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Versatile CO-assisted direct reductive amination of 5-hydroxymethylfurfural catalyzed by a supported gold catalyst†

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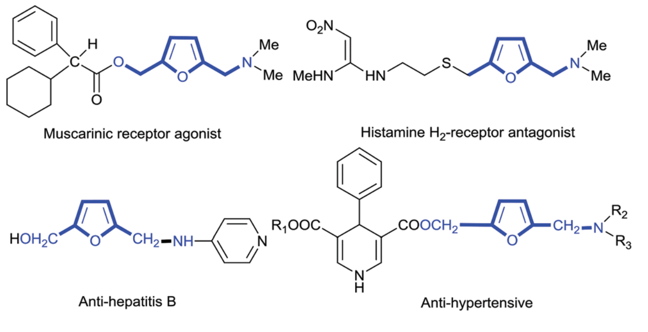
Reductive amination (RA) constitutes an attractive and practical strategy for discovering protocols capable of converting biomass into valuable *N*-containing compounds. Described herein is a versatile and sustainable RA of 5-hydroxymethyl-furfural (HMF), an important biomass-derived aldehyde, using abundant and cheaply available CO and water as reductants. A single phase rutile titania supported gold (Au/TiO_2-R) catalyst is shown to efficiently catalyze this CO/H_2O-mediated RA under mild and convenient conditions. With this system, a broad spectrum of primary and secondary amines can be used as suitable substrates and the desired reaction can proceed favourably in a highly chemoselective, efficient and atom-economical fashion. In particular, this protocol can also allow convenient access to bis(hydroxylmethylfurfuryl)-amines, a new group of furan-based monomers with great potential to form functional biopolymers with tunable properties. Moreover, this CO-assisted RA is more efficient (higher TON and TOF) and more eco-friendly (increased resource efficiency) than the previous state-of-the-art technique.

Introduction

The depletion of readily available fossil fuel reserves and global climate change concerns have prompted efforts to make chemical production more benign and hence contribute to a more sustainable future.[1] Compared to other alternative feedstock choices, the production of chemicals from biorenewable resources, such as biomass, has attracted increasing interest in recent years due to the vast potential availability of lignocellulosic materials and the versatility of adaptating existing technologies that potentially enable the production of useful chemicals in commercial scales in a shorter time frame.[2] Owing to the inherent oxygen-rich nature of lignocellulosics, significant attention has been directed to processes for converting bio-based feedstocks into a variety of oxygenates, such as furfurals,[3] diols,[4] hexitols,[5] ketones,[6] various organic acids,[7] *etc*. In contrast, transformation of biomass into more value-added *N*-containing compounds has remained largely under-developed,[8] despite the huge untapped potential to create novel functional molecules with unusual properties which might not be achievable with the use of conventional fossil-based methods.

Aminofurans, in particular aminoalkylfuran derivatives, are key structural units in many biologically active natural products and are also an indispensable class of industrially sought-after compounds known for their wide range of pharmacological activities (Scheme 1).[9] Therefore, the development of efficient and environmentally benign methods for the synthesis of aminoalkylfurans from readily available starting materials has long been an active area of research.[10] In this respect, the utilization of bio-based feedstocks like 5-hydroxymethylfurfural (HMF) derived from abundantly available non-edible lignocellulosic biomass[11] could be an ideal option for accessing this class of compounds. Indeed, several recent studies have shown that it is possible to achieve the amino



Scheme 1 Selected bioactive molecules incorporating the aminoalkylfuran core structure.

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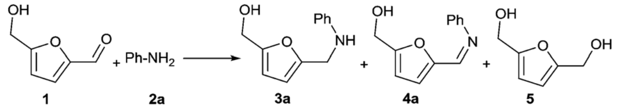
functionalization of HMF by reductive amination (RA) using $NaBH_4$[10b] or molecular H_2[12] as the reducing agent. Despite these encouraging results, there are still major incentives to develop alternative strategies capable of facilitating more efficient and reliable RA, especially given that the fossil-dependent nature of H_2 is nowadays recognized as being a less sustainable part of the biorefinery concept.[13]

Driven by the huge potential of CO as a key intermediate in the chemical industry, mainly as a C1 building block, there is continuous interest in the development of novel transformations that can expand the utility of the existing methods for CO valorization. Particularly, given that CO is also a steel-work off-gas, produced in multi-ton quantities,[14] it represents an abundant and inexpensive source for large-scale chemical synthesis.[15] We recently introduced an Au-CO/H_2O reduction system where the transient Au^0–H formed by the CO-induced H_2O reduction is believed to be the key active species for H_2-free reduction. This system performed well in the chemoselective reduction of substituted nitro and carbonyl compounds as well as in the semireduction of alkynes under very mild conditions.[16] Following the publication of our work, examples of CO-assisted reduction or deoxygenation by other types of transition metal-based catalysts were also reported.[17] Our continuing interest in finding new applications of this Au-CO/H_2O reduction system led us to investigate the possibilities offered by CO/H_2O-assisted RA to obtain aminoalkylfurans from HMF.

Table 1 Catalytic reductive amination of HMF with aniline over different catalysts[a]



Entry	Catalysts	Conv. [%]	Yield[b] [%] 3a	4a	5
1	Au/TiO_2-P25	96	81	15	0
2	Au/TiO_2-A	89	43	46	0
3[c]	Au/TiO_2-A	95	79	16	0
4	Au/TiO_2-R	>99	>99	0	0
5[d]	Au/TiO_2-R	>99	>99	0	0
6[e]	Au/TiO_2-R	>99	97	3	0
7[f]	Au/TiO_2-R	>99	87	0	13
8[g]	Au/TiO_2-R	>99	98	2	0
9	Au/CeO_2	84	53	31	0
10	Au/ZrO_2	79	25	54	0
11	Au/Al_2O_3	78	4	74	0
12	Au/SiO_2	68	1	66	0
13	$HAuCl_4$	76	0	76	0
14	Au^0 colloid	70	0	70	0

[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mmol), catalysts (Au 0.5 mol%), MeOH–H_2O (1 : 1 v/v, 3 mL), CO (20 bar), 60 °C, 2.5 h. [b] GC-MS yields using anisole as the internal standard. [c] 4 h. [d] 60 bar CO, 1 h. [e] 25 °C, 22 h. [f] 20 bar H_2, 1.5 h. [g] 10 mmol **1**, 10 mmol **2a**, MeOH : H_2O (1 : 1 v/v, 10 mL) Au/TiO_2-R (Au 0.05 mol%), 60 bar CO, 15 h.

Results and discussion

Our initial investigations focused on using aniline (**2a**) as the aminating reagent for direct RA of HMF showed that the suitable choice of an underlying support material stands out as one of the most important parameters that determine the conversion of the substrate and the desired product selectivity over various gold-based catalysts. A promising lead result was observed when using a commercial titania P25 supported gold catalyst (Au/TiO_2-P25, Fig. S1 and S4†), yielding 81% of the desired amination product upon reaction under 20 bar CO for 2.5 hours at 60 °C (Table 1, entry 1). In this case, 15% imine (**4a**) remained unreduced. Further investigation revealed, however, that the use of phase pure anatase TiO_2 as the supporting material was much less successful, providing the expected RA product in only very moderate yields, even after an extended reaction time of 4 h under identical conditions (Table 1, entries 2 and 3). Nevertheless, to our delight, the related catalyst comprising gold deposited on single phase rutile TiO_2 (Au/TiO_2-R) turned out to be much more efficient, yielding the desired aminated product in a near-quantitative yield under similar conditions (Table 1, entry 4).

This is remarkable given that, on the research idea described herein,[18] there had previously been no studies that could utilize only an equimolar amount of aminating reagent to accomplish the intended reaction.[10b,12a,18c,f] Of yet further interest is that in this particular case the specific activity based on HMF conversion is up to 79.2 mol mol_{Au}^{-1} h^{-1}, which is over 2 times more active than the previously established homogeneous Ru-based catalytic systems.[12a] The subsequent study revealed that a binary solution system comprising a 1 : 1 volumetric ratio of methanol/H_2O was the optimal solvent for this catalyst (Table S1†).[19] Control experiments lacking the Au/TiO_2-R catalyst, CO, or H_2O provided none of the desired adducts (Table S2†). Additional investigations into the various reaction parameters revealed that both CO pressure and temperature have a profound influence on the reaction outcome. The reaction time can be greatly shortened from 2.5 to 1 h as the P_{CO} was increased from 20 to 60 bar (Table 1, entries 4 and 5). Of particular note is that, at a temperature as low as 25 °C, the reaction can also proceed efficiently without affecting the **3a** yield (Table 1, entry 6).

One scenario that deserves special mention is the beneficial selectivity control of this Au-CO/H_2O-driven RA system capable of delivering the expected reaction product in an almost exclusive manner. As revealed in Fig. 1, the conversion of HMF with Au/TiO_2-R proceeds smoothly and reaches complete conversion after approximately 2.5 h at 60 °C, with **4a** being the sole transient intermediate. During the whole reaction process, the carbonyl group of HMF remains unreduced, which highlights the robustness and effectiveness of our protocol (Scheme 2). This is striking, considering that a competitive reduction of the carbonyl group into the corresponding alcohol is in fact an issue that has long plagued traditional RA systems,[20] thus leaving ample opportunities for functional group manipu-

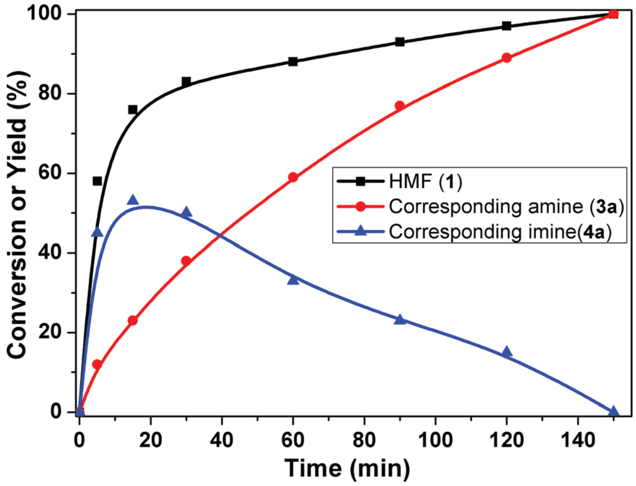
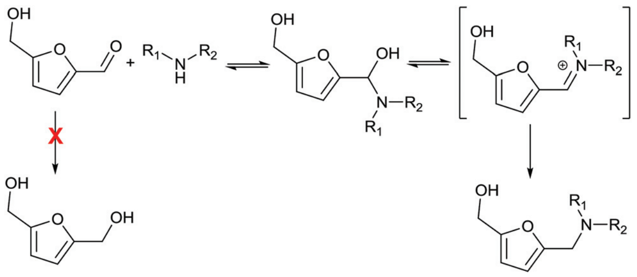


Fig. 1 Reaction profile for aminoalkylfuran formation from HMF and aniline. Reaction conditions: HMF (**1**) (0.5 mmol), aniline (**2a**) (0.5 mmol), MeOH–H_2O (1 : 1 v/v, 3 mL), Au/TiO_2-R (Au: 0.5 mol%), CO (20 bar), 60 °C.



Scheme 2 Synthesis of aminoalkylfurans *via* direct RA of HMF with amines assisted by CO.

lation *via* CO-assisted reductive chemistry. This point is nicely illustrated by the fact that when the reaction was comparatively carried out by replacing CO with H_2 under otherwise identical conditions, 2,5-bis-(hydroxylmethyl)furan (BHMF) (**5**) is formed at appreciable levels even at low HMF conversion levels, albeit with a much higher **3a** formation rate (Fig. S5;† Table 1, entry 7).

As a further illustration of the efficacy of this Au-CO/H_2O-mediated RA catalysis, the use of lower Au loadings (S/C = 2000) proved to be equally effective in the model reaction with aniline (Table 1, entry 8). Thus, in a gram-scale reaction of **1** and **2a** (10 mmol scale up) for 15 h, 98% yield of **3a** was obtained. Under the aforementioned optimized conditions, some of the common supporting materials, such as CeO_2, ZrO_2, Al_2O_3 and SiO_2 (Table 1, entries 9–12; Fig. S1 and S2†), can deliver appreciable conversion of 1, despite their lack of sufficient capability to facilitate the eventual transformation of **4a** to **3a**. We also tested other gold-based precursors or materials such as $HAuCl_4$ and bulk Au^0 colloid (mean particle size, *ca.* 50 nm, Fig. S3†), but all of them gave no **3a** (Table 1, entries 13 and 14). Herein it is important to point out that we did not observe any formation of humins when $HAuCl_4$ was used in the reaction, despite the notoriously unstable nature of HMF,[21] presumably due to the presence of only a minimal amount of $HAuCl_4$ which can hardly influence the pH value of the reaction medium. It is also revealed that neither the Pt, Pd, nor Ru catalysts were effective for this reaction (Table S3†). Altogether, these results show that the combination of CO and Au NPs strongly associated with rutile TiO_2 is essential for achieving a high catalytic activity for selective RA of HMF and **2a** into **3a** under mild conditions.

A leaching test was performed to evaluate the potential durability and to exclude the possible contribution of leached Au species. When Au/TiO_2-R was removed from the reaction mixture after 1 h, no extra products were detected by continuing this reaction for another 1.5 h (Fig. S6†). The remaining solution was checked by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and indeed there was no leaching of Au (see the ESI†). In addition, reusability tests confirmed that Au/TiO_2-R could be recovered and reused up to five times without any appreciable loss of activity (Fig. S7†). The X-ray diffraction (XRD) analysis displayed that both the fresh and used Au/TiO_2-R catalysts showed a similar crystal phase, with no obvious distinguishing Au features being identified in these two samples, suggesting that the Au particle sizes were quite small (Fig. 2c). The transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS) measurements further confirmed the stable crystalline and electronic structure of Au (Fig. 2a, b and d). These results account for the remarkable durability of Au/TiO_2-R in the recycling test.

Having demonstrated the suitability of the present CO/H_2O-mediated approach for a practical and efficient HMF amination, we sought to further elucidate the fundamental aspects underlying the Au-CO/H_2O-driven phenomenon. In this respect, it was confirmed in a separate set of experiments that the direct conversion of HMF and **2a** to **4a** under an inert N_2 atmosphere occurred at a much faster rate than the reduction of **4a** to **3a** under otherwise identical conditions (Tables S4 and S5†). These results indicate that the direct synthesis of **3a** would proceed through a series of consecutive steps in a cascade mode, in which the rate-determining step must be the CO/H_2O-mediated reduction of **4a** to **3a**. The critical role of Au/TiO_2-R in promoting this CO/H_2O-mediated RA process is further clarified by comparing the direct condensation of HMF with aniline as well as the direct reduction of **4a** with CO/H_2O for Au NPs deposited on different supports (Tables S4 and S5†), wherein it is revealed that all relevant reactions, in particular the direct reduction of **4a** with CO/H_2O (Table S5†) over Au/TiO_2-R occurred with much higher rates than that over other catalysts.

Essentially, these observations demonstrate the critical role of Au/TiO_2-R in promoting the crucial imine reduction step for an efficient CO/H_2O-mediated RA process. To gain an insight into the origin of the enhanced CO-assisted direct RA activity achieved by using rutile TiO_2 as a support, the temperature-programmed surface reaction (TPSR) in the presence of CO and H_2O (CO/H_2O-TPSR)[22] has been investigated for Au de-

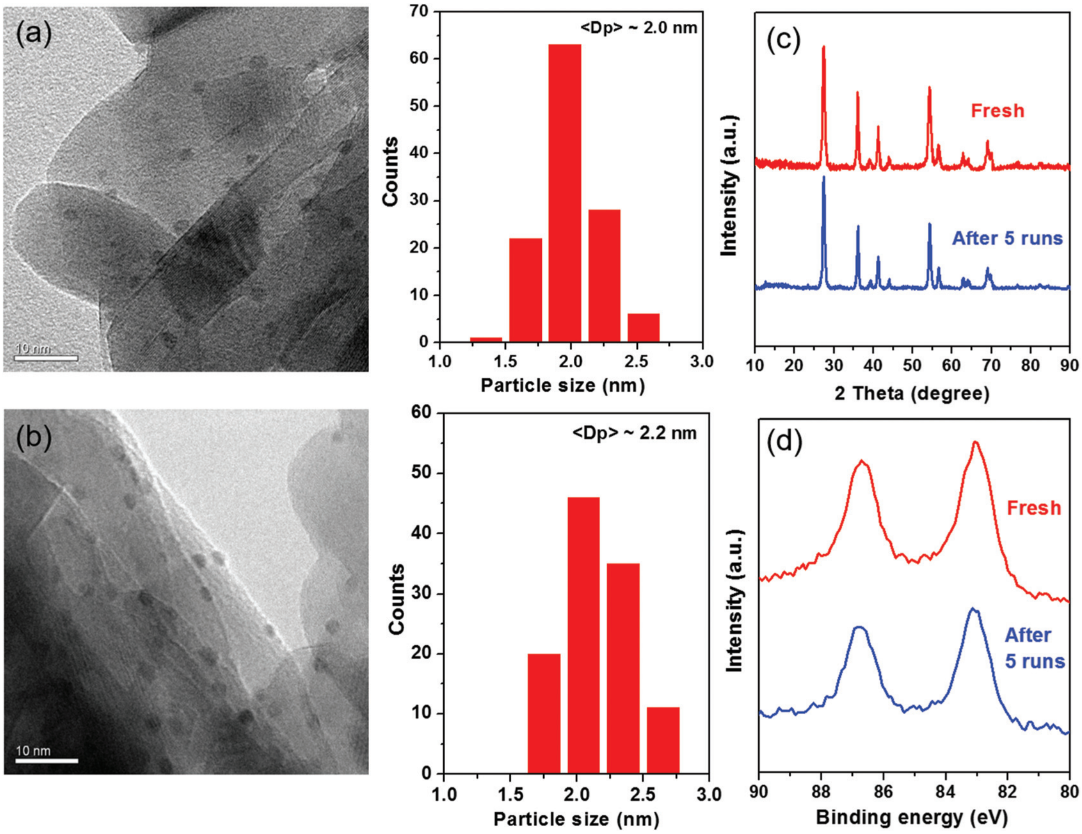


Fig. 2 (a) and (b) TEM images and particle distribution of fresh and used Au/TiO_2-R; (c) and (d) XRD and XPS of fresh and used Au/TiO_2-R.

posited on several different supports. Based on the results from Fig. 3, the lower performance observed with Au/TiO_2-A, Au/CeO_2, Au/ZrO_2, Au/Al_2O_3 and Au/SiO_2 can be rationalized by the fact that the rate of transient Au^0–H or H_2 formation catalyzed by these catalysts is significantly lower than that over the Au/TiO_2-R sample. This scenario is further reinforced by the observation that the low temperature H_2 production rate over Au/TiO_2-R also occurred with a much higher rate than those over biphasic P25 and anatase TiO_2 supported Au. Altogether, these results unambiguously demonstrate that the present Au-catalyzed CO/H_2O-mediated **4a** reduction may proceed *via* a sequential water-gas-shift/**4a**-reduction pathway (Scheme S1†) in which the generation of transient Au^0–H species formed by CO-induced H_2O activation is the central step.

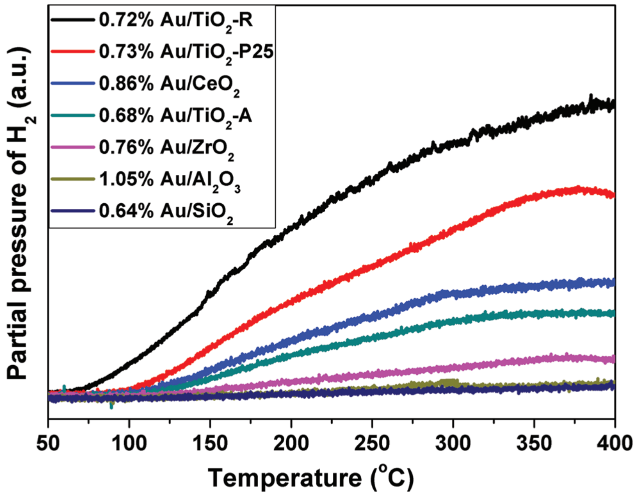
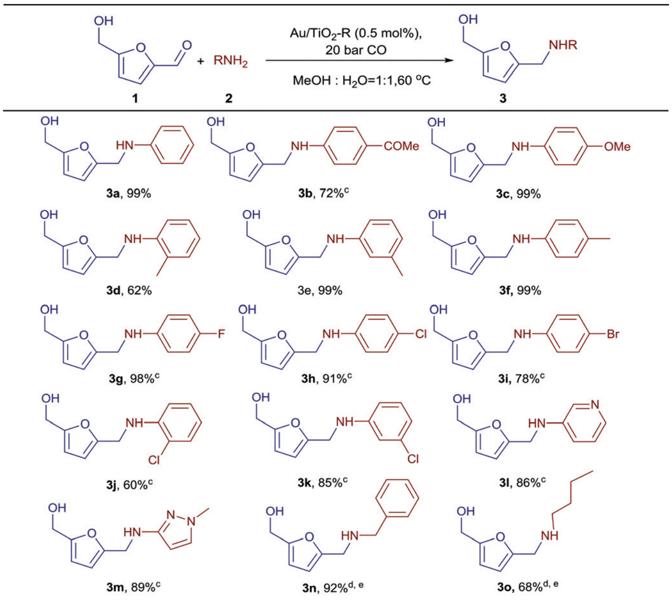


Fig. 3 CO/H_2O-TPSR over various supported Au catalysts, conditions: 100 mg sample, 1% CO–3% H_2O–He (20 mL min^{-1}), 5 °C min^{-1}.

The preceding results highlight the distinct capability of Au/TiO_2-R in enabling a facile CO-assisted RA synthesis of **3a** from **1** and **2a** *via* intermediacy of **4a**, apparently due to an unusual and extraordinary metal-support synergy that can markedly suppress the undesired pathways and favor the product formation under the above-mentioned conditions. At this point it is important to note that in the two related precedents to this work, Rh/C[17c] and Co_2Rh_2/C[17d] were shown to be efficient catalysts for reductive transformation of a set of carbonyl compounds by using carbon monoxide as a deoxygenative agent. However, either a high CO pressure (50 bar) and/or extended reaction times at elevated temperatures (up to 20 h at 160 °C) were required to obtain high yields of the desired secondary or tertiary amines. Thus, the most distinctive aspect of the present Au/TiO_2-R catalyst system is that effective CO-mediated direct RA can be readily achieved by using substantially milder conditions compared with prior-art methods. Notably, the specific activity based on carbonyl conversion using the Au/TiO_2-R catalyst is up to 79.2 mol mol_{Au}^{-1} h^{-1} (corresponding to the HMF conversion level ~99%), which is over 19 and 24 times more active than the previously reported Rh/C and Co_2Rh_2/C catalytic systems.

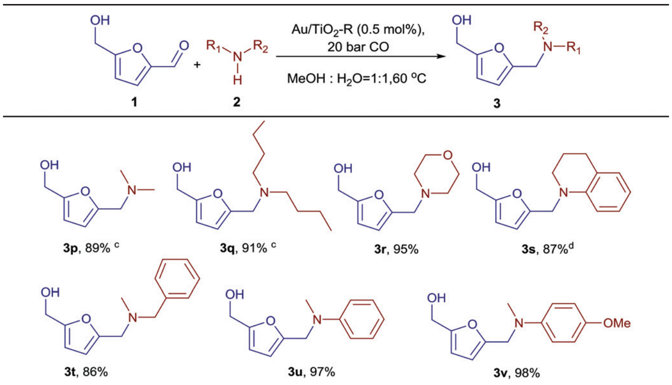
We next set out to expand the substrate scope of this Au-CO/H_2O-mediated RA process. As revealed in Table 2, various structurally diverse anilines, regardless of the presence of electron-withdrawing or donating functional groups, could be mono-alkylated with HMF to yield the corresponding secondary amines in good to excellent yields at 60 °C. It is important to note that this procedure tolerates the presence of halogens (**3g**–**3k**), thereby permitting further transformations of the present HMF-derived aminoarylfuran product using cross-coupling technologies. Additionally, a variety of nitrogen heterocycles that are frequently found in medicinally active agents, including pyridine and pyrazole,[23] could be applied with this RA process and the corresponding amino-alkylfurans (**3l**, **3m**) could be obtained in 85–90% yields. Moreover, it was found that aliphatic amines could also be effectively converted into their corresponding secondary aminoalkylfurans with excellent selectivity (**3n**, **3o**), showcasing the generality of the current CO/H_2O-based methodology for direct HMF amination. Contrastingly, a previously reported dichlorobis(2,9-dimethyl-1,10-phenanthroline) ruthenium(II) ($Ru(DMP)_2Cl_2$) complex system is found to be totally inactive for this substrate, owing to a strong coordination of the primary alkylamine groups to the Ru(II) complex.[12a]

Table 2 Au-catalyzed direct reductive amination of HMF with primary amines[a,b]



[a] Reaction conditions: **1** (0.5 mmol), **2** (0.5 mmol), Au/TiO_2-R (Au 0.5mol%), MeOH–H_2O (1 : 1 v/v, 3 mL), CO (20 bar), at 60 °C for 2.5 h. [b] GC yields using anisole as the internal standard. [c] 18 h. [d] At 70 °C for 8 h. [e] Bi-*N*-alkylation products were detected.

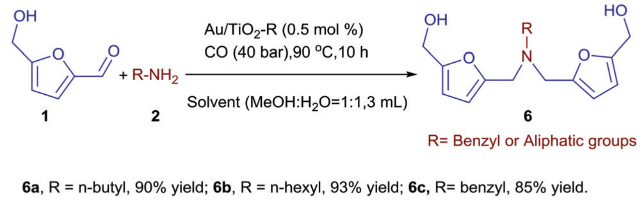
Table 3 Au-catalyzed direct reductive amination of HMF with secondary amines[a,b]



[a] Reaction conditions: 1 (0.5 mmol), 2 (0.5 mmol), Au/TiO_2-R (Au 0.5 mol%), MeOH–H_2O (1 : 1 v/v, 3 mL), CO (20 bar), at 60 °C for 6 h. [b] GC yields using anisole as the internal standard. [c] 5 h. [d] 20 h.

To further evaluate the potential of this Au-CO/H_2O-mediated RA reaction, we turned our attention toward tertiary amine formation *via* direct amination of HMF with secondary amines, which are challenging aminating agents compared with primary amines using the RA strategy because of the difficulty associated with the *in situ* formation and rapid hydrogenation of the relevant imine intermediates.[20b] To the best of our knowledge, a heterogeneous catalytic system capable of delivering RA with only equivalent amounts of secondary amines as aminating agents has so far been elusive.[20b,24] To our delight, with the current heterogeneous Au-catalyzed RA system, sec-benzylic amines as well as secondary anilines gave excellent yields for direct amination of HMF under mild conditions (Table 3, **3t**–**3v**). Remarkably, secondary aliphatic secondary amines also proved to be excellent aminating agents (**3p**, **3q**). Under the present catalyst system, sterically more hindered heterocyclic amines can also be used as the aminating agent, and up to 95% (**3r**) and 87% (**3s**) yields were achieved when morpholine and tetrahydroquinoline were used as the aminating agents.

Given the superb efficiency observed for Au/TiO_2-R toward HMF amination, we were thus prompted to check whether this CO/H_2O-driven Au catalysis would also allow the direct synthesis of bis-(hydroxylmethylfurfuryl)amines (BHMFAs) from HMF by reacting primary amines with two equivalents of HMF. Owing to their attractive malleability and self-healing ability, BHMFAs has recently been advocated as a new group of furan-based monomers that hold great potential to form functional biopolymers with tunable properties.[25] We have performed a straightforward process that subjects two equivalents of HMF to several typical primary amines by adopting the above-mentioned RA procedure. The results presented in Scheme 3 show that it is possible to achieve a yield up to 93% through this simple CO/H_2O-based procedure. In a precedent study, Zhang and co-workers have demonstrated that a high yield (*ca.* 90%) of BHMFAs can be attained from HMF and a number of primary amines *via* a homogeneous



Scheme 3 CO-assisted one-pot synthesis of BHMFAs.

ruthenium-catalyzed RA using H_2 as the hydrogen source.[25] In addition to the lower process productivity, this homogeneous catalytic RA system necessitated the addition of HMF in excess of that required to ensure the desired reaction process as proceeded.

Conclusions

In conclusion, we have successfully developed a facile and environmentally friendly CO/H_2O-driven RA approach that can provide an effective means to access an array of aminoalkyl based furans, a valuable structure in medicinal and materials chemistry, directly from biogenic HMF under very mild conditions. This RA method, using only equimolar amounts of amines as the aminating reagent and a robust and reusable gold catalyst with inexpensive and abundantly available CO and H_2O as the appealing reductant under mild conditions, would be useful for further applications in the synthesis of new bio-based amines and is currently in progress.

Experiments

General procedure for direct reductive amination of HMF with amines

A mixture of HMF (0.5 mmol), amines (0.5 mmol), supported metal catalysts (metal 0.5 mol%), anisole (0.5 mmol, internal standard), methanol (1.5 mL) and water (1.5 mL) was charged into a 25 mL Hastelloy-C high pressure Parr reactor. After the reactor was sealed, the remaining air was purged by flushing with CO five times. The reactor was pressured to 20 bar CO and then heated to 60 °C. The mixture of substrates and catalyst was stirred at a rate of 800 rpm for a given reaction time. After completion of the reaction, the liquid products were separated by centrifugation and then analyzed on an Agilent 7820A gas chromatograph equipped with a capillary column HP-INNO Wax (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID). The identification of the products was performed by using a GC-MS spectrometer. After that, the crude product was purified by column chromatography [silica gel (300–400 mesh); petroleum ether (60–90 °C)/ethyl acetate mixture] to afford the pure product. All the products were identified by ^{1}H-NMR and ^{13}C-NMR and the spectra obtained were compared with the standard spectra (see the ESI†).

Procedure for large-scale direct reductive amination of HMF with aniline

A mixture of HMF (10 mmol), aniline (10 mmol), supported metal catalysts (metal 0.05 mol%), anisole (10 mmol, internal standard), methanol (5 mL) and water (5 mL) was charged into a 100 mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm under 60 bar CO for 15 h. The mixture of substrates and catalyst was heated to the desired temperature in less than 15 minutes. After completion of the reaction, the liquid products were separated by centrifugation. The conversion and yield were determined by using an Agilent 7820A gas chromatograph equipped with a HP-INNOWax column (30 m × 0.32 mm × 0.25 μm) and a flame ionization detector (FID).

Physicochemical characterization

The metal loading of the catalysts was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer. The BET specific surface areas of the prepared catalysts were determined by adsorption–desorption of nitrogen at liquid nitrogen temperature, using Micromeritics TriStar 3000 equipment. Sample degassing was carried out at 300 °C prior to acquiring the adsorption isotherm. The crystal structures of various catalysts were characterized with powder X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu Kα radiation source at 40 kV and 40 mA. Field emission scanning electron microscopy (FESEM) measurements were carried out on a Nova NanoSem 450 field-emission scanning electron microscope, operating at 3 kV and using a TLD detector. TEM images for various noble metal catalysts were obtained with a JEM 2011 electron microscope operating at 200 kV. Before being transferred into the TEM chamber, the samples dispersed with ethanol were deposited onto a carbon-coated copper grid and then quickly moved into the vacuum evaporator. The size distribution of the metal nanoparticles was determined by measuring about 120 random particles in the images. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained on a Tecnai G2 F20 S-Twin electron microscope, operating at 200 kV and using a HAADF detector. XPS measurements were performed with a PerkinElmer PHI 5000C spectrophotometer with Mg Kα radiation (1253.6 eV). The samples were pressed into a pellet and transferred to a test chamber. The spectra were collected with an analyzer pass energy of 23.5 eV and an electron takeoff angle of 45°. The vacuum in the test chamber was maintained below 10^{-9} Torr. The binding energy scale was calibrated taking, as a reference, the adventitious C 1s peak at 284.6 eV. CO/H_2O-TPSRs were run in a Micromeritics ChemiSorb 2750 instrument equipped with a mass spectrometer (OmniStar TM, QMS 200). The gas mixture (1% CO–3% H_2O–He) was obtained by flowing 1% CO–He through a water bubbler with a flow rate of 70 mL min^{-1}. In each experiment, the catalyst was stabilized in 1% CO–3% H_2O–He for 20 min at 50 °C before being heated up to 400 °C at 5 °C min^{-1}. The effluent gas was analyzed by online mass spectrometry.

Acknowledgements

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