View Article Online
View Journal

Green Chemistry

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: T. Zhang, L. Zhang, W. Wang, A. Wang, Y. Cui, X. Yang, Y. Huang, X. Liu, W. Liu, J. Son and H. Oji, *Green Chem.*, 2013, DOI: 10.1039/C3GC41117F.

Green Chemistry

Cutting-edge research for a greener sustainable future

www.rsc.org/greenchem

Volume 12 | Number 9 | September 2010 | Pages 1481–1676

ISSN 1463-9262

RSCPublishing

COMMUNICATION
Luque, Varma and Baruwati
Magnetically seperable organocatalyst for homocoupling of arylboronic acids

CRITICAL REVIEW
Dumesic et al.
Catalytic conversion of biomass to biofuels

1463-9262(2010)12:9;1-U

This is an *Accepted Manuscript*, which has been through the RSC Publishing peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, which is prior to technical editing, formatting and proof reading. This free service from RSC Publishing allows authors to make their results available to the community, in citable form, before publication of the edited article. This *Accepted Manuscript* will be replaced by the edited and formatted *Advance Article* as soon as this is available.

To cite this manuscript please use its permanent Digital Object Identifier (DOI®), which is identical for all formats of publication.

More information about *Accepted Manuscripts* can be found in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics contained in the manuscript submitted by the author(s) which may alter content, and that the standard **Terms & Conditions** and the **ethical guidelines** that apply to the journal are still applicable. In no event shall the RSC be held responsible for any errors or omissions in these *Accepted Manuscript* manuscripts or any consequences arising from the use of any information contained in them.

Green Chemistry

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

View Article Online
DOI: 10.1039/C3GC41117F

COMMUNICATION

Aerobic Oxidative Coupling of Alcohols and Amines over Au-Pd/resin in Water: Au/Pd Molar Ratios Switch the Reaction Pathways to Amides or Imines

Leilei Zhang,[a,b] Wentao Wang,[a] Aiqin Wang,[a] Yitao Cui,[c] Xiaofeng Yang,[a] Yanqiang Huang,[a] Xiaoyan Liu,[a] Wengang Liu,[b] Jin-Young Son,[c] Hiroshi Oji,[c] and Tao Zhang*[,a]

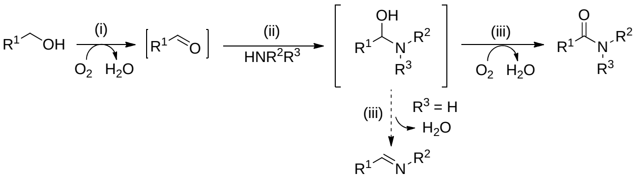
Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX

DOI: 10.1039/b000000x

Facile switch of the reaction pathways of aerobic oxidative coupling of alcohols and amines from amidation to imination was realized for the first time by tuning the Au/Pd ratios in ion-exchange resin supported Au-Pd alloy catalysts (Au-Pd/resin). Amides were obtained with high yields on Au_6Pd/resin while imines over $AuPd_4$/resin. Various alcohols and amines underwent oxidative coupling smoothly in water to afford the desired products with good to excellent yields. Further investigation on the reaction mechanism suggested the synergistic effect between Au and Pd determined the adsorption strength of aldehyde intermediate, which in turn dictated the reaction pathways. That is, on Au-riched alloys (e.g., Au_6Pd) absorbed aldehyde species was formed, and followed by further oxidation to yield amides while on Pd-riched alloys (e.g., $AuPd_4$) free aldehyde was generated, which then underwent condensation with amines to produce imines. The discovery might provide avenue to develop new efficient catalysts for green synthesis of special chemicals.

Introduction

Amides and imines represent two important classes of N-containing intermediates and functional groups for organic synthesis.[1] Amides play a major role in the pharmaceutical industry, biological system and material science[1a-1c] while imines are widely applied as electrophiles in many organic transformations such as cyclization, reduction, addition and condensation[1d,1e]. Traditional synthesis of amides and imines involves the reactions of carboxylic acid or derivatives such as acid chlorides and anhydrides with amine, which suffers from toxicity issues and harsh reaction conditions.[2] Lately, new methodologies towards the green synthesis of amides and imines have been developed,[3] such as oxidative coupling of aldehydes and amines,[3a] hydrolyzation of nitriles,[3b] and dehydrogenative coupling of alcohols and amines[3c-3e]. Among others, aerobic oxidative coupling of alcohols and amines offers prominent advantages of mild reaction conditions, high efficiency, and wide scope of the substrates.[4] This reaction is a tandem process composed of three consecutive steps: (i) oxidative dehydrogenation of alcohol to aldehyde, (ii) oxidative coupling of aldehyde and amine to form hemiaminal, and (iii) further oxidation of hemiaminal to yield amide or dehydration to yield imine, as shown in Scheme 1. Kobayashi and co-workers successfully explored this reaction by employing their unique PICB (polymer-incarcerated carbon black)-supported gold bimetallic catalysts.[4a,4d] According to their reports, Au-Co/PICB catalyzed the selective formation of amide[4a] while Au-Pd/PICB promoted the selective production of imine[4d]. The results suggested that the selectivity of reaction catalyzed by gold could be tuned by changing the second metal.[5] However, the respective mechanism of Co and Pd in this reaction is to be clarified yet, which would be highly desirable for the rational design of new catalysts. Moreover, some intrinsic defects may exist in PICB-supported metal catalysts: (1) the PICB catalyst is not readily available and involves a multi-step and expensive synthesis procedure; and (2) possibly due to the weak interaction between PICB and metal species, the leaching of metal species appeared unavoidable in water, which necessitated the employment of organic solvent.[6] From a environmentally benign point of view, developing efficient and durable catalyst that can be used for organic transformations in aqueous media is highly desirable.



Scheme 1 pathways of oxidative coupling of alcohols and amines.

Supported Au and Au-containing bimetallic nanoparticles have shown great potentials as catalysts in green synthesis of fine chemicals.[7,8] In particular, Au-Pd alloy catalysts often outperform monometallic counterparts owing to the synergistic interplay between Au and Pd in terms of ensemble effect and ligand effect.[9] Ensemble effect arises when Au and Pd atoms,

View Article Online
DOI: 10.1039/C3GC41117F

individually or together, activate distinct substrates in a reaction mechanism while ligand effect is derived from the modification of electronic structure of Au and Pd through charge transfer between dissimilar neighbouring atoms.[10] It is obvious that the composition, namely, the Au/Pd molar ratios of Au-Pd alloys plays a critical role in dictating the synergistic effect and hence tuning the catalytic performance.[10e,11] Therefore, it would be highly desirable to employ strong ensemble and/or ligand effect to achieve selective organic synthesis, or even better, to switch the reaction pathways by tuning the Au/Pd molar ratios in Au-Pd alloys. However, currently, no reports have been deliverd that the reaction pathways could be switched merely by the Au/Pd molar ratios in organic transformations.

Herein, we used cheap and commercially available anion-exchange resin as the support to prepare a series of Au-Pd alloy catalysts (denoted as Au-Pd/resin hereafter) and then employed them for the oxidative coupling of alcohols and amines in water. To our delight, our Au-Pd/resin catalysts were highly active and robust for this reaction. More importantly, by tuning Au/Pd molar ratios, the reaction pathways could be switched facilely from amidation to imination. Amides and imines were obtained with good to excellent yields over Au_6Pd/resin and $AuPd_4$/resin, respectively. To the best of our knowledge, this is the first example in organic transformations that the reaction pathways can be switched by the Au/Pd molar ratios of Au-Pd alloys.

Results and discussion

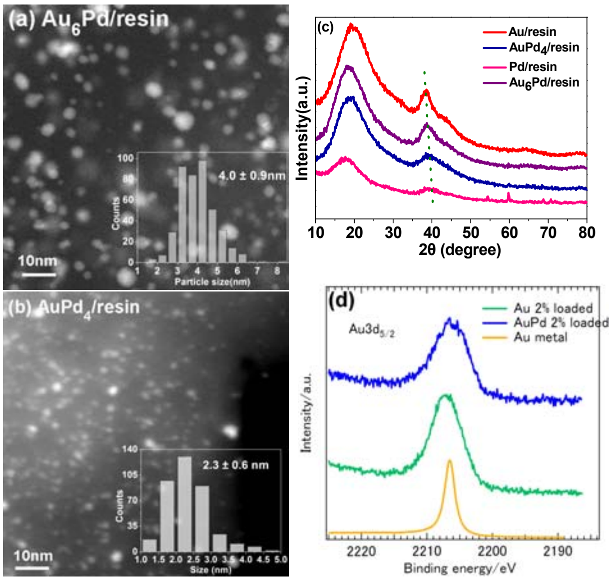
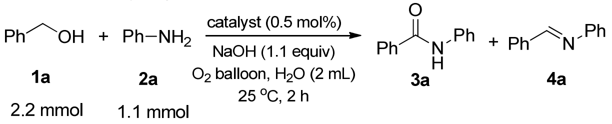


Fig. 1 HAADF images of Au_6Pd/resin (a) and $AuPd_4$/resin (b); XRD patterns of Au-Pd/resin (c); HAXPES spectra of Au $3d_{5/2}$ of Au_6Pd/resin (d).

Au-Pd/resin catalysts were prepared with ion exchange-$NaBH_4$ reduction method. Fig. 1((a), (b), (c)) shows HAADF images and XRD patterns of samples with different Au/Pd ratios. Au-Pd nanoparticles are highly dispersed on the support, and the average particle size decreased with decreasing the Au/Pd ratio, indicating Pd helps to stabilize alloy nanoparticles against aggregation.[10a,10d] The gradual shift of (111) reflection towards higher angles with a decrease of Au/Pd ratio suggests the formation of Au-Pd alloy. Oxidative coupling of alcohols and amines were carried out in aqueous media under O_2 balloon. First, the reaction of benzyl alcohol **1a** and aniline **2a** was tested to investigate the effect of Au/Pd ratio and the results are shown in Table 1. It was found that both the activity and selectivity changed remarkably with Au/Pd ratios. For monometallic gold and gold-rich alloy catalysts (Au/Pd > 1, Table 1, entries 1-4), the main product was amide **3a** and the best result was achieved with Au_6Pd/resin (Table 1, entry 3). On the other hand, for monometallic Pd and Pd-rich alloy catalysts (Au/Pd ≤ 1, Table 1, entries 5-8), the main product turned out to be imine **4a** and the best result was obtained with $AuPd_4$/resin (Table 1, entry 7). Thus, we have provided a new opportunity to switch the reaction pathways of oxidative coupling of alcohols and amines, from amides to imines merely by tuning the Au/Pd molar ratios. After optimizations of the reaction conditions (Table S2-S7, ESI†), 91% and 80% isolated yields of amide **3a** and imine **4a** could be obtained over Au_6Pd/resin and $AuPd_4$/resin, respectively. It was also noted that the catalytic activity went up first with a decrease of Au/Pd ratio until Au/Pd = 6/1, and then dropped significantly with further decreasing the Au/Pd ratio. This trend implies that Au is much more active than Pd in the coupling reaction. Accordingly, we speculate that Au acts as the main active component and Pd functions as a switch to direct the reaction pathway.

Table 1 Catalytic performance of Au-Pd/resin.



Entry	Catalysts	Conversion (%)[a]	Selectivity (%)[a]	
			3a	**4a**
1	Au/resin	47	93	6
2	$Au_{10}Pd$/resin	63	91	8
3	Au_6Pd/resin	77	97	2
4	Au_2Pd/resin	51	71	28
5	AuPd/resin	28	33	66
6	$AuPd_2$/resin	12 (60[b])	4 (32[b])	95 (67[b])
7	$AuPd_4$/resin	12 (42[b])	0 (5[b])	99 (94[b])
8	Pd/resin	1 (16[b])	0 (0[b])	99 (99[b])

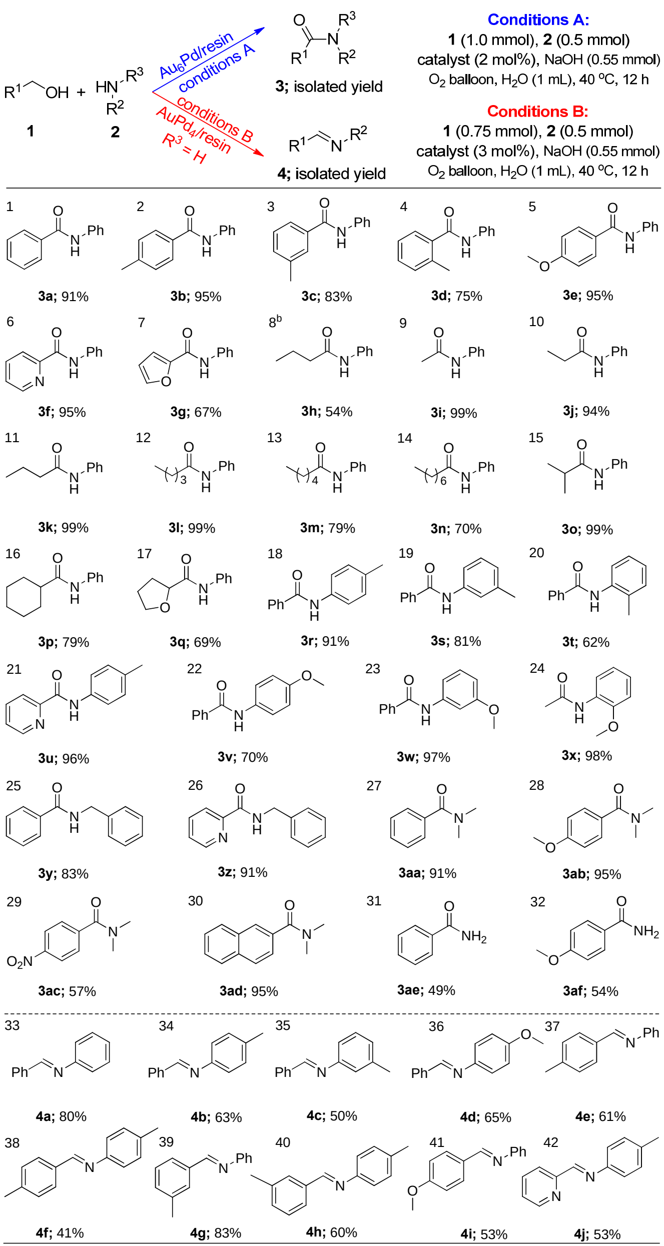
[a] Determined by GC using 1,3,5-trimethylbenzene as an internal standard and calculated based on **2a**. [b] **1a** (1.0 mmol), **2a** (0.5 mmol), catalyst (2 mol%), H_2O (1 mL), 5 h.

After establishing suitable catalysts and optimum reaction conditions, we focused on the issues of scope and functional group tolerance. Amidation reaction was further studied over the best catalyst Au_6Pd/resin and various alcohols **1** and amines **2** were tested (Table 2). As for alcohols **1**, benzyllic alcohols bearing both electron-withdrawing and -donating groups (Table 2, entries 2-5, 29) were successfully converted to the corresponding amides **3b-3e** and **3ac** with high yields. The Au_6Pd/resin was also tolerant to alcohols when the aromatic rings were naphthyl (Table 2, entry 30) and pyridyl (Table 2, entries 6, 21, 26), and the amidation reaction proceeded very well to afford the desired products **3ad, 3f, 3u** and **3z**. Specifically, for biomass derived ethanol, *n*-butanol and furyl alcohols (Table 2, entries 7, 9, 11, 17), the corresponding amides **3g**, **3i**, **3k** and **3q** were also achieved with good to excellent yields. This would open up a new

View Article Online
DOI: 10.1039/C3GC41117F

route to the synthesis of valuable fine chemicals from renewable biomass-derived materials. Importantly, for aliphatic alcohols that are difficult to oxidize, the amidation reaction could also proceed smoothly (Table 2, entries 9-17). Allylic alcohol (Table 2, entry 8) was also investigated. To our surprise, saturated N-phenylbutyramide **3h** was obtained when 2-buten-1-ol was employed as the starting alcohol. Obviously, hydrogen transfer occurred during the oxidative process, which is quite different from the result obtained with Au/Co[4a] catalysts. This result will provide some hints for the underlying mechanism and therefore be discussed in the following part. Besides alcohols, a series of amines **2a** were also investigated (Table 2, entries 18-32) and the reaction proceeded smoothly. Notably, for sterically hindered secondary amines that are sluggish to perform amidation (Table 2, entries 27-30), good to excellent yields of the corresponding amides **3aa-3ad** were obtained. Ammonia could also be good substrate (Table 2, entries 31-32) though moderate yields of benzamides **3ae-3af** were achieved. Gram-scale experiment was also performed with ethanol and aniline, and acetanilide, an important intermediate in pharmaceutical industry, was achieved with 96% yield (Scheme S1, ESI†), indicating our Au_6Pd/resin catalyst could be tolerant to large-scale production and therefore showed great potentials for industrial application.

Table 2 Oxidative coupling reactions over Au-Pd/resin.[a]

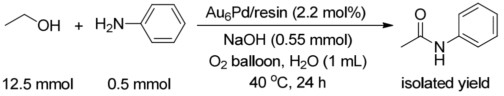


[a] For experimental details, see Electronic Supplementary Information (ESI†). [b] Obtained from coupling of aniline and 2-buten-1-ol.

The reaction pathway was completely switched to imination when Au_6Pd/resin was replaced by $AuPd_4$/resin while the other reaction conditions were almost identical. Various aromatic alcohols **1** and amines **2** bearing a broad scope of substitution groups on the benzene ring (Table 2, entries 33-41) could be converted into the desired imines **4b-4i**. Pyridyl alcohol (Table 2, entry 42) was also tolerated and the reaction proceeded very well. It is noted that though the selectivity of imines determined by GC was very high, only moderate to good isolated yields of imines were obtained when the products were purified by chromatography because the products decomposed to some extent over silica gel.

Hot filtration test was carried out to rule out the possible contribution of homogeneous catalysis.[12] The Au_6Pd/resin was separated from the reaction system by filtration at a conversion of 52% and the filtrate was examined by ICP-AES. The results showed that only negligible amounts of Au (0.4 ppm corresponding to 0.02 wt% of initial charge) and Pd (0.1 ppm corresponding to 0.09 wt% of initial charge) were detected in the solution and no further reaction took place when new batch of substrates was added into the filtrate. Evidently, the oxidative coupling reaction indeed took place on the surface of solid catalyst. The catalysts also exhibited good recyclability and stability. For instance, the Au_6Pd/resin could be recovered by simple filtration and reused for 6 times (Table 3) and could be stored for 7 months under air atmosphere without significant loss of catalytic activity.

Table 3 Recovery and reuse of Au_6Pd/resin.

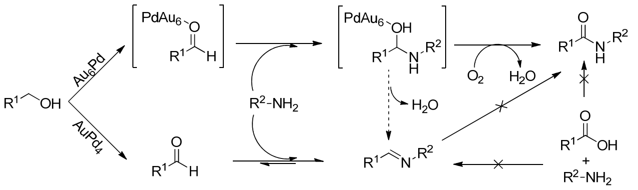


Run	1	2	3	4	5	6
Yield (%)	99	99	97	96	89	84

How are the reaction pathways switched from amidation to imination with decreasing the Au/Pd ratios? To address this issue, we designed following control experiments. First, the oxidation of benzyl alcohol was performed on catalysts with different Au/Pd ratios (Table S8, ESI†). The selectivity of benzaldehyde increased with a decrease of Au/Pd ratio, and no benzaldehyde was formed over Au_6Pd/resin. This result was well consistent with the observation that no aldehyde was detected in Au_6Pd/resin system while a quantity of free aldehyde was always detected in the case of $AuPd_4$/resin during the oxidative coupling reaction. Second, the coupling reaction of benzaldehyde and aniline was performed, and it resulted in the exclusive formation

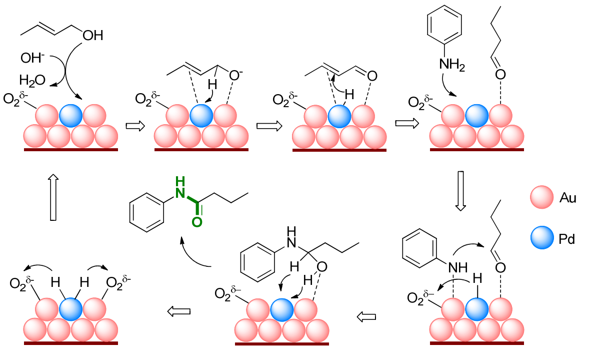
View Article Online
DOI: 10.1039/C3GC41117F

of imine either with Au_6Pd/resin or without any catalyst (Scheme S3-S4, ESI†). Taking these results together, we can propose that the reaction pathway to amidation or imination depends on the adsorption strength of aldehyde intermediate on catalyst surface, which in turn relies on the Au/Pd ratio. In the case of gold-rich alloy catalyst (e.g., Au_6Pd), an adsorbed aldehyde species would be formed at the initial stage of the reaction due to the strong affinity of Au to acyl group.[13] The adsorbed aldehyde then reacted with amine to generate adsorbed hemiaminal, followed either by further oxidation to yield amide or dehydration to imine.[4] Nevertheless, dehydration process is significantly inhibited in aqueous media, thus amidation turns out to be the main reaction pathway on the Au_6Pd/resin. In contrast, free aldehyde was preferentially formed with Pd-rich alloy (e.g., $AuPd_4$) probably owing to the isolation of Au atoms by Pd which weakens the adsorption of aldehyde on Au atoms. Upon formation, the free aldehyde then underwent condensation with amine smoothly to produce imine. The possible mechanisms of amidation and imination are shown in Scheme 2.



Scheme 2 Proposed reaction pathways of amidation and imination over Au-Pd/resin.

To gain insight into the synergistic interplay between Au and Pd, further control experiments and hard x-ray photoemission spectroscopy (HAXPES) characterizations were carried out.[14] As mentioned before, transfer hydrogenation occurred during amidation of 2-buten-1-ol and aniline (Table 2, entry 8). To clarify the dependence of hydrogen transfer capability on the Au/Pd ratios, this reaction was further investigated over a series of catalysts with different Au/Pd ratios (Table S9, ESI†). The fact that hydrogen transfer occurred on all Pd-containing catalysts except Au/resin suggested that β-H of alcohol was abstracted directly on Pd rather than Au atoms and the Pd-H species was probably formed.[15] The HAXPES results of Au_6Pd/resin (Fig. 1(d)) showed the Au atoms were negatively charged. These experimental results, combined with the conclusion in literature that Au had strong affinity to acyl group,[13] helps us to understand the synergistic effect in Au-Pd alloy. For the Au_6Pd catalyst (Scheme 3), Au served as the main active sites to adsorb acyl group-containing intermediates and O_2, while addition of Pd facilitated the abstraction of β-H, a step that is usually sluggish to proceed directly over Au.[16] Moreover, electron transfer from Pd to Au made the Au atoms slightly negatively charged, and consequently promoted the activation of O_2 on Au[17] to generate superoxo-like species,[18] which in turn facilitated the H elimination from Pd-H species through a H_2O_2 route.[19] Through such synergistic interplay between Au and Pd, the Au_6Pd catalyst exhibited the best performance for amidation. Distinct from the Au_6Pd catalyst, in the case of $AuPd_4$ catalyst, the catalyst surface might be covered by H atoms to a great extent during the reaction, which will weaken the adsorption of the aldehyde intermediates on Pd atoms and thereby hinder further oxidative dehydrogenation. Meanwhile, the isolation of Au by Pd atoms also results in the weak adsorption of the aldehyde intermediates on Au atoms. Taken together, the aldehyde intermediate desorbs readily from the $AuPd_4$ catalyst surface, which directs the reaction towards imination pathway.



Scheme 3 Schematic illustration of synergistic interplay between Au and Pd in amidation of 2-buten-1-ol and aniline over Au_6Pd/resin.

Conclusions

We have developed ion exchange resin supported Au-Pd nano-alloy catalysts that afforded high activity, tunable selectivity, wide substrate variety, and good reusability for oxidative coupling of alcohols and amines to synthesis of amides and imines. The reaction pathways could be facilely switched by the Au/Pd molar ratios; amides were obtained over Au_6Pd/resin while imines on $AuPd_4$/resin. Through deliberate design of control experiments as well as the catalyst characterization, we also provided insightful understanding of the reaction mechanisms responsible for the switch-like behavior of the Au/Pd ratio. The synergistic interplay between Au and Pd revealed in this work may offer a new guide for the design of other gold-bimetallic catalysts towards the green synthesis of fine chemicals.

Acknowledgments

This work is supported by grants from the National Science Foundation of China (21176235, 21203182, 21202163), Hundred Talents Program of Dalian Institute of Chemical Physics (DICP). HAXPES experiment was performed at Spring-8 with the approval of JASRI (Proposal No. 2013A1400).

Notes and references

[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, 116023, China.*
[b] *University of Chinese Academy of Sciences, Beijing, 100049, China.*
[c] *Industrial Application Division, Japan Synchrotron Radiation Research Institute, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo, 679-5198, Japan.*

† Electronic Supplementary Information (ESI) available: Experimental details, ^1H NMR and ^{13}C NMR spectra are provided. See DOI: 10.1039/b000000x/

1 (a) E. Valeur and M. Bradley, *Chem. Soc. Rev.*, 2009, **38**, 606; (b) M. A. Mintzer and E. E. Simanek, *Chem. Rev.*, 2009, **109**, 259; (c) C. L. Allen and J. M. J. Williams, *Chem. Soc. Rev.*, 2011, **40**, 3405; (d) R.

View Article Online
DOI: 10.1039/C3GC41117F

W. Layer, *Chem. Rev.*, 1963, **63**, 489; (e) J. Gawronski, N. Wascinska and J. Gajewy, *Chem. Rev.*, 2008, **108**, 5227.

2 M. B. Smith, *Compendium of Organic Synthetic Methods*, Wiley: New York, 2001.

3 (a) W.-J. Yoo and C.-J. Li, *J. Am. Chem. Soc.*, 2006, **128**, 13064; (b) Y.-M. Liu, L. He, M.-M. Wang, Y. Cao, H.-Y. He and K.-N. Fan, *ChemSusChem*, 2012, **5**, 1392; (c) C. Gunanathan, Y. Ben-David and D. Milstein, *Science*, 2007, **317**, 790; (d) L. U. Nordstrøm, H. Vogt and R. Madsen, *J. Am. Chem. Soc.*, 2008, **130**, 17672; (e) L. Tang, H. Sun, Y. Li, Z. Zha and Z. Wang, *Green Chem.*, 2012, **14**, 3423.

4 (a) J.-F. Soulé, H. Miyamura and S. Kobayashi, *J. Am. Chem. Soc.*, 2011, **133**, 18550; (b) Y. Wang, D. Zhu, L. Tang, S. Wang and Z. Wang, *Angew. Chem. Int. Ed.*, 2011, **50**, 8917; (c) S. Kegnæs, J. Mielby, U. V. Mentzel, C. H. Christensen and A. Riisager, *Green Chem.*, 2010, **12**, 1437; (d) J.-F. Soulé, H. Miyamura and S. Kobayashi, *Chem. Commun.*, 2013, **49**, 355.

5 K. Kaizuka, H. Miyamura and S. Kobayashi, *J. Am. Chem. Soc.*, 2010, **132**, 15096.

6 W.-J. Yoo, H. Miyamura and S. Kobayashi, *J. Am. Chem. Soc.*, 2011, **133**, 3095.

7 (a) A. S. K. Hashmi and G. J. Hutchings, *Angew. Chem. Int. Ed.*, 2006, **45**, 7896; (b) A. Corma and H. Garcia, *Chem. Soc. Rev.*, 2008, **37**, 2096; (c) Y. Zhang, X. Cui, F. Shi and Y. Deng, *Chem. Rev.*, 2012, **112**, 2467.

8 (a) M. Sankar, N. Dimitratos, P. J. Miedziak, P. P. Wells, C. J. Kielye and G. J. Hutchings, *Chem. Soc. Rev.*, 2012, **41**, 8099; (b) A. Villa, G. M. Veith and L. Prati, *Angew. Chem. Int. Ed.*, 2010, **49**, 1; (c) W. Li, A. Wang, X. Liu and T. Zhang, *Appl. Catal. A*, 2012, **433–434**, 146.

9 (a) M. Chen, D. Kumar, C.-W. Yi and D. W. Goodman, *Science*, 2005, **310**, 291; (b) D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight and G. J. Hutchings, *Science*, 2006, **311**, 362.

10 (a) X. Liu, A. Wang, X. Yang, T. Zhang, C.-Y. Mou, D.-S. Su and J. Li, *Chem. Mater.*, 2009, **21**, 410; (b) P. Strasser, S. Koh, T. Anniyev, J. Greeley, K. More, C. Yu, Z. Liu, S. Kaya, D. Nordlund, H. Ogasawara, M. F. Toney and A. Nilsson, *Nat. Chem.*, 2010, **2**, 454; (c) X. Liu, A. Wang, L. Li, T. Zhang, C.-Y. Mou and J.-F. Lee, *J. Catal.*, 2011, **278**, 288; (d) X. Wei, X.-F. Yang, A.-Q. Wang, L. Li, X.-Y. Liu, T. Zhang, C.-Y. Mou and J. Li, *J. Phys. Chem. C*, 2012, **116**, 6222; (e) D. A. Slanac, W. G. Hardin, K. P. Johnston and K. J. Stevenson, *J. Am. Chem. Soc.*, 2012, **134**, 9812.

11 F. Cárdenas-Lizana, S. Gómez-Quero, A. Hugon, L. Delannoy, C. Louis and M. A. Keane, *J. Catal.*, 2009, **262**, 235.

12 M. Lamblin, L. Nassar-Hardy, J.-C. Hierso, E. Fouquet and F.-X. Felpin, *Adv. Synth. Catal.*, 2010, **352**, 33.

13 (a) K.-Q. Sun, Y.-C. Hong, G.-R. Zhang and B.-Q. Xu, *ACS Catal.*, 2011, **1**, 1336; (b) J. Zheng, H. Lin, Y.-N. Wang, X. Zheng, X. Duan and Y. Yuan, *J. Catal.*, 2013, **297**, 110.

14 K. Kobayashi, *Nucl. Instr. and Meth. A*, 2005, **547**, 98.

15 (a) T. Mallat and A. Baiker, *Chem. Rev.*, 2004, **104**, 3037; (b) W. Hou, N. A. Dehm and R. W. J. Scott, *J. Catal.*, 2008, **253**, 22; (c) A. Abad, A. Corma and H. García, *Pure Appl. Chem.*, 2007, **79**, 1847.

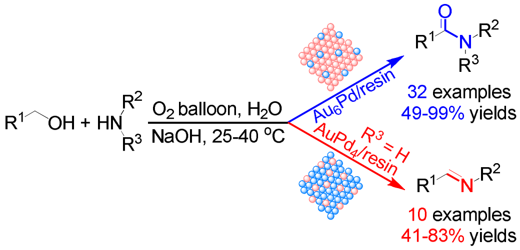
16 M. Conte, H. Miyamura, S. Kobayashi and V. Chechik, *J. Am. Chem. Soc.*, 2009, **131**, 7189.

17 H. Tsunoyama, N. Ichikuni, H. Sakurai and T. Tsukuda, *J. Am. Chem. Soc.*, 2009, **131**, 7086.

18 (a) H. Tsunoyama, H. Sakurai, Y. Negishi and T. Tsukuda, *J. Am. Chem. Soc.*, 2005, **127**, 9374; (b) H. Zhang, T. Watanabe, M. Okumura, M. Haruta and N. Toshima, *Nat. Mater.*, 2012, **11**, 49.

19 (a) B. N. Zope, D. D. Hibbitts, M. Neurock and R. J. Davis, *Science*, 2010, **330**, 74; (b) C. Shang and Z.-P. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 9938.

View Article Online
DOI: 10.1039/C3GC41117F



Facile switch of the reaction pathways from amidation to imination was realized by tuning the Au/Pd ratios in Au-Pd/resin.