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Heterogeneous Catalysis

Sustainable Heterogeneous Platinum Catalyst for Direct Methylation of Secondary Amines by Carbon Dioxide and Hydrogen

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Abstract: Pt and MoO_x co-loaded TiO_2 is found to be highly effective for direct methylation of aliphatic and aromatic secondary amines by CO_2 and H_2 under solvent-free conditions. This is the first additive-free and reusable heterogeneous catalytic system with acceptable turnover number.

Continuous efforts have been focused on reductive fixation of carbon dioxide (CO_2), because it could be an abundant and renewable carbon resource for the production of valuable chemicals, such as methanol, formic acid and amides.[1–3] A recent advance in this area is the discovery of new catalytic methods to utilize CO_2 as a as a methylation reagent in fine chemical synthesis. Cantat et al.[4] and Beller et al.[5] independently reported the methylation of amines by CO_2 and silanes by homogeneous catalysts. Although the methods are not practical due to the use of silanes as the reductant, they show a possible use of CO_2 as a methylation reagent. Later, Klankermayer et al.[6] developed a more practical method, that is, direct methylation of aromatic amines by CO_2 and H_2 using a homogeneous Ru catalyst, [Ru(triphos)(tmm)], with an acidic additive ($HNTf_2$). Beller et al.[7] also reported an improved catalyst for this reaction with wider scope, in which aliphatic amines as well as aromatic amines were tolerated by a homogeneous Ru catalyst with triphos ligand and additives (methanesulfonic acid or LiCl). This new catalytic pathway can be a practical alternative to the current industrial methylation of amines with methanol or formaldehyde,[8] since methylamines can be directly produced from inexpensive and renewable chemicals and H_2O is the only byproduct. For practical applications, these homogeneous catalysts have serious problems, such as difficult catalyst/product separation, the inability to reuse the catalyst, and the necessity of additives (ligands, acids, and salts) in the reaction mixture. As for heterogeneous catalysts, Baiker et al.[9] previously reported Cu-catalyzed gas-phase methylation of NH_3 by CO_2 and H_2, but the system suffered from drawbacks such as low yield and the necessity of high temperatures (200–300 °C). Very recently, Shi et al.[10] reported the first reusable catalyst ($CuAlO_x$) for methylation of amines with CO_2 and H_2. However, this system requires substoichiometric amount of Cu (38 mol% Cu with respect to amine). To our knowledge, there are no examples of additive-free and reusable catalytic systems with acceptable turnover numbers (TONs). We report herein a new heterogeneous Pt catalyst, Pt and MoO_x co-loaded TiO_2, for methylation of aliphatic and aromatic secondary amines by CO_2 and H_2 under solvent-free conditions that shows an order of higher TON than previous systems and high reusability.

Motivated by the fact that some oxide-supported transition metal nanoparticles catalyze amide formation from CO_2, H_2, and amines[3d,f] and hydrogenation of amides to amines,[11] we screened various oxide-supported transition metal catalysts (containing 0.02 mmol of active metals) for methylation of *N*-methyl aniline (1 mmol) with CO_2 and H_2 at 200 °C (24 h) as a model reaction. Table 1 lists the conversion and yield of *N*,*N*-dimethyl aniline. First, we tested a well-established CO_2 hydrogenation catalyst,[3c,d] $CuZnAlO_x$, prepared by the co-precipitation method according to the literature.[3d] The Cu catalyst (entry 1, Table 1) was nearly inactive, showing only 2% yield. Then, we tested supported Pt catalysts (entries 2–11, Table 1) and found that some Pt catalysts such as Pt/Nb_2O_5 showed higher yield of the desired product. Pt/C as a conventional Pt catalyst resulted in low yield of the product partly due to aromatic ring reduction. Inspired by previous reports that transition metals, such as Mo and Re, act as effective promoters of heterogeneous Ru, Rh, and Ir catalysts for hydrogenation of oxygen-containing compounds,[11–13] we tested supported Pt catalysts co-loaded with oxides of transition metals (V, Mo, W, Re). Among various catalysts tested (entries 13–21, Table 1), $Pt-MoO_x/TiO_2$ (entry 13, Table 1) showed the highest yield (85%). Next, we tested a series of transition metal and MoO_x co-loaded TiO_2 (entries 13, 22–26, Table 1). Among various metals (Pt, Pd, Rh, Ru, Ni, Cu), $Pt-MoO_x/TiO_2$ showed the highest yield. MoO_x-loaded TiO_2 (entry 12, Table 1) was nearly inactive and Pt/TiO_2 (entry 4, Table 1) and Pt/MoO_3 (entry 5, Table 1) showed markedly lower yield (6–10%) than $Pt-MoO_x/TiO_2$. These results indicate that co-presence of Pt and Mo species on TiO_2 is critical. The effect of the prereduction temperature (200–600 °C) of $Pt-MoO_x/TiO_2$ showed that the catalyst reduced at 300 °C gave the highest activity (result not shown).

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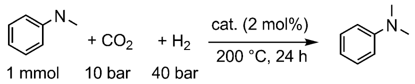
Table 1. Methylation of *N*-methyl aniline with CO_2 and H_2 by various catalysts.



Entry	Catalysts	Conv. [%]	Yield[a] [%]
1	Cu-ZnO/Al_2O_3	6	2
2	Pt/Nb_2O_5	41	39
3	Pt/HMFI	27	10
4	Pt/TiO_2	7	6
5	Pt/MoO_3	10	10
6	Pt/SiO_2	16	4
7	Pt/ZrO_2	16	3
8	Pt/Al_2O_3	11	3
9	Pt/CeO_2	3	2
10	Pt/MgO	5	2
11	Pt/C	100	0
12	MoO_x/TiO_2	1	1
13	Pt-MoO_x/TiO_2	85	85
14	Pt-VO_x/TiO_2	49	48
15	Pt-WO_x/TiO_2	27	22
16	Pt-ReO_x/TiO_2	16	12
17	Pt-MoO_x/Al_2O_3	34	32
18	Pt-MoO_x/ZrO_2	32	20
19	Pt-MoO_x/SiO_2	25	11
20	Pt-WO_x/ZrO_2	34	29
21	Pt-MoO_x/Nb_2O_5	43	39
22	Pd-MoO_x/TiO_2	25	10
23	Rh-MoO_x/TiO_2	54	49
24	Ru-MoO_x/TiO_2	20	0
25	Ni-MoO_x/TiO_2	29	1
26	Cu-MoO_x/TiO_2	9	8

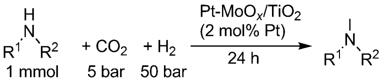
[a] GC yield based on amine (using *n*-dodecane as an internal standard).

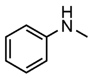
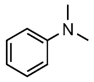
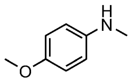
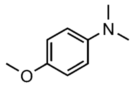
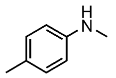
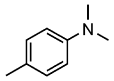
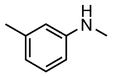
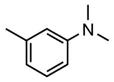
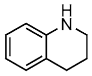
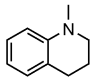
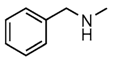
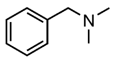
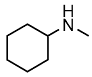
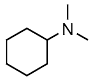
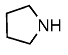
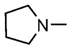
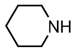
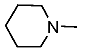
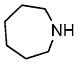
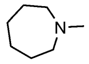
Next, we show the characterization results of the representative catalyst, Pt-MoO_x/TiO_2 prereduced at 300 °C. Figure S1 (in the Supporting Information) show X-ray absorption near edge spectroscopy (XANES) spectra of Pt-MoO_x/TiO_2 (reduced at 300 °C) and a reference compound (Pt foil). The XANES spectrum of Pt-MoO_x/TiO_2 is nearly identical to that of Pt foil, which indicates that the electronic state of the Pt species in Pt-MoO_x/TiO_2 is metallic. Temperature-programmed reduction of the unreduced catalyst precursor under H_2 (Figure S2) shows a H_2 consumption peak due to the reduction of oxidic Pt to metallic Pt below 200 °C. Thus, Pt species in Pt-MoO_x/TiO_2 are completely metallic after the standard prereduction at 300 °C, which is consistent with the XANES result. From the CO adsorption experiment on Pt-MoO_x/TiO_2, the mean diameter of Pt metal particles is estimated to be 4.1 nm, based on the assumption that CO is adsorbed on the surface of spherical Pt particles at a stoichiometry of CO/(surface Pt atom) of 1:1. Summarizing the structural results, the dominant Pt species in Pt-MoO_x/TiO_2 are Pt metal nanoparticles with average size of 4.1 nm.

With the most effective catalyst, Pt-MoO_x/TiO_2 reduced at 300 °C, we studied the optimization of reaction conditions. First, we tested the reaction in different solvents (Table S1 in the Supporting Information). The reaction in dodecane, water, and toluene gave moderate to good yield (45–72%), and methanol gave the lowest yield (34%). The reaction under neat conditions (without solvent) gave the highest yield of 85%. The time-conversion profile (Figure S3) under the neat conditions shows that a reaction time of 24 h is appropriate.

The heterogeneous nature and reusability of this catalytic system is confirmed by the following results. For the standard reaction (entry 1, Table 2), the catalyst was removed from the reaction mixture at 26% yield ($t = 3$ h). Then, further heating of the filtrate under 5 bar CO_2 and 40 bar H_2 for 21 h at 200 °C did not increase the yield. inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis of the filtrate confirmed that the content of Pt and Mo in the solution was below the detection limits. These results confirm that the reaction is attributed to the heterogeneous catalysis of Pt-MoO_x/TiO_2. Figure 1 shows the result of catalyst recycling. After the standard reaction for 24 h, the catalyst was separated from reaction mixture by centrifugation and was dried at 90 °C for 3 h and then reduced in H_2 at 300 °C for 0.5 h. The catalyst showed high yield (80–90%) for at least 10 cycles. A total TON during the successive 10 cycles reached 433, which is higher than TONs (40[6] and 80[7]) of the state-of-the-art homogeneous Ru catalysts for the same reaction.

Table 2. Methylation of amines with CO_2 and H_2 by Pt-MoO_x/TiO_2.



Entry	Substrate	Product	T [°C]	Pt [mol%]	Conv. [%]	Yield [%][a]
1[b]			200	2	85	85(82)[c]
2			200	1	98	90
3			230	1	87	85
4			200	1	85	77
5			250	1	96	96
6			170	2	84	67
7			180	3	92	64
8			200	0.1	100	99
9			200	2	100	63
10			220	2	100	96

[a] GC yield based on amine (using *n*-dodecane as an internal standard). [b] 40 bar H_2. [c] Yield of isolated product.

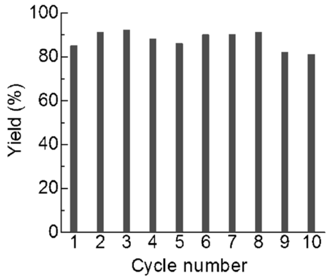
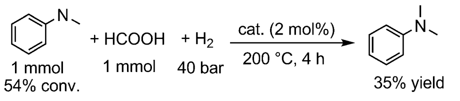


Figure 1. Catalyst reuse for methylation of *N*-methyl aniline with CO_2 and H_2 by Pt-MoO_x/TiO_2. Conditions are the same as those in entry 1 in Table 2.

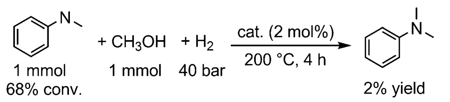
Next, we studied general applicability of the present catalytic system. Table 2 shows the scope of methylation of various secondary amines under 5 bar CO_2 and 50 bar H_2 using Pt-MoO_x/TiO_2 (2 mol% Pt with respect to amine). When methyl anilines with electron-donating groups (entries 2–4, Table 2) and tetrahydroquinoline (entry 5, Table 2) were used, the desired products were obtained in good to high yields (77–96%). Benzylic and aliphatic secondary amines (entries 6–10, Table 2) also underwent catalytic methylation with CO_2 and H_2, giving good to high yield of the tertiary amine products (63–99%). Methylation of pyrrolidine with small amount (0.1 mol%) of the catalyst resulted in 99% yield of 1-methylpyrrolidine, corresponding to a TON of 990. This value is 470 times higher than that of the $CuAlO_x$ catalyst (2.1).[10]

To discuss the key intermediates and pathway of this reaction, we studied the following control experiments. First, we tested Pt-MoO_x/TiO_2-catalyzed reductive methylation of *N*-methyl aniline with formic acid or methanol, because formic acid or methanol are general products of heterogeneous CO_2 hydrogenation.[3] The reaction with formic acid for 4 h resulted in 35% yield of *N*,*N*-dimethyl aniline [Eq. (1)], which is close to the yield (38%) of the standard reaction of *N*-methyl aniline, CO_2 and H_2 for 4 h. In contrast, the reaction with methanol gave only 2% yield of the product [Eq. (2)].

As shown in [Eq. (3)], amidation of formic acid with *N*-methyl aniline under catalyst-free condition resulted in 93% yield of *N*-methylformanilide, which then underwent Pt-MoO_x/TiO_2-catalyzed hydrogenation to give *N*,*N*-dimethyl aniline (55% yield) as the major product. These results suggest that formic acid and *N*-methylformanilide can act as key intermediates. A plausible mechanism is given in Scheme 1. Formic acid, first formed by Pt-catalyzed hydrogenation of CO_2, reacts with amine to give *N*-methylformanilide, which undergoes Pt-catalyzed hydrogenation to give tertiary amine. Mechanistic studies are ongoing to clarify the role of Mo in the catalytic cycle.



(1)



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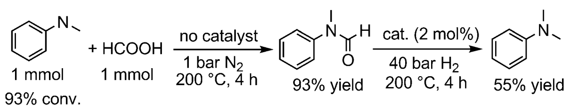

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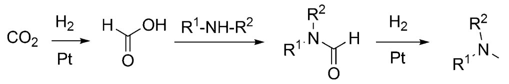

Scheme 1. Reaction pathway of Pt-catalyzed methylation of *N*-methyl aniline with CO_2 and H_2.

In conclusion, we have found that Pt and MoO_x co-loaded TiO_2 is effective for catalytic methylation of aliphatic and aromatic secondary amines by CO_2 and H_2 under solvent-free conditions. This method is the first additive-free and reusable heterogeneous catalytic system with an acceptable TON. If hydrogen is provided from renewable sources, this system can provide a sustainable and practical method for production of tertiary amines.

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Keywords: carbon dioxide · heterogeneous catalysis · hydrogenation · methylation · platinum

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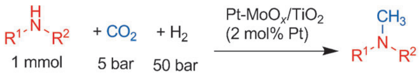
COMMUNICATION

Over and over: A heterogeneous Pt catalyst for direct methylation of aromatic amines by CO_2 and H_2 with high reusability and an order of magnitude higher turnover number than previous catalysts has been demonstrated (see scheme).



Heterogeneous Catalysis

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Sustainable Heterogeneous Platinum Catalyst for Direct Methylation of Secondary Amines by Carbon Dioxide and Hydrogen