Selective synthesis of *N*-methylaniline from CO_2, H_2 and aniline over CeO_2-supported Cu sub-nanoparticle catalyst

Yu Gu,[a] Masazumi Tamura,[a]* Ayaka Miura,[a] Yoshinao Nakagawa,[a] Keiichi Tomishige[a,]*

[a]*Department of Applied Chemistry, Graduate School of Engineering, Tohoku University, Sendai, 980-8579, Japan*

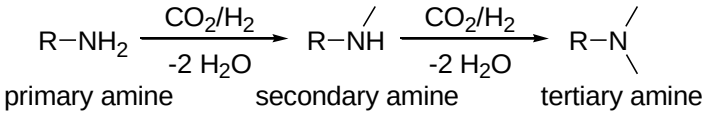
**+81-22-795-7214, mtamura@erec.che.tohoku.ac.jp; +81-22-795-7215, tomi@erec.che.tohoku.ac.jp*

Abstract: CeO_2-supported Cu (Cu/CeO_2) was a very effective heterogeneous catalyst in the selective synthesis of *N*-methylaniline from aniline, CO_2 and H_2. High selectivity to *N*-methylaniline and moderate activity were achieved by the catalyst. Copper sub-nanoparticles are responsible for the high activity of the catalyst, and the CeO_2 support plays an important role in suppression of over-*N*-methylation of the target product, leading high selectivity to *N*-methylaniline.

Keywords: *N*-Methylation of amines, Carbon dioxide utilization, Copper sub-nanoparticle.

1. Introduction

N-Methylated amines are widely used chemicals as solvents and important intermediates for dyes, surfactants, pesticides, etc. Conventionally, *N*-methylated amines are prepared using methyl iodide, formaldehyde, or formic acid derivatives as a methyl source.[1] Considering the high price of these methylation reagents, *N*-methylation of amines with CO_2 and H_2 will be an attractive alternative for *N*-methylated amines production. However, selective synthesis of secondary amines by *N*-methylation of primary amines with CO_2 and H_2 is difficult because of the successive *N*-methylation of the produced *N*-methylamines to the tertiary *N*,*N*-dimethylamines (Scheme 1). To solve the problem, heterogeneous catalysts with high activity for mono-*N*-methylation are desired to be developed.



Scheme 1. *N*-Methylation of primary amines with CO_2/H_2

Recently, we found that Cu/CeO_2 acted as an effective heterogeneous catalyst for hydrogenation of dimethyl carbonate to methanol.[2] The catalyst was obtained by impregnation method and the size of Cu particles on the support was found to be at sub-nanoscale. The Cu sub-nanoparticles are formed by the interaction with CeO_2 support. Considering that carbamic acid can easily generate from CO_2 and amines and the Cu/CeO_2 catalyst will be effective for the hydrogenation, we tested the Cu/CeO_2 catalyst in *N*-methylation of aniline to *N*-methylaniline with CO_2 and H_2.[3]

2. Experimental

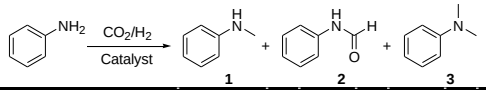
CeO_2 used as support was obtained by calcining cerium oxide HS (Daiichi Kigenso, Japan) for 3 hours under air at 873 K. Cu/CeO_2 and Cu/support catalysts were prepared by impregnation method with an aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$. Other CeO_2 supported monometallic catalysts were prepared by similar method using the corresponding precursors. All prepared catalysts were calcined at 773 K for 3 h. Carbon-supported 5 wt% metal catalysts were commercially available.

Activity tests were performed in a 190 mL stainless-steel autoclave with an inserted glass vessel. Reaction conditions were as follows: catalyst 0.3 g, aniline 0.19 g, toluene (solvent) 5 g, dodecane (internal standard) 0.15 g; CO_2 1 MPa, H_2 7 MPa; 433 K; 4 h. The products in the gas phase and liquid phase were analyzed by GC with Porapak N (GL Science) and DB-1 (Agilent J&W), respectively. Conversion of the substrate, and yield and selectivity of the products were determined on the basis of aniline by internal standard method.

3. Results and discussion

At first, catalytic performance of various CeO_2-supported metal catalysts (M/CeO_2, M = Cu, Ir, Rh, Ru, Pd, Pt, and Ni) (Table 1, Entries 1-7) was compared in *N*-methylation of aniline with CO_2 and H_2. Among CeO_2-supported metal catalysts, Cu/CeO_2 acted as the most effective catalyst, showing moderate conversion, and high selectivity to *N*-methylaniline (**1**). Formanilide (**2**) was also produced, while *N*,*N*-dimethylaniline (**3**) was hardly observed (Entry 1). Although Ru/CeO_2 and Pd/CeO_2 exhibited higher conversion of aniline (Entrie 4 and 5), other products such as *N*-cyclohexylaniline and dicyclohexylamine were mainly formed, which indicates that hydrogenation of the aromatic ring in aniline to cyclohexylamine and coupling of the produced cyclohexylamines took place over these catalysts. In addition to the CeO_2-supported noble metal catalysts, commercial carbon-supported noble metal catalysts (M/C, M = Pt, Pd, Rh and Ru) (data not shown) were also tested. Pt/C, Pd/C and Rh/C showed low conversion for the reaction, while Ru/C exhibited high conversion, but the products were similar to those achieved by using Ru/CeO_2. Other screened CeO_2-supported metal catalysts showed low conversion (Entries 2, 3, 6, and 7). Since Cu/CeO_2 was the most effective catalyst among the above catalysts, other Cu/support catalysts (support = Al_2O_3, ZrO_2, TiO_2, SiO_2, ZnO, MgO, and Y_2O_3) were also investigated (Table 1, Entries 8-14). Cu/Al_2O_3 and Cu/ZrO_2 catalysts (Entries 8 and 9) showed two-fold higher activity than that of the Cu/CeO_2 catalyst with higher selectivity to **1**, while catalysts using other supports exhibited lower conversion (Entries 10-14). Therefore, Al_2O_3, ZrO_2, and CeO_2 are selected as effective supports in this reaction. In order to obtain high yield of **1**, catalytic performance of Cu/CeO_2, Cu/Al_2O_3 and Cu/ZrO_2 were compared at similar high conversion level (70-80%), and the result is shown in Figure 1. Obviously, Cu/CeO_2 showed higher selectivity to **1** up to 98%, and formation of **3** caused by over-*N*-methylation was suppressed.

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



Entry	Catalyst	Conv. /%	Selectivity /%			
			1	2	3	Others[a]
1	Cu/CeO_2	16	88	12	<1	<1
2	Ir/CeO_2	2	43	57	<1	<1
3	Rh/CeO_2	2	14	20	<1	66
4	Ru/CeO_2	>99	<1	<1	<1	>99
5	Pd/CeO_2	60	<1	6	<1	94
6	Pt/CeO_2	< 1	-	-	-	-
7	Ni/CeO_2	< 1	-	-	-	-
8	Cu/Al_2O_3	36	97	1	2	<1
9	Cu/ZrO_2	30	94	6	<1	<1
10	Cu/TiO_2	6	97	<1	3	<1
11	Cu/SiO_2	6	58	42	<1	<1
12	Cu/ZnO	5	84	15	<1	1
13	Cu/MgO	3	87	8	2	3
14	Cu/Y_2O_3	1	68	32	<1	<1

Reaction conditions: aniline 0.19 g (2mmol), M/support (M: 1wt%) 0.3 g, toluene 5 g, 433 K, 1 MPa CO_2, 7 MPa H_2, 4 h. [a]Others are mainly *N*-cyclohexylaniline and dicyclohexylamine.

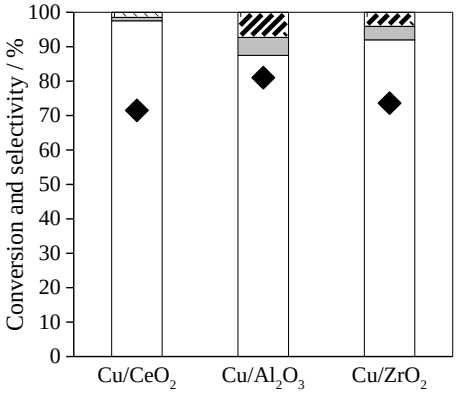


Figure 1. Comparison of the catalytic performance of Cu/CeO_2 (42 h), Cu/Al_2O_3 (16 h) and Cu/ZrO_2 (16 h) at similar high conversion level in *N*-methylation of aniline with CO_2 and H_2 (◆ : Conversion of aniline, white bar: selectivity to **1**, gray bar: selectivity to **2**, stripe bar: selectivity to **3**). Reaction conditions: aniline 0.19 g, catalyst 0.5 g (Cu: 1wt%), toluene 5 g, 433 K, 1 MPa CO_2, 7 MPa H_2.

4. Conclusions

We demonstrated that Cu/CeO_2 catalyst has excellent catalytic performance towards selective synthesis of *N*-methylaniline by *N*-methylation of aniline with CO_2 and H_2. Cu sub-nanoparticles were the main active species over CeO_2 support, which was responsible for the high selectivity.

References

1. R.N. Salvatore, C. Hwan, K.W. Jung, Tetrahedron 57 (2001) 7785.
2. M. Tamura, T. Kitanaka, Y. Nakagawa, K. Tomishige, ACS Catal. 6 (2016) 376.
3. M. Tamura, A. Miura, Y. Gu, Y. Nakagawa, K. Tomishige, Chem. Lett. 46 (2017) 1243.