec and S. Z. Qiao, *Nat. Commun.*, 2014, **5**, 3738; (b) H. Tabassum, W. Guo, W. Meng, A. Mamood, R. Zhao, Q. Wang and R. Zou, *Adv. Energy Mater.*, 2017, **7**, 1601671.
10. L. He, F. Weniger, H. Neumann and M. Beller, *Angew. Chem. Int. Ed.*, 2016, **55**, 12582.
11. Z. Li, X. Yang, N. Tsumori, Z. Liu, Y. Himeda, T. Autrey and Q. Xu, *ACS Catal.*, 2017, **7**, 2720.

12. (a) A. Boddien, D. Mellmann, F. Gärtner, R. Jackstell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig, M. Beller, *Science*, 2011, **333**, 1733, (b) M. Yadav and Q. Xu, *Energy Environ. Sci.*, 2012, **5**, 9698, (c) J. F. Hull, Y. Himeda, W. H. Wang, B. Hashiguchi, D. J. Szalda, J. T. Mucherman and E. Fujita, *Nat. Chem.*, 2012, **18**, 383, (d) S. Moret, P. J. Dyson and G. Laurenczy, *Nat. Commun.*, 2014, **4**, 4017, (e) W. H. Wang, M. Z. Rrtem, S. Xu, N. Onishi, Y. Manaka, Y. Suna, H. Kambayashi, J. T. Muckerman, E. Fujiata and Y. Himeda, *ACS Catal.*, 2015, **5**, 5496, (f) Z. Li and Q. Xu, *Acc. Chem. Res.*, 2017, **50**, 1449, (g) C. Tang, F. Chen, M. -M. Pohl, G. Agostini, M. Schneider, H. Junge and M. Beller, *Angew. Chem. Int. Ed.*, 2017, **56**, 16616.

Chapter 5

Conclusions

Liquid chemical hydrides, such as FA and AB, as a class of clean, effective, renewable and promising hydrogen carrier, have attracted much attention. The purpose of the research work presented in this dissertation is development of ultrafine metal NPs and exploring their applications as catalysts for hydrogen generation from liquid chemical hydrides. The bimetallic AuPd NPs supported on reduced graphene oxide using a non-noble metal sacrificial approach (*NNMSA*) exhibited high activity for dehydrogenation of FA. The Pd NCs encapsulated within organic molecular cage using a reverse double solvents approach (*RDSA*) exhibited highly efficient for methanolysis of AB. Especially, the alloys composed of classically immiscible Au and Rh metals synthesized using the functionalized carbon showed great promising for dehydrogenation of FA. The main findings of this dissertation are summarized as follows:

(i) Immobilization of highly catalytically active bimetallic AuPd NPs on reduced graphene oxide for hydrogen generation from formic acid

A $(\text{Co}_3)_\text{E}\text{Au}_{0.6}\text{Pd}_{0.4}/\text{rGO}$ catalyst has been synthesized using a simple non-noble metal sacrificial method (*NNMSA*). The obtained catalyst shows efficient catalytic activity for hydrogen generation from the FA/SF system with the highest TOF of 4840 h^{-1} at 323 K and possesses high selectivity, durability and stability over 5 cycles. It is believed that the way to the utilization of FA as a hydrogen carrier will be paved by the practical use of the

presently provided catalyst.

(ii) Encapsulation of highly catalytically active Pd nanoclusters inside porous organic cages for hydrogen generation from ammonia borane

A facile, scalable and effective reverse double solvents approach (*RDSA*) has been developed for synthesizing Pd@RCC3 hybrids with Pd NCs encapsulated inside the cavities of RCC3 cages for the first time. The excellent solubility of RCC3 with open skeletons has resulted in extremely high dispersion of soluble Pd NCs in solutions and favored mass transfer, and thus is beneficial for various liquid-phase catalytic reactions including AB methanolysis, nitroarenes hydrogenation and dyes reduction. Moreover, the as-prepared catalysts possess excellent stability and durability owing to the good confinement of Pd NCs within the discrete POC matrix. The present results provide a new perspective to the catalysis field in terms of the exploration of advanced catalysts through the use of flexible functionalized cavities of soluble microporous materials as matrix for highly dispersed ultrasmall MNPs.

(iii) Solid solution alloying of classically immiscible Au and Rh metals for highly efficient catalysis of hydrogen generation from formic acid

Heterometallic NPs containing two or more metals are important in various heterogeneous catalytic reactions. Solid-solution alloying between different metals enables, in most of cases, the excellent synergistic effects in alloy NPs, enhancing their intrinsic performance or even endowing them with

unpredictable properties. Herein, we have demonstrated a relatively simple, effective and general method for solid-solution alloying of the entirely immiscible Au and Rh at room temperature. The obtained Au-Rh are ultrafine, high-dispersed and well-alloyed, showing significantly enhanced catalytic activity, selectivity, stability and durability for the dehydrogenation of FA in comparison with their monometallic parents. Our success relies on the design of ideal functionalized carbon through heating of urea at an appropriate temperature, and more importantly, the simple *in situ* formation of discrete metal species from the strong electrostatic adsorption during the solid-solution alloying process.

In conclusion, this dissertation focuses on the development of ultrafine MNPs for catalytic hydrogen generation from liquid chemical hydrides such as formic acid and ammonia borane. We hope that the way to the utilization of liquid chemical hydrides as the hydrogen carriers will be paved by the practical use of the presently provided catalysts.

List of Publications

Journal Publications

- ✧ Highly efficient hydrogen generation from formic acid using a reduced graphene oxide-supported AuPd nanoparticle catalyst.

Xinchun Yang, Pradip Pachfule, Yao Chen, Nobuko Tsumori and Qiang Xu*

Chemical Communications, 2016, **52**, 4171-4174.

- ✧ Gold-containing metal nanoparticles for catalytic hydrogen generation from liquid chemical hydrides (Invited mini-review).

Xinchun Yang and Qiang Xu*

Chinese journal of Catalysis, 2016, **37**, 1594-1599.

- ✧ Bimetallic metal-organic frameworks for gas storage and separation (Invited perspective).

Xinchun Yang and Qiang Xu*

Crystal Growth & Design, 2017, **17**, 1450-1455.

- ✧ Encapsulating highly catalytically active metal nanoclusters inside porous organic cages.

Xinchun Yang, Jian-Ke Sun, Mitsunori Kitta, Huan Pang and Qiang Xu*

Nature Catalysis, 2018, accepted.

- ✧ Solid-solution alloying of classically immiscible Au and Rh for highly efficient catalysis of hydrogen generation.

Xinchun Yang, Zhangpeng Li, Nobuko Tsumori and Qiang Xu*

To be submitted.

Conference Presentations

- ✧ Ultrafine metal nanoparticles for catalytic hydrogen generation from formic acid.

Xinchun Yang and Qiang Xu*

The 1st International Symposium on Nanotechnology and Mesophase Engineering (ISNME2017), Poster, Osaka, Japan, 2017/6/10.

Doctoral Dissertation, Kobe University

“Development of ultrafine metal nanoparticles for catalytic hydrogen generation from liquid chemical hydrides”, 89 pages

Submitted on January 18, 2018

The date of publication is printed in cover of repository version published in Kobe University Repository Kernel.

© YANG XINCHUN

All Right Reserved, 2018