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ARTICLE TYPE

NaF Regulated Aqueous Phase Synthesis of Aromatic Amides and Imines Catalyzed by Au/HT

Qianqian Wang[a,b], Youquan Deng[a] and Feng Shi[a]*

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An Au/HT catalyst was found to be an efficient heterogeneous catalyst for the coupling reaction of aromatic alcohols and amines. The amides and imines can be selectively synthesized with up to 99% yield with or without the addition of NaF as cocatalyst.

The nitrogen-containing compounds such as amides and imines play a key role in organic and biological chemistry.[1] Generally, the alkyl amides are produced through the reaction of amides and alkyl halides with the addition of stoichiometric amounts of inorganic bases or by the reaction of carboxylic acid or ester and amine.[2-5] These methods often suffer from the drawbacks such as the generation of inorganic waste.[6] For the production of imines, the condensation of amines with aldehydes or ketones was an effective way.[7] However, this method is usually limited by the use of dehydrating agents or apparatus. In the last years, the direct synthesis of amides and imines via oxidative coupling of alcohols with amines was developed rapidly benefiting from its high atom efficiency.[5, 8-12] This procedure experiences the following steps. First, alcohol is converted into the corresponding aldehyde by catalytic oxidation. Afterwards, hemiaminal was generated via the coupling of amine and aldehyde. Finally, the hemiaminal is converted to amides or imines.

In 2007, Milstein reported the transformation of alcohols and amines into amides and hydrogen catalyzed by a ruthenium pincer complex.[13] Subsequently, a series of Ru catalyst systems were developed.[14,15] On the other hand, homogeneous catalysts show high activity on imines formation from alcohols and amines, too.[16,17] Although the homogeneous catalyst is very efficient for amides or imines generation selectively, there are disadvantages of ligand dependence, complicated operation and non-reusability.[16] A more efficient and feasible heterogeneous catalyst for the coupling reaction from alcohols and amines is highly desirable.[18] In 2009, Satsuma and co-workers reported a heterogeneous Ag/Al_2O_3, which can catalyze the amide synthesis from secondary amines and alcohols with a good yield, and the catalyst can be recycled.[17] Since then, Au/DNA,[19] PICB-Au,[20] OMS-2,[21] Au/PVP,[22] Au/HT,[23] Au-Pd/resin[24] and Au/HAP[25] were reported. Although there are gratifying achievements in the direct coupling from amines and alcohols catalyzed by heterogeneous catalysts, but one limitation is the low yield if aromatic amine and aromatic alcohol were used as starting materials. In the existing literature reports, normally high alcohols/amines ratio is needed for the coupling reactions of alcohols and amines to form substituted amides in the heterogeneous catalyst systems.

Hydrotalcite, especially Mg-Al hydrotalcite, was widely used as catalyst in different reactions.[26,27] In addition hydrotalcite supported nano-metal catalysts had gradually played an important role in the field of catalysis, such as oxidation of alcohols in the presence of oxygen.[28, 29] Here, we report an Au/HT catalyst system, which is prepared by precipitation-deposition-reduction method, for the synthesis of alkyl amides and imines. Importantly, alkyl amides and imines can be selectively generated by tuning the catalyst systems with or without the addition of NaF as cocatalyst.

In this work, water was chosen as the reaction media because it has been considered as a "green solvent" in organic chemistry, and it has attracted extensive attentions in the last years.[30,31] Additionally, since the first report on the insoluble Diels-Alder reactions using water as a solvent,[31] "on-water chemistry" has also been investigated.[32-34] In the current work, the synthesis of amide or imine might be in-water or on-water organic reaction.

The structure and physicochemical properties of Au/HT-1 (Mg/Al = 1 : 1), Au/HT-2 (Mg/Al = 3 : 1) and Au/HT-3 (Mg : Al = 5 : 1) catalysts were characterized by XRD, XPS, TEM, BET and ICP-AES. From the BET analysis (Table S1), Au/HT-2 exhibited the biggest BET area accompanied by the minimum pore size and pore volume compared with Au/HT-1 and Au/HT-3. In addition, an ordered meso-porous structure was formed in Au/HT-2, which might contribute to the high surface area and be beneficial for the preparation of active catalyst. According to the XRD diffraction patterns (Figure 1), the typical diffraction peaks at 11.7, 23.5, 34.7, and 46.4, which were related to the (003), (006), (009) and (018) reflections of hydrotalcite, were observable. Another featured peak at 38.4 was related to crystal lattice of Au (111). Noteworthy, the Au (111) diffraction peak in sample Au/HT-2 was much weaker, which suggested the gold species in Au/HT-2 was less crystallized. The X-ray photoelectron spectroscopy (XPS) was used to clarify the chemical state of the gold species formed on the catalyst surface (Figure 2). It can be seen that the binding energy of $Au4f_{7/2}$ for Au/HT-1, Au/HT-2 and Au/HT-3 were 83.6, 83.3 and 83.6 eV respectively. Another peak was attributed to Mg_{2s} and the binding energies were 89.2, 88.9 and 88.8 eV. Therefore, metallic gold formed on the catalyst surface. TEM images showed that the structure of the catalysts were nano-Au particles anchored on the surface of hydrotalcite (Figure 3). It can be seen that all the supported nano-Au particles were even distribution, and the

average particle sizes were 7.7, 20.1 and 14.0 nm, respectively. So the properties of the supports influence the structure of the final catalyst samples remarkably. ICP-AES analysis showed that the loadings of gold in these catalysts were 3.4 wt%, 3.7 wt% and 3.4 wt%.

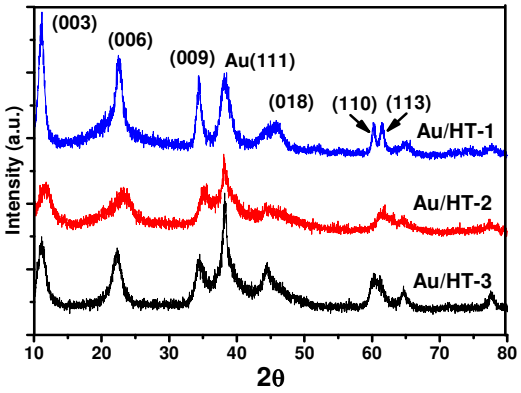


Figure 1. XRD diffraction patterns of the prepared catalysts

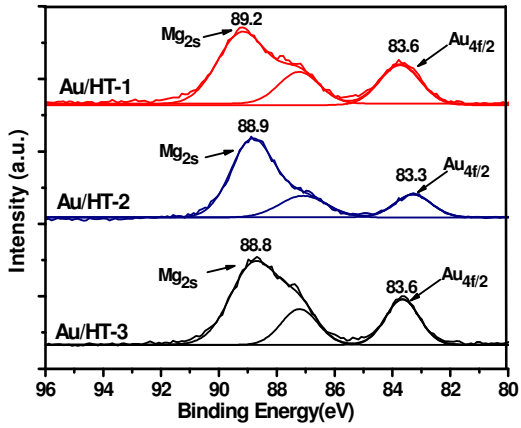


Figure 2. XPS spectra of the prepared catalysts

Next, we chose the amidation of benzylamine and benzyl alcohol as the model reaction to optimize the reaction conditions (alcohol : amine = 1.5, mol/mol). As given in (Table 1), N-phenylbenzamide was not obtained when using Au/HT-2 itself as catalyst and the major product was N-benzylideneaniline (Entry 1). This result is similar as the former report that alcohol imination can be realized with Au/Mg_2Al-HT as catalyst and with molecular oxygen as oxidant.[35] It has been shown that amides can be synthesized efficiently with the addition of Cs_2CO_3.[12] However, our reaction was not significantly improved and the selectivity to amide product was only 37% (Entry 2). Other bases such as NaOH and Na_2CO_3 were also tested and the selectivity increased to 96% and 84% but the conversions of aniline were not high enough (Entries 3, 4). Interestingly, the conversion and selectivity increased remarkably if using NaF as additive and 95% aniline conversion was obtained (Entry 5). With the addition of KF and $NaBF_4$ as cocatalyst, the amidation of aniline with benzyl alcohol can be carried out as well (Entries 6, 7). The coupling reaction can not occur if using NaCl as an additive which indicated that the reaction was promoted by fluoride (Entry 8). When the ratios of Mg to Al of the catalysts support were changed to 1 : 1 and 5 : 1, the conversions and selectivities of the amidation reaction decreased remarkably (Entries 9, 10). So 3 : 1 should be a suitable Mg/Al ratio. In order to explore the catalytic behavior of leached catalyst species, the catalyst was removed by filtration when it reacted for 12 h and the aniline conversion maintained at 77% after reacted for another 12 h. Therefore, the real catalyst should be the supported nano-Au. Additionally, only 50% amide was formed when the catalyst was reused at the second run. ICP-AES analysis showed that the Au loading was 3.1 wt% after use. Possibly the catalyst structure variation but not Au leaching should be responsible for the deactivation.

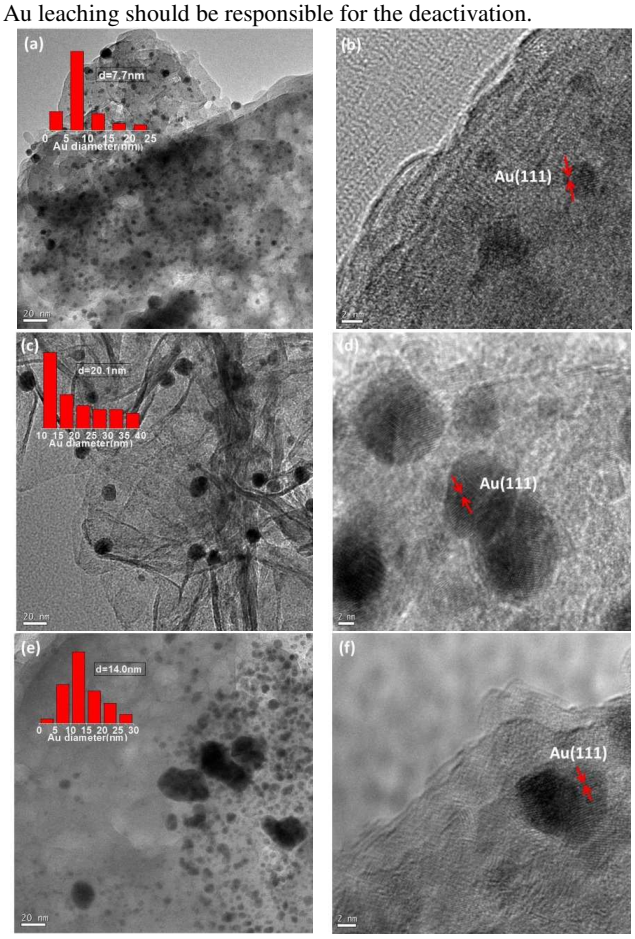
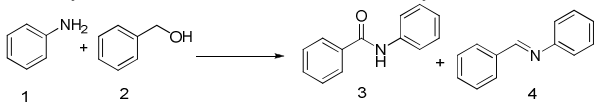


Figure 3. TEM pictures of the prepared catalysts Au/HT-1 (a, b), Au/HT-2 (c, d) and Au/HT-3 (e, f)

Table 1: Synthesis of amides from aniline and benzyl alcohol[a]



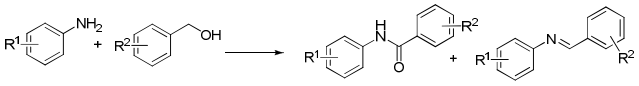
Entry	Cat.	Additive	Con. % of 1[b]	Sel. % of 3[b]	Sel.% of 4[b]
1	Au/HT-2	/	80	16	84
2[c]	Au/HT-2	Cs_2CO_3	79	36	74
3	Au/HT-2	NaOH	45	96	4
4	Au/HT-2	Na_2CO_3	87	84	6
5	Au/HT-2	NaF	95	98	2
6	Au/HT-2	KF • $2H_2O$	90	95	5
7	Au/HT-2	$NaBF_4$	83	86	14
8	Au/HT-2	NaCl	9	3	97
9	Au/HT-1	NaF	69	82	18
10	Au/HT-3	NaF	76	66	34

11[d]	Au/HT-2	NaF	95	50	50

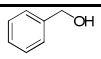
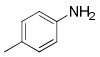
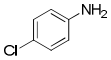
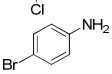
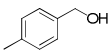
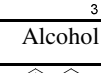
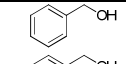
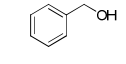
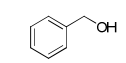
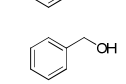
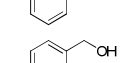
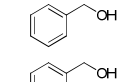
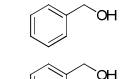
[a] Aniline (0.5 mmol), benzyl alcohol (0.75 mmol), Au/HT (50 mg), additive (2 mmol), 2 mL H_2O, O_2, 40 °C, 12 h.
[b] The conversion and selectivity were detected by GC-FID according to the peak area.
[c] Cs_2CO_3: 20 mol%.
[d] The catalyst was reused in the second run.

Then, the generality of the amidation reaction from amines and alcohols was investigated under the optimized reaction conditions and the results were summarized in Table 2. First, N-phenylbenzamide was synthesized with 86% yield (Entry 1). Then, we investigated the scope of the amidation of benzyl alcohol and anilines containing different functional groups. Clearly, the catalyst can catalyze the amidation reactions of various aromatic amines, which contain electron-donating as well as electron-withdrawing substituents, to synthesize the corresponding amides with moderate to good isolated yields (46%-81%, Entries 2-7). However, lower yield was obtained if o-toluidine was used as starting material, which might be caused by the steric hindrance. If using benzyl alcohol derivatives as starting materials, the catalyst showed good catalytic activity as well with 47-78% isolated yields to the desired products (Entries 8-16). Further on, alcohols with electron-donating substituents such as methyl, methoxyl and isopropyl were more favorable in the amidation reactions than those with electron-withdrawing substituents such as chlorine, bromine, fluorine and trifluoromethyl. Similarly, the catalysts exhibited lower activity in the amidation of o-methyl benzyl alcohol compared with m-methyl benzyl alcohol and p-methyl benzyl alcohol (Entries 8-10). The (4-(trifluoromethyl) benzyl alcohol and 3,4-(methylenedioxy)aniline were converted into the corresponding amides with 50% and 47% isolated yields (Entries 16 and 17).

Table 2: Synthesis of amides from alcohols and amines[a]



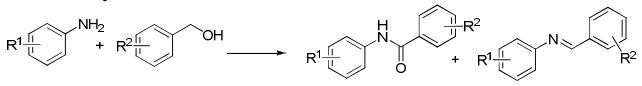
1 2 3 4

Entry	Amine	Alcohol	Yield of 3[b] (%)
1			86
2			70
3			72
4			46
5			62
6			60
7			81
8			73
9			77
10			48
11			78
12			77
13			63
14			68
15			73
16			50
17			47

[a] Reaction Condition: amine (0.5 mmol), Alcohol (0.75 mmol), Au/HT-2 (50 mg), NaF (2 mmol), H_2O (2 mL), O_2, 40 °C, t = 24 h.
[b] Isolated Yields.

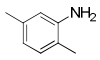
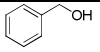
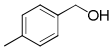
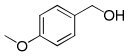
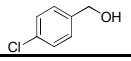
During the optimization of the reaction conditions for amidation reaction, we found that benzyl alcohol and aniline can be converted into N-benzylideneaniline in the absence of NaF (Table 1, Entry 1). It inspired us that our catalyst might be suitable for the imination of amines and alcohols without the addition of NaF. As expected, the anilines with various substituents such as methyl, methoxyl, chlorine, and bromine were converted into the corresponding imines with benzyl alcohol (Table 3, Entries 1-9). Moreover, the electron-donating substituents on the aromatic ring are slightly favorable for the imination reaction than the electron-withdrawing substituents while steric effect made a negative influence. 80% yield was obtained if using 2,5-dimethylaniline as starting material (Entry 9). In addition, the reactions of anilines with different aromatic alcohols were progressed well with 82-97% yields (Entry 10-12).

Table 3: Synthesis of imines from alcohols and amines[a]

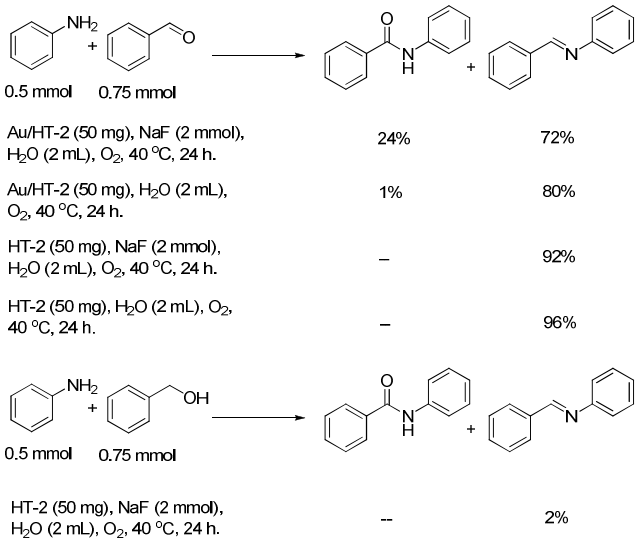


1 2 3 4

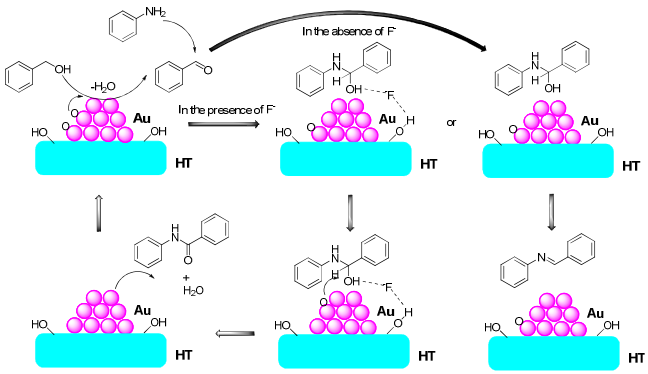
Entry	Amine	Alcohol	Yield of 4[b] (%)
1			98
2			85
3			99
4			84
5			63
6			94
7			71
8			70

9			80
10			82
11			87
12			97

[a] Reaction Condition: amine (0.5 mmol), Alcohol (0.75 mmol), Au/HT-2 (50 mg), H_2O (2 mL), O_2, 40 °C, t = 24 h.
[b] Yields were determined by GC with internal biphenyl.



Scheme 1. The mechanism investigation of alcohol amidation and imination with alcohol.



Scheme 2. The proposed reaction mechanism of amidation and imination reactions catalyzed by Au/HT-2 with or without the addition of NaF.

In order to explore the reaction mechanism, several control reactions were carried out (Scheme 1). Full conversion of aniline was obtained with 24% amide and 72% imine under the given reaction conditions if using benzaldehyde as starting material catalyzed by Au/HT-2 and NaF, and no amidation product was observed if NaF or gold was excluded. Similarly, almost no reaction occurred if using benzyl alcohol and aniline as starting materials with HT and NaF as catalysts. These results suggested that the co-presence of nano-Au and fluoride were crucial for amide formation. Moreover, the amidation reaction might happen promptly after the formation of hemiaminal on the surface of Au/HT in the presence of fluoride. For the imination reaction, it can be carried out in the absence of the fluoride (Scheme 2).

Conclusions

In summary, an active Au/HT catalyst was prepared by precipitation-deposition-reduction method for the coupling reaction of amines and alcohols. The amidation and imination reactions can be realized efficiently with moderate to good yields with or without the addition of NaF as co-catalyst. In addition, the mechanism of the reaction was investigated, too.

Acknowledgements

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Experiment Section

Generals

All the solvents and chemicals were obtained commercially and were used as received. Mass spectra were in general recorded on an HP 6890/5973 GC-MS. High-resolution TEM analysis was carried out on a JEM 2010 operating at 200 KeV. The catalyst samples after pretreatment were dispersed in methanol, and the solution was mixed ultrasonically at r.t. A part of solution was dropped on the grid for the measurement of TEM images. XRD measurements are conducted by a STADI P automated transmission diffractometer (STOE) equipped with an incident beam curved germanium monochromator selecting Cu Kα1 radiation and a 6° position sensitive detector (PSD). The XRD patterns are scanned in the 2θ range of 10-80°. For the data interpretation the software WinXpow (STOE) and the database of Powder Diffraction File (PDF) of the International Centre of Diffraction Data (ICDD) were used. The XPS measurements were performed with a VG ESCALAB 210 instrument provided with a dual Mg/Al anode X-ray source, a hemispherical capacitor analyser and a 5 keV Ar^+ ion-gun. All spectra were recorded using non-monochromatic Mg Ka (1253.6 eV) radiation. Nitrogen adsorption-desorption isotherms were measured at 77 K using Micromeritics 2010 instrument. The pore-size distribution was calculated by Barrett, Joyner and Halenda (BJH) method from desorption isotherm. The Cu and Al contents of the catalyst were measured by inductively coupled plasma-atomic emission spectrometry (ICP-AES), using an Iris advantage Thermo Jarrel Ash device.

Typical procedure for HT-2 preparation[36]: 7.69 g (30 mmol) $Mg(NO_3)_2{\cdot}6H_2O$ and 3.75 g (10 mmol) $Al(NO_3)_3{\cdot}9H_2O$ were dissolved into 100 mL deionized water. Then the solution was dropwise added into 100mLNa_2CO_3 solution (0.3 mol/L) in 1 h under magnetic stirring and the pH value of the solution was maintained at 10 by adding aqueous solution of NaOH (1 M). After aging for 1 h at 65 °C, the white solid was filtered and washed with deionized water (2 L). The obtained solid was dried at 100 °C in air overnight and ~3.3 g HT-2 was obtained. HT-1 and HT-3 were prepared with similar operation.

General procedure for Au/HT preparation: 500 mg HT was added to 4 mL $HAuCl_4$ solution (24 mM) under magnetic stirring

in 2 min. The pH value of the solution was tuned to 10 with the addition of aqueous NH_3 (~25 wt%), and the mixture was stirred at room temperature for 12 h. Then, it was centrifuged and washed with 100 mL deionized water. The obtained solid sample was dispersed in 10 mL deionized water and 20 mL $NaBH_4$ solution (26 mmol/L) was added in 1 h under magnetic stirring. Au/HT catalyst was obtained after centrifugation, washing by deionized water and drying at 80 ^oC for 1 h.

General procedure for the amidation of amines and alcohols: All the reactions were carried out in a shrek tube. Typically, 0.5 mmol aniline, 0.75 mmol benzyl alcohol, 50 mg Au/HT (3.7 wt% Au, 1.9 mol% to aniline) and 2 mmol NaF were added, respectively. Then, the reaction mixture was stirred (300 rpm) at 40 ^oC under 1 atm oxygen (O_2 balloon) for 24 h. Then it was cooled down to room temperature. The reaction mixture was analyzed by GC-MS (Agilent 6890-5973)/GC-FID (Agilent 7890A) and 86% yield was obtained by column chromatography (ethyl acetate/petroleum ether = 9/1, v/v; Silica Gel: 200-300 mesh; white solid. m.p. 162-163 ^oC). For reusability test, the catalyst was separated by centrifugation, washed by ethanol and water, and was used for the next run with the same operation as mentioned above.

General procedure for the imination of amines and alcohols: All the reactions were carried out in a shrek tube. Typically, 0.5 mmol aniline, 0.75 mmol benzyl alcohol, 50 mg Au/HT (3.7 wt% Au, 1.9 mol% to aniline) and 2 mmol NaF were added, respectively. Then, the reaction mixture was stirred (300 rpm) at 40 ^oC under 1 atm oxygen (O_2 balloon) for 24 h. Then it was cooled down to room temperature and quantitatively analyzed by GC-FID (Agilent 7890A) using biphenyl as standard material.

Notes and references

[a] *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Center for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China. Fax: +86-931-8277088; Tel: +86-931-4968142; E-mail: fshi@licp.cas.cn*

[b] *Graduate School of the Chinese Academy of Sciences. Beijing, 100049, China*

†Electronic Supplementary Information (ESI) available: catalyst preparation procedure and characterization details. See DOI: 10.1039/b000000x/

1 M. A. Mintzer and E. E. Simanek, *Chem. Rev.*, 2008, **109**, 259.
2 E. Valeur and M. Bradley, *Chem. Soc. Rev.*, 2009, **38**, 606.
3 V. R. Pattabiraman and J. W. Bode, *Nature*, 2011, **480**, 471.
4 C. Chen and S. H. Hong, *Org. Biomol. Chem.*, 2011, **9**, 20.
5 J. E. Anderson, R. Davis, R. N. Fitzgerald and J. M. Haberman, *Synth. Commun.*, 2006, **36**, 2129.
6 C. Montalbetti and V. Falque, *Tetrahedron*, 2005, **61**, 10827.
7 M. H. S. A. Hamid, C. L. Allen, G. W. Lamb, A. C. Maxwell, H. C. Maytum, A. J. A. Watson and J. M. J. Williams, *J. Am. Chem. Soc.*, 2009, **131**, 1766.
8 S. Kegns, J. Mielby, U. V. Mentzel, T. Jensen, P. Fristrup and A. Riisager, *Chem. Commun.*, 2012, **48**, 2427.
9 T. Ishida, H. Watanabe, T. Takei, A. Hamasaki, M. Tokunaga and M. Haruta, *Appl. Catal. A: Gen.*, 2012, **425**, 85.
10 J. Mielby, A. Riisager, P. Fristrup and S. Kegnaes, *Catal. Today*, 2013, **203**, 211.
11 S. K. Klitgaard, K. Egeblad, U. V. Mentzel, A. G. Popov, T. Jensen, E. Taarning, I. S. Nielsen and C. H. Christensen, *Green Chem.*, 2008, **10**, 419.
12 X. Y. Liu and K. F. Jensen, *Green Chem.*, 2013, **15**, 1538.
13 C. Gunanathan, Y. Ben-David and D. Milstein, *Science*, 2007, **317**, 790.
14 B. Gnanaprakasam and D. Milstein, *J. Am. Chem. Soc.*, 2011, **133**, 1682.
15 J. Zhang, M. Senthilkumar, S. C. Ghosh and S. H. Hong, *Angew. Chem. Int. Ed. Engl.*, 2010, **49**, 6391.
16 C. L. Allen and J. M. J. Williams, *Chem. Soc. Rev.*, 2011, **40**, 3405.
17 K. Shimizu, K. Ohshima and A. Satsuma, *Chem. Eur. J.*, 2009, **15**, 9977.
18 B. J. Xu, R. J. Madix and C. M. Friend, *Chem. Eur. J.*, 2012, **18**, 2313-2318.
19 Y. Wang, D. Zhu, L. Tang, S. Wang and Z. Wang, *Angew. Chem. Int. Ed. Engl.*, 2011, **50**, 8917.
20 J.-F. Soule , H. Miyamura and S. Kobayashi, *J. Am. Chem. Soc.*, 2011, **133**, 18550.
21 K. Yamaguchi, H. Kobayashi, T. Oishi and N. Mizuno, *Angew. Chem. Int. Ed. Engl.*, 2012, **51**, 544.
22 P. Preedasuriyachai, H. Kitahara, W. Chavasiri and H. Sakurai, *Chem. Lett.*, 2010, **39**, 1174.
23 J. Zhu, Y. Zhang, F. Shi and Y. Deng, *Tetrahedron Lett.*, 2012, **53**, 3178.
24 L. L. Zhang, W. T. Wang, A. Q. Wang, Y. T. Cui, X. F. Yang, Y. Q. Huang, X. Y. Liu, W. G. Liu, J. Y. Son, H. S. Oji and T. Zhang, *Green Chem.*, 2013, **15**, 2680.
25 W. Wang, Y. Cong, L. Zhang, Y. Huang, X. Wang and T. Zhang, *Tetrahedron Lett.*, 2014, **55**, 124.
26 A. Takagaki, M. Ohara, S. Nishimura and K. Ebitani, *Chem. Commun.*, 2009, 6276.
27 A. Takagaki, K. Iwatani, S. Nishimura and K. Ebitani, *Green Chem.*, 2010, **12**, 578.
28 V. V. Costa, M. Estrada, Y. Demidova, I. Prosvirin, V. Kriventsov, R. F. Cotta, S. Fuentes, A. Simakov and E. V. Gusevskaya, *J. Catal.*, 2012, **292**, 148.
29 K. Ebitani, K. Motokura, T. Mizugaki and K. Kaneda, *Angew. Chem. Int. Ed.*, 2005, **44**, 3423.
30 C. J. Li and L. Chen, *Chem. Soc. Rev.,* 2006, **35**, 68.
31 D. C. Rideout and R. Breslow, *J. Am. Chem. Soc.,* 1980, **102**, 7816.
32 M. B. Gawande, V. D. B. Bonifacio, R. Luque, P. S. Branco and R. S. Varma, *Chem. Soc. Rev.,* 2013, **42**, 5522.
33 M. O. Simon and C. J. Li, *Chem. Soc. Rev.,* 2012, **41**, 1415.
34 M. B. Gawande, V. D. B. Bonifácio, R. Luque, P. S. Branco and R. S. Varma, *ChemSusChem,* 2014, **7**, 24.
35 P. Liu, C. Li, E. J. M. Hensen, *Chem. Eur. J.*, 2012, **18**, 12122.
36 A. Tsuji, K. T. V. Rao, S. Nishimura, A. Takagaki and K. Ebitani, *ChemSusChem*, 2011, **4**, 542.

Supporting Information

NaF Regulated Aqueous Phase Synthesis of Aromatic Amides and Imines Catalyzed by Au/HT

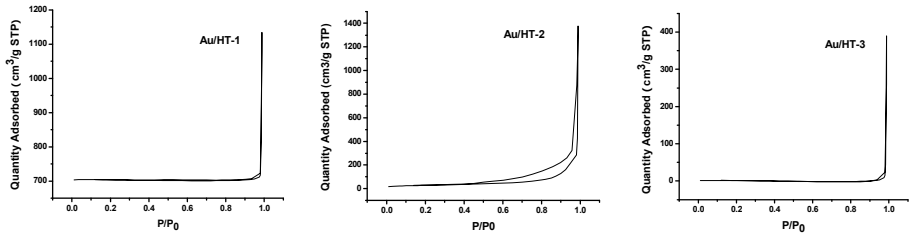
Qianqian Wang[a,b], Youquan Deng[a] and Feng Shi[a]*

[a] *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Center for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China. Fax: +86-931-8277088; Tel: +86-931-4968142; E-mail: fshi@licp.cas.cn*

[b] *Graduate School of the Chinese Academy of Sciences. Beijing, 100049, China*

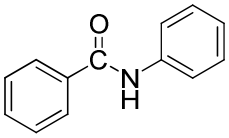
Table S1 Composition and porosity parameters of Au/HT with various Mg/Al molar ratios.

Catalyst	Au loading (wt.%)	S_{BET}(m^2 g^{-1})[b]	Pore Size(nm)[b]	Pore Volume (cm^3 g^{-1})[b]
Au/HT-1	3.40	7.1	116.2	0.67
Au/HT-2	3.67	96.2	34.88	2.1
Au/HT-3	3.39	2.6	111.9	0.60



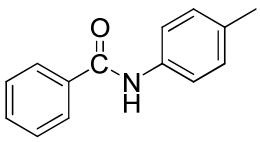
HMR

N-phenylbenzamide**: (Table 2, Entry 1)**



This compound was prepared following the above general procedure and purified by column chromatography (ethyl acetate / petroleum ether = 21/9, v/v; Silica Gel: 200-300 mesh;) to give the product as a white solid. m.p. 162-163 ^{o}C. ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 7.11-7.15 (t, 1H), δ 7.33-7.37 (t, 2H), δ 7.43-7.47 (t, 2H), δ 7.51-7.54 (t, 1H), δ 7.62-7.64 (d, 2H), δ 7.83-7.85 (d, 2H), δ 7.91 (s, 1H); *m/z* (rel. int.) 198(7), 197(5), 106(8), 105(100), 77(46), 51(11).

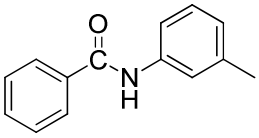
N-p-phenylbenzamide**: (Table 2, Entry 2)**



This compound was prepared following the above general procedure and purified

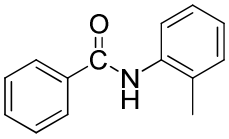
by column chromatography (ethyl acetate / petroleum ether = 1/9, v/v; Silica Gel: 200-300 mesh;) to give the product as a white solid. m.p. 157-158 °C. ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 2.34 (s, 3H), δ 7.15-7.17 (d, 2H), δ 7.46-7.53 (m, 5H), δ 7.82-7.86 (m, 3H); *m/z* (rel. int.) 212(11), 211(67), 106(9), 105(100), 77(41), 51(7).

N-m-phenylbenzamide**: (Table 2, Entry 3)**



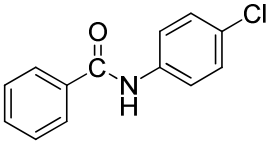
This compound was prepared following the above general procedure and purified by column chromatography (ethyl acetate / petroleum ether = 1/9, v/v; Silica Gel: 200-300 mesh;) to give the product as a white solid. m.p. 119-120 °C. ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 2.36 (s, 3H), δ 6.95-6.97 (d, 1H), δ 7.22-7.26 (m, 1H), δ 7.40-7.55 (m, 5H), δ 7.86-7.88 (d, 3H); *m/z* (rel. int.) 212(11), 211(71), 106(9), 105(100), 77(41), 51(7)

N-o-phenylbenzamide**: (Table 2, Entry 4)**



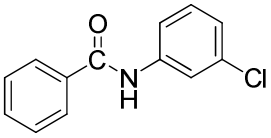
This compound was prepared following the above general procedure and purified by column chromatography (ethyl acetate / petroleum ether = 1/9, v/v; Silica Gel: 200-300 mesh;) to give the product as a white solid. m.p. 142-143 °C. ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 2.33 (s, 3H), δ 7.10-7.14 (t, 1H), δ 7.22-7.24 (m, 2H), δ 7.47-7.58 (m, 3H), δ 7.70 (s,1H), δ 7.87-7.89 (m, 2H), δ 7.93-7.94 (d, 1H); *m/z* (rel. int.) 212(10), 211(65), 106(12), 105(100), 77(41), 51(7)

N-(4-chlorophenyl)phenylbenzamide**: (Table 2, Entry 5)**



This compound was prepared following the above general procedure and purified by column chromatography (ethyl acetate / petroleum ether = 1/9, v/v; Silica Gel: 200-300 mesh;) to give the product as a white solid. m.p. 199-200 °C. ^{1}H NMR (400MHz, D^6-DMSO, ppm): δ 7.36-7.39 (m, 2H), δ 7.48-7.59 (m, 3H), δ 7.77-7.80 (m, 2H), δ 7.90-7.92 (t, 2H), δ 10.36 (s, 1H); *m/z* (rel. int.) 233(14), 232(7), 231(41), 106(8), 105(100), 77(39), 51(8)

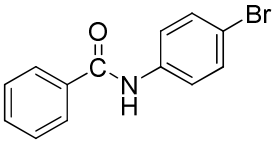
N-(3-chlorophenyl)phenylbenzamide**: (Table 2, Entry 6)**



This compound was prepared following the above general procedure and purified

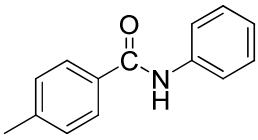
by column chromatography (ethyl acetate / petroleum ether = 1/9, v/v; Silica Gel: 200-300 mesh;) to give the product as a white solid. m.p. 122-123 ^{o}C. ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 7.11-7.13 (d, 1H), δ 7.25-7.29 (m, 1H), δ 7.46-7.49 (t, 3H), δ 7.63-7.67 (m, 1H), δ 7.77 (s, 1H), δ 7.83-7.85 (d, 2H), δ 7.93 (s, 1H); *m/z* (rel. int.) 233(9), 231(25), 106(8), 105(100), 77(46), 51(12)

N-(4-bromophenyl)phenylbenzamide**: (Table 2, Entry 7)**



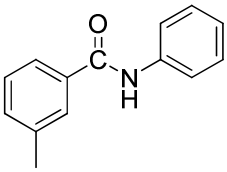
This compound was prepared following the above general procedure and purified by column chromatography (ethyl acetate / petroleum ether = 1/9, v/v; Silica Gel: 200-300 mesh;) to give the product as a white solid. m.p. 201-202 ^{o}C. ^{1}H NMR (400MHz, D^6-DMSO, ppm): δ 7.11 (s, 1H), δ 7.36 (s, 2H), δ 7.76 (s, 4H), δ 7.90-7.92 (d, 2H), δ 10.31 (s, 1H); *m/z* (rel. int.) 277(17), 275(19), 227(8), 207(11), 106(8), 105(100), 77(38), 51(11)

4-methyl-N-phenylbenzamide**: (Table 2, Entry 8)**



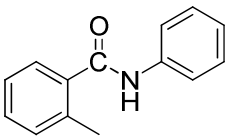
This compound was prepared following the above general procedure and purified by column chromatography (ethyl acetate / petroleum ether = 1/9, v/v; Silica Gel: 200-300 mesh;) to give the product as a white solid. m.p. 147-148 ^{o}C. ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 2.39 (s, 3H), δ 7.10-7.14 (t, 1H), δ 7.23-7.25 (t, 2H), δ 7.32-7.35 (t, 2H), δ 7.61-7.63 (d, 2H), δ 7.73-7.75 (d, 2H), δ 7.88 (s, 1H); *m/z* (rel. int.) 212(7), 211(44), 120(10), 119(100), 91(37), 90(5), 65(18), 39(5)

3-methyl-N-phenylbenzamide**: (Table 2, Entry 9)**



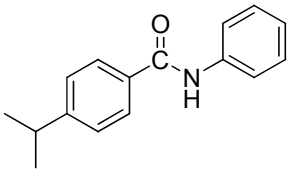
This compound was prepared following the above general procedure and purified by column chromatography (ethyl acetate / petroleum ether = 1/9, v/v; Silica Gel: 200-300 mesh;) to give the product as a white solid. m.p. 124-125 ^{o}C. ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 2.41 (s, 3H), δ 7.12-7.16 (t, 1H), δ 7.34-7.38 (t, 4H), δ 7.83-7.88 (t, 4H), δ 7.87 (s, 1H); *m/z* (rel. int.) 212(9), 211(60), 120(9), 119(100), 91(37), 65(13).

2-methyl-N-phenylbenzamide**: (Table 2, Entry 10)**



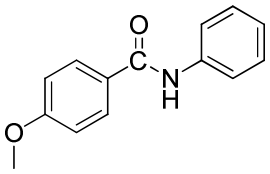
This compound was prepared following the above general procedure and purified by column chromatography (ethyl acetate / petroleum ether = 1/9, v/v; Silica Gel: 200-300 mesh;) to give the product as a white solid. m.p. 125-126 ^{o}C. ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 2.48 (s, 3H), δ 7.12-7.15 (t, 1H), δ 7.21-7.25 (m, 2H), δ 7.33-7.37 (t, 3H), δ 7.44-7.46 (d, 1H), δ 7.55 (s, 1H), δ 7.59-7.61 (d, 2H); *m/z* (rel. int.) 211(24), 194(8), 120(9), 119(100), 91(46), 65(20), 39(7).

4-isopropyl-N-phenylbenzamide**: (Table 2, Entry 11)**



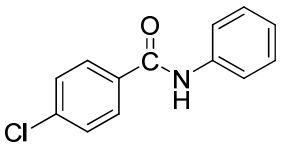
This compound was prepared following the above general procedure and purified by column chromatography (ethyl acetate / petroleum ether = 1/9, v/v; Silica Gel: 200-300 mesh;) to give the product as a white solid. m.p. 1117-118 ^{o}C. ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 1.26-1.28 (m, 6H), δ 2.93-3.00 (m, 1H), δ 7.11-7.15 (t, 1H), δ 7.30-7.37 (m, 4H), δ 7.63-7.66 (d, 2H), δ 7.78-7.80 (d, 2H), δ 7.90 (s, 1H), δ 7.59-7.61 (d, 2H); *m/z* (rel. int.) 239(32), 148(12), 147(100), 91(9).

4-methoxy-N-phenylbenzamide**: (Table 2, Entry 12)**



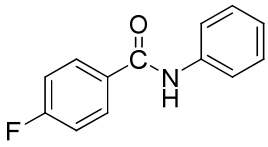
This compound was prepared following the above general procedure and purified by column chromatography (ethyl acetate / petroleum ether = 1/9, v/v; Silica Gel: 200-300 mesh;) to give the product as a white solid. m.p. 173-174 ^{o}C. ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 3.87 (s, 3H), δ 6.96-6.97 (d, 2H), δ 7.12-7.15 (t, 1H), δ 7.34-7.38 (d, 4H), δ 7.62-7.64 (d, 2H), δ 7.79 (s, 1H), δ 7.83-7.85 (d, 2H); *m/z* (rel. int.) 227(21), 136(9), 135(100), 107(6), 92(12), 77(15), 65(5), 64(6).

4-chloro-N-phenylbenzamide**: (Table 2, Entry 13)**



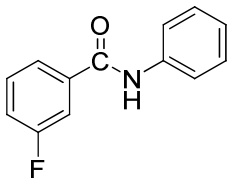
This compound was prepared following the above general procedure and purified by column chromatography (ethyl acetate / petroleum ether = 1/9, v/v; Silica Gel: 200-300 mesh;) to give the product as a white solid. m.p. 200-201 ^{o}C. ^{1}H NMR (400MHz, D^6-DMSO, ppm): δ7.10-7.13 (t, 1H), δ 7.34-7.38 (t, 2H), δ 7.60-7.62 (d, 2H), δ 7.76-7.78 (d, 2H), δ 7.98-8.00 (d, 2H), δ 10.31 (s, 1H); *m/z* (rel. int.)

4-fluoro-N-phenylbenzamide**: (Table 2, Entry 14)**



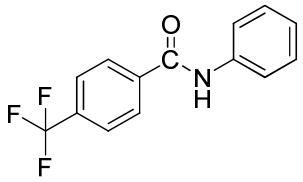
This compound was prepared following the above general procedure and purified by column chromatography (ethyl acetate / petroleum ether = 1/9, v/v; Silica Gel: 200-300 mesh;) to give the product as a white solid. m.p. 182-183 ^{o}C. ^{1}H NMR (400MHz, D^{6}-DMSO, ppm): δ 7.08-7.12 (t, 1H), δ 7.33-7.39 (m, 4H), δ 7.75-7.77 (d, 2H), δ 8.02-8.05 (m, 2H), δ 10.28 (s, 1H); *m/z* (rel. int.) 215(39), 207(14), 124(8), 123(100), 95(35), 75(8), 28(7).

3-fluoro-N-phenylbenzamide**: (Table 2, Entry 15)**



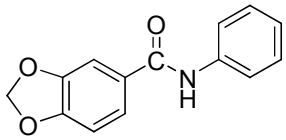
This compound was prepared following the above general procedure and purified by column chromatography (ethyl acetate / petroleum ether = 1/9, v/v; Silica Gel: 200-300 mesh;) to give the product as a white solid. m.p. 151-152 ^{o}C. ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 7.14-7.18 (t, 1H), δ 7.22-7.26 (m, 1H), δ 7.35-7.38 (t, 2H), δ 7.41-7.47 (m, 1H), δ 7.56-7.83 (m, 4H), δ 7.88 (s, 1H); *m/z* (rel. int.) 216(15), 215(39), 207(14), 124(8), 123(100), 95(35), 75(8), 28(7).

N-phenyl-4-(trifluoromethyl)benzamide**: (Table 2, Entry 16)**



This compound was prepared following the above general procedure and purified by column chromatography (ethyl acetate / petroleum ether = 1/9, v/v; Silica Gel: 200-300 mesh;) to give the product as a white solid. m.p. 194-195 ^{o}C. ^{1}H NMR (400MHz, D^{6}-DMSO, ppm): δ 7.09-7.11 (t, 1H), δ 7.32-7.36 (t, 2H), δ 7.74-7.76 (d, 2H), δ 7.87-7.90 (d, 2H), δ 8.10-8.12 (d, 2H), δ 10.46 (s, 1H); *m/z* (rel. int.) 266(8), 265(47), 174(9), 173(100), 145(53), 95(6), 65(6).

N-phenylbenzo[d][1,3]dioxole-5-carboxamide**: (Table 2, Entry 17)**



This compound was prepared following the above general procedure and purified by column chromatography (ethyl acetate / petroleum ether = 1/9, v/v; Silica Gel: 200-300 mesh;) to give the product as a white solid. m.p. 145-146 ^{o}C. ^{1}H NMR (400MHz, $CDCl_3$, ppm): δ 6.02 (s, 2H), δ 6.81-6.83 (d, 1H), δ

7.09-7.13 (t, 1H), δ 7.31-7.37 (m, 4H), δ 7.58-7.60 (d, 2H), δ 7.81 (s, 1H); *m/z* (rel. int.) 227(21), 136(9), 135(100), 107(6), 92(12), 77(15), 65(5), 64(6).