Heterogeneous Platinum Catalysts for Direct Synthesis of Trimethylamine by *N*-Methylation of Ammonia and Its Surrogates with CO₂/H₂

Takashi Toyao,^{*1,2} S. M. A. Hakim Siddiki,¹ Keisuke Ishihara,¹ Kenichi Kon,¹ Wataru Onodera,¹ and Ken-ichi Shimizu^{*1,2}

¹Institute for Catalysis, Hokkaido University, N-21, W-10, Sapporo, Hokkaido 001-0021

²Elements Strategy Initiative for Catalysts and Batteries, Kyoto University, Katsura, Kyoto 615-8520

(E-mail: toyao@cat.hokudai.ac.jp, kshimizu@cat.hokudai.ac.jp)

Direct synthesis of trimethylamine through *N*-methylation of NH₃ or its surrogate (NH₄HCO₃) with both CO₂ and H₂ has been achieved by employing Pt and MoO_x coloaded TiO₂ (Pt-MoO_x/TiO₂). Pt-MoO_x/TiO₂ was found to be superior to other supported Pt and transition-metal-loaded MoO_x/TiO₂ catalysts for the trimethylamine synthesis process.

Keywords:	Carbon dioxide (CO ₂) <i>N</i> -Methylation		
	Trimethylamine synthesis		

Much effort has been devoted to the utilization of carbon dioxide (CO_2) as a renewable carbon resource for the production of chemicals such as methanol, formic acid, and value-added chemicals.¹⁻³ One of the important advances in this research area is catalytic methods for the utilization of CO₂/H₂ mixtures as a methylation reagent in fine chemical synthesis.^{2–10} Recent studies have shown the direct N-methylation of amines by CO₂/H₂ mixtures using homogeneous Ru catalysts^{4,5} or heterogeneous Cu,⁶ Pd,⁷ Pt,⁸ or Au⁹ catalysts. More recently, Klankermayer et al.¹⁰ have succeeded in the direct synthesis of an industrially important chemical, trimethylamine, by N-methylation of ammonia (NH₃) and its surrogate (NH₄Cl) by CO₂/H₂ using a homogeneous Ru catalyst, [Ru(triphos)(tmm)] (triphos: tridentate phosphine; tmm: trimethylene methane) under batch conditions. Since methylamines are industrially produced by zeolitecatalyzed *N*-methylation of NH₃ by methanol,¹¹ this catalytic system can be a sustainable alternative route for the synthesis of methylamines using CO₂ as a renewable carbon resource. For a practical application, however, it is strongly desired that a heterogeneous catalytic system is developed. Previously, Baiker et al. reported heterogeneous Cu catalysts for the direct synthesis of methylamines from NH₃/CO₂/H₂ in gas phase at 200-300 °C using a high-pressure flow reactor.¹² Although these reports represent important contributions to the synthesis of methylamines, the system suffered from drawbacks such as low yield (<1%) and low selectivity to trimethylamine. Herein, we report a heterogeneous Pt catalyst, Pt and MoO_x coloaded TiO₂ (Pt- MoO_x/TiO_2), for the direct synthesis of trimethylamine through *N*-methylation of NH₃ or its surrogate (NH₄HCO₃) with CO_2/H_2 under batch conditions.

Pt-MoO_x/TiO₂ (5 wt % Pt, 7 wt % Mo) was prepared by a sequential impregnation method. First, MoO₃-loaded TiO₂ (MoO_x/TiO₂) was prepared by impregnation of TiO₂ (JRC-TIO-4 supplied from the Catalysis Society of Japan) with an aqueous solution of (NH₄)₆Mo₇O₂₄•4H₂O, followed by evaporation to dryness, and by calcination in air at 500 °C for 3 h. Subsequently, for the deposition of Pt nanoparticles, MoO_x/TiO₂ was added to an aqueous HNO₃ solution containing Pt(NH₃)₂(NO₃)₂. After stirring at room temperature for 15 min, the solution was subjected to evaporation to dryness and subsequent reduction under a flow of H₂ (20 mL min⁻¹) at 300 °C for 0.5 h in a glass tube. The prepared Pt-MoO_x/TiO₂ was characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) measurements (see the Supporting Information). XRD patterns of TiO₂, MoO_x/TiO₂, and Pt-MoO_x/TiO₂ were found to be essentially identical, with peaks arising from TiO₂ having both anatase and rutile phases (Figure S1). This fact suggests that the introduced MoO_x and Pt species exist in amorphous and/or as very small particles that cannot be identified by XRD. TEM images shown in Figure S2 revealed that Pt-MoO_x/TiO₂ contains Pt nanoparticles with average size of 4.7 ± 1.1 nm, as previously reported.¹³ Other supported catalysts were prepared in a similar manner. After the H₂-reduction, the catalyst (5 mol % on the basis of the Pt loading amount), and a mixture of ammonium hydrogen carbonate (NH₄HCO₃) and octane (0.29 mmol) were added to a stainless steel autoclave (10 cm^3) . Soon after being sealed, the reactor was flushed with H₂ and charged with 1 MPa CO₂ and 5 MPa H₂ at room temperature. The autoclave was heated at 250 °C under stirring (500 rpm) for 24 h. The yields of trimethylamine were determined on the basis of N content in the substrate by GC using octane as the internal standard.

In the initial phase of this effort, we carried out catalyst screening for the methylation of an NH₃ surrogate (NH₄HCO₃) using various oxide-supported transition-metal catalysts, containing 5 wt % of active metals. Table 1 shows the yield of trimethylamine from 1 mmol of NH₄HCO₃ under 1 MPa of CO₂ and 5 MPa of H₂ in the presence of the catalyst containing 0.05 mmol (5 mol %) of active metals. Pt-MoO_x/TiO₂ showed the highest yield (65%) among the supported Pt catalysts explored in this study (Entries 1–12). We also tested a series of transition metal and MoO_x coloaded TiO₂ catalysts (Entries 1 and 13–20). Among various metals (Pt, Pd, Re, Ir, Rh, Ru, Ni, Co, and Cu) tested, Pt-MoO_x/TiO₂ exhibited the highest yield for the trimethylamine synthesis. It was confirmed that MoO₃/TiO₂ (Entry 21) showed 0% yield, indicating that the presence of Pt is essential for progression of the reaction.

Next, we further optimized the reaction conditions by employing the best catalyst, Pt-MoO_x/TiO₂. Table 2 shows the catalytic results employing different solvents. The reactions in 1,4-dioxane, glyme (1,2-dimethoxyethane), THF (tetrahydrofuran), heptane, and H₂O resulted in low to moderate yields (20–53%). The reaction under solvent-free conditions gave the highest yield of 65%. Under the solvent-free conditions, a reaction at a lower temperature (200 °C) gave 54% yield. Furthermore, a reaction using a lower amount of the catalyst (3 mol % Pt) was found to result in a lower product yield (54%).

Reactions using various NH_3 surrogates such as $(NH_4)_2CO_3$, urea, and NH_4Cl instead of using NH_4HCO_3 as a N source were also performed, as shown in Table 3. The reactions were carried

NH₄HCO ₃	+ CO ₂ + H ₂ 5 mol% cat.	→ N CH ₃
1 mmol	1 MPa 5 MPa ²⁵⁰ °C, 24 h	H ₃ C ¹¹ CH ₃
Entry	Catalyst	Yield/%
1	$Pt-MoO_x/TiO_2$	65
2	Pt/MoO ₃	43
3	Pt/WO_3 - ZrO_2	38
4	Pt/SiO ₂ -Al ₂ O ₃	10
5	Pt/TiO ₂	9
6	Pt/SnO_2	7
7	Pt/Nb_2O_5	6
8	Pt/MgO	2
9	Pt/Al_2O_3	4
10	Pt/SiO_2	4
11	Pt/HBEA	3
12	Pt/C	1
13	$Pd-MoO_x/TiO_2$	19
14	$\text{Re-MoO}_x/\text{TiO}_2$	8
15	$Ir-MoO_x/TiO_2$	2
16	Rh-MoO _x /TiO ₂	1
17	$Ru-MoO_x/TiO_2$	1
18	$Ni-MoO_x/TiO_2$	4
19	$Co-MoO_x/TiO_2$	2
20	$Cu-MoO_x/TiO_2$	2
21	MoO_x/TiO_2	0

Table 1. Synthesis of trimethylamine from $\rm NH_4HCO_3,\ \rm CO_2,$ and $\rm H_2{}^a$

^aReaction conditions: 5 mol % catalyst, $1 \text{ mmol } \text{NH}_4\text{HCO}_4$, $1 \text{ MPa } \text{CO}_2$, $5 \text{ MPa } \text{H}_2$, $250 \,^{\circ}\text{C}$, 24 h. Yields were determined on the basis of N atom in the substrate by using GC with octane as an internal standard.

Table 2. Synthesis of trimethylamine from NH₄HCO₃, CO₂, and H₂ under different conditions over Pt-MoO_x/TiO₂^a

NH₄HCO₃ ↔ 1 mmol	+ CO ₂ + H ₂ (5 mol% Pt) + CO ₂ + H ₂ (5 mol% Pt) 5 mL solvent 250 °C, 24 h	→ CH ₃ H ₃ C N CH ₃
Entry	Solvent	Yield/%
1	No solvent	65
2	1,4-Dioxane	53
3	Glyme	45
4	THF	35
5	Heptane	31
6	H ₂ O	20

^aReaction conditions: Pt-MoO_x/TiO₂ (5 mol % Pt), 1 mmol NH₄HCO₄, 5 mL solvent, 1 MPa CO₂, 5 MPa H₂, 250 °C, 24 h. Yields were determined on the basis of N atom in the substrate by using GC with octane as an internal standard.

out with 1 MPa of CO₂ and 5 MPa of H₂ using Pt-MoO_x/TiO₂ (5 mol % Pt with respect to the N atom in the substrate). Among the surrogates in Table 3, NH₄HCO₃ gave the highest yield (65%). While (NH₄)₂CO₃ and urea were converted to trimethylamine even with low yields (13 and 31%, respectively), the yield obtained for NH₄Cl was 0%. Note that 0.5 M NH₃ dissolved in 1,4-dioxane was transformed to trimethylamine in 64% yield under the standard condition, as shown in eq 1. These results

Table 3. Synthesis of trimethylamine from ammonia surrogates, CO₂, and H₂ over Pt-MoO_x/TiO₂^a

Entry	N source	Yield/%
1	NH ₄ HCO ₃	65
2	$(NH_4)_2CO_3$	13
3	Urea	31
4	NH ₄ Cl	0

^aReaction conditions: Pt-MoO_x/TiO₂ ($5 \mod \%$ Pt), NH₃ surrogate corresponding to 1 mmol of N atom, 1 MPa CO₂, 5 MPa H₂, 250 °C, 24 h. Yields were determined on the basis of N atom in the substrate by using GC with octane as an internal standard.

demonstrate that the present catalytic system is effective for the selective synthesis of trimethylamine from NH_3 or its surrogate (NH_4HCO_3) with CO_2/H_2 .

In our previous study on the catalytic N-methylation of Nmethyl aniline with CO₂/H₂ over Pt-MoO_x/TiO₂,⁸ we proposed a reaction pathway involving initial formation of formate. Moreover, we have reported that the same catalyst is effective for the hydrogenation of amides to amines.¹⁴ Taking these things into consideration, the direct catalytic methylation of ammonia presented here may involve the initial formation of formic acid or formate, subsequent condensation with NH₃, and hydrogenation to amine.¹⁰ This is supported by following control reactions using 0.5 M NH₃ in 1,4-dioxane as a substrate. As shown in eq 2, the reaction of NH₃ with formic acid under 5 MPa H₂ with Pt-MoO_x/TiO₂ gave trimethylamine in 42% yield. In addition, dimethylamine underwent N-methylation with CO_2/H_2 by Pt-MoO_x/TiO₂ to give trimethylamine in 56% yield (eq 3). Although we have not fully understood the reaction mechanism and the role of the catalyst support, it is expected that the strong Lewis acidity of MoO_x/TiO₂ plays an important role for the steps involving hydrogenation of the formed amides to amines as is the case with our previous study.¹⁴

$$\begin{array}{c} NH_{3} + HCO_{2}H + H_{2} \\ 1 \text{ mmol} \quad 10 \text{ mmol} \quad 5 \text{ MPa} \end{array} \xrightarrow[250]{(5 \text{ mol}\% \text{ Pt})} \begin{array}{c} CH_{3} \\ 1 \text{ mol} & 10 \text{ mmol} \quad 5 \text{ MPa} \end{array} \xrightarrow[250]{(5 \text{ mol}\% \text{ Pt})} \\ (0.5 \text{ M in } 1,4\text{-dioxane}) \end{array} \xrightarrow[42\%]{(5 \text{ mol}\% \text{ Pt})} \begin{array}{c} H_{3}C \\ 42\% \\ H_{3}C \\ N \\ CH_{3} + CO_{2} + H_{2} \\ \hline \begin{array}{c} 05 \text{ mol}\% \text{ Pt} \\ \frac{5 \text{ mol}\% \text{ Pt}}{250 \text{ C} 24 \text{ h}} \\ \frac{16 \text{ mol}\% \text{ Pt}}{250 \text{ C} 24 \text{ h}} \\ H_{3}C \\ N \\ CH_{3} \\ CH_$$

In conclusion, the direct catalytic methylation of ammonia and its surrogates with CO_2/H_2 was found to be catalyzed by Pt-MoO_x/TiO₂ to give trimethylamine. With a renewable hydrogen source, in the near future, this system could provide a sustainable method for production of trimethylamine from non-fossil resources.

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