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Amine formylation *via* carbon dioxide recycling catalyzed by a simple and efficient heterogeneous palladium catalyst†

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A simple and efficient Pd/Al$_2$O$_3$-NR-RD catalyst was prepared by depositing palladium on a shape controllable Al$_2$O$_3$-NR support through a two-step process that involves hydrothermal synthesis of Al$_2$O$_3$-NRs followed by reductive-deposition of palladium. This catalyst showed high activity in the catalytic formylation of amines by CO$_2$–H$_2$ under mild conditions with up to 96% yield.

Carbon dioxide (CO$_2$) chemistry is the subject of increased attention in both academic and industrial fields.[1,2] In order to reduce the emission of CO$_2$ and utilize the carbon source, various technologies have been explored. The catalytic hydrogenation of CO$_2$ to high value-added chemical fuels,[3] such as alcohols, gasoline, and related higher hydrocarbons, is one of the attractive approaches. Another direction is the synthesis of carbonyl containing chemicals, such as carbonate, formamide, carboxylic acid, ester or lactone, urea or carbamate, polymer *etc.*,[4] through a catalytic carbonylation reaction, among which the production of formamide has attracted much attention because it plays an important role in industry.[5] Commonly, formamides are synthesized using CO as the carbonyl source under rigorous reaction conditions. The catalytic formylation of amines using CO$_2$ is inviting yet challenging because of the thermodynamic and kinetic stability of CO$_2$. Recently, conversion of amines to the corresponding formamides through the reduction of CO$_2$ using polymethylhydrosiloxane as the hydrogen source has come into notice with homogeneous catalysts.[2b,6] Besides, the catalytic transformation of amines to formamides using CO$_2$ and H$_2$ as feedstock is another known process.[2b,7] However, the reported systems often require rigorous reaction conditions with limited generality especially over heterogeneous catalysts.[8]

Nano-materials are regarded as either efficient catalysts themselves or as a structure-directing support to gain specific activity. For example, Tsang and co-workers reported the significant shape effect of plate-like ZnO on the catalytic activity of Cu nanoparticles in the synthesis of methanol by CO$_2$ hydrogenation.[3b] Trunschke and co-workers

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investigated the role of lattice strain and defects in Cu–ZnO–Al$_2$O$_3$ catalyzed methanol synthesis.[3c] These results inspired us to develop active heterogeneous catalysts for amine formylation with CO$_2$–H$_2$ by tuning the nano-structure of the catalyst support. In this work, we describe the preparation of a Al$_2$O$_3$ nano-rod (Al$_2$O$_3$-NR) supported nano-palladium catalyst for the formylation of amines by CO$_2$–H$_2$.

The Al$_2$O$_3$-NR was prepared by a modified hydrothermal method using AlCl$_3$ as a precursor, 1-butyl-3-methyl imidazolium chloride (BMImCl) as a template and (NH$_4$)$_2$CO$_3$ as a precipitant.[9] After washing, drying and calcining, the Al$_2$O$_3$-NR was obtained and used as a support. The Pd/Al$_2$O$_3$-NR-RD catalyst was prepared by the reductive deposition (RD) of nano-Pd particles on Al$_2$O$_3$-NRs, Fig. 1. Furthermore, the Pd/Al$_2$O$_3$-NR-RD catalyst was characterized in detail. SEM and TEM images showed that the diameter of the Al$_2$O$_3$-NR was in the range of 60–100 nm and most of the Pd NPs were in the range of 2.5–3.5 nm, and the Pd NPs are well dispersed on the surface of Al$_2$O$_3$-NR (Fig. 2a–c). Moreover, only the crystal lattice of the Pd(110) plane is observable by HR-TEM (Fig. 2d). The Pd content was 0.53 wt%, suggested by ICP-AES. According to the XRD characterization (Fig. S1, ESI†), there are no observable diffraction patterns of Pd species, which also suggested that the Pd species were highly dispersed. BET analysis showed that its BET surface area was 177.9 m^2 g^{-1}. Other catalysts were characterized by BET, XPS,
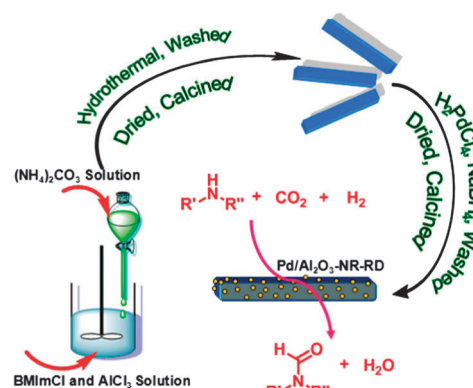

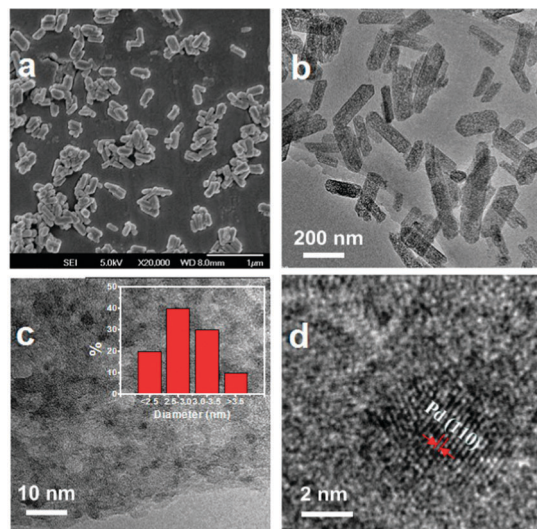**Fig. 1** An illustration for the preparation of Pd/Al$_2$O$_3$-NR-RD.

Fig. 2 SEM (a), TEM (b and c) and HR-TEM (d) images of Pd/Al$_2$O$_3$-NR-RD.

XRD, ICP-AES, SEM and TEM as well and the palladium loadings were in the range of 0.47–0.85 wt% with BET surface areas of 154–281 m^2 g^{-1} (Tables S1 and S2, Fig. S1, S3–S8, ESI†).

The redox properties of the catalysts were investigated by Temperature-Programmed-Reduction (TPR) and the results are given in Fig. S2, ESI.† The TPR profiles of Pd/γ-Al$_2$O$_3$ and Pd/Al$_2$O$_3$-NR-RD showed well defined positive peaks centered at 45 °C (H$_2$ consumption: 9.5 μmol g$_{cat}^{-1}$) and 47 °C (H$_2$ consumption: 13 μmol g$_{cat}^{-1}$) respectively, which were attributed to the reduction of supported PdO. It indicated that more active Pd species existed and was highly dispersed on Pd/Al$_2$O$_3$-NR-RD. The consumption peak shifted to higher temperature and appeared at 70 °C (H$_2$ consumption: 15 μmol g$_{cat}^{-1}$) in Pd/α-Al$_2$O$_3$, which indicates the strong interaction between Pd and the support. In comparison with Pd/Al$_2$O$_3$-NR-RD, the TPR profile of Pd/Al$_2$O$_3$-NR-DP, which was prepared by the deposition precipitation (DP) method, showed an increase in H$_2$ consumption (15 μmol g$_{cat}^{-1}$) and the reduction temperature started at 44 °C but centered at 65 °C. Moreover, a broader peak of H$_2$ consumption (45 μmol g$_{cat}^{-1}$) was observed for Pd/Al$_2$O$_3$-NR-IP prepared by an impregnation method. The peak of PdO reduction was in the range of 53–173 °C and centered at 112 °C, indicating the formation of different reducible Pd species. These results were consistent with the catalytic performance shown below.

Subsequently, the formylation of 1-methylpiperazine was chosen as the model reaction to optimize the reaction conditions, Table S3, ESI.† Clearly, no reaction occurred under catalyst free conditions or in the presence of Al$_2$O$_3$-NRs (entries 1 and 2). Exhilaratingly, remarkably high conversion of morpholine and good selectivity to the desired product were obtained when Pd/Al$_2$O$_3$-NR-RD was employed but Pd/Al$_2$O$_3$-NR-IP, Pd/Al$_2$O$_3$-NR-DP, Pt, Ru or Rh/Al$_2$O$_3$-NR-RD, Pd/α-Al$_2$O$_3$-RD and Pd/γ-Al$_2$O$_3$-RD exhibited poor activity (entries 3–10). Then, the pressure ratio of CO$_2$ to H$_2$, solvents and reaction temperatures were screened (entries 11–22). Finally, under the optimized reaction conditions, i.e. P_{CO_2}:P_{H_2} = 1:2 Mpa, 50 mg Pd/Al$_2$O$_3$-NR-RD, 3 mL octane, 130 °C and 24 h, 96% yield of 4-methylpiperazine-1-carbaldehyde was obtained. Next, if the catalyst

Table 1   Results of the formylation of amines using CO$_2$–H$_2$ ^{a}

Entry	Substrates	Products	Yields^b (%)
1			89 (83%^{c})
2			93
3			84
4			92
5			86
6			71
7			96
8			79
9			85
10			83
11			86
12			84
13			79
14			86
15			83
16			37
17			0^d
18			10^d
19			18^d

^{a} Reaction conditions: 1 mmol (100 mg) amine, 50 mg catalyst, 3 mL octane, 1 MPa CO$_2$, 2 MPa H$_2$, 130 °C, 24 h. ^{b} Isolated yields. ^{c} The catalyst was reused in the 3rd run. ^{d} Determined by GC-FID using biphenyl as the standard material.

was removed by filtration after heating the reaction mixture for 2 h under the reaction conditions, the reaction did not proceed any

further even if it was reacted for another 22 h, and ICP-AES measurements showed that the Pd concentration was out of detection limit. These results excluded the possible contribution of the leached palladium species. Moreover, the catalyst can be easily separated by centrifugation and can be reused three times without deactivation, and 83% yield was maintained (entry 23 and Table 1, entry 1).

Furthermore, the gaseous phase was checked by GC-TCD after the reaction of 1-methylpiperazine with CO_2–H_2 and the CO concentration was out of the TCD test limit. So the formation of CO should be negligible and the selectivity based on CO_2 conversion should be >99%. If the formylation reaction was performed with CO, the yield of the desired product was only 15%, suggesting that CO should not be the reaction intermediate. Also we checked the catalytic performance of homogeneous $PdCl_2$ (2 mol%)/1,2-bis(diphenylphosphino) ethane (5 mol%) but only <1% desired product was formed as determined by GC-MS. So the catalytic behavior of Pd/Al_2O_3-NR-RD is unique.

Having a highly efficient catalyst in hand, we further explored the formylation of various amines to examine the scope and limitations of the current catalyst system, Table 1. By using 1-methylpiperazine and 1-ethylpiperazine as substrates, the reaction proceeded successfully and furnished the desired products with 89–93% yields (entries 1 and 2). In addition, other cyclic secondary amines, such as pyrrolidine, piperidine and 4-methylpiperidine, were also converted into the formamides with 84–92% yields under the optimized conditions (entries 3–5). Moreover, the steric hindrance might decrease the reactivity of amine and the desired product was obtained in 71% yield for the formylation of 2,6-dimethylpiperidine (entry 6). It should be mentioned that morpholine, which has an oxygen on its ring, was also used and 96% yield was obtained (entry 7). Interestingly, the increase of reaction sites on the ring did not reduce the reactivity of amine, and piperazine was formylated with 79% yield (entry 8). Thus, it was not surprising that the formylation of 1,3-di(piperidin-4-yl)propane was also realized with high yield (entry 9). Furthermore, 8-oxa-3-azabicyclo[3.2.1]octane and 1,2,3,4-tetrahydroisoquinoline were converted into the corresponding formamides smoothly with 83–86% yields (entries 10, 11). The employment of other dialkylamines, such as Me_2NH, Et_2NH, Bu_2NH and Oc_2NH, led to excellent yields, too (entries 12–15). Clearly, the yields of the formamides decreased with the increase of the alkyl chain. Secondary aromatic amines were proved to be active as well with 49% conversion and 37% yield of PhMeNHCO. GC-MS analysis suggested that the major byproduct was N,N-dimethyl aniline, which indicated that the existence of the aromatic ring increased the hydrogenation of formyl groups and formation of N,N-dimethyl substrates (entry 16). However, two aromatic substituents on the nitrogen completely deactivated diphenylamine and there was no observable product (entry 17). By applying primary amines such as hexan-1-amine and aniline as substrates, the reactivity was found to be low and only 18% and 10% yields were obtained, respectively (entries 18–19).

In conclusion, we have prepared a simple and efficient Pd/Al_2O_3-NR-RD catalyst by depositing palladium on a shape controllable Al_2O_3-NR support through a two-step process that involves hydrothermal synthesis of Al_2O_3-NR followed by reductive-deposition of palladium. This catalyst showed high activity in the catalytic formylation of amines by CO_2–H_2 under mild conditions. The influence of the Al_2O_3 structure and the preparation method of catalysts on the catalytic performance was also studied.

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