



N-methylation of *N*-methylaniline with Carbon Dioxide and Molecular Hydrogen over a Heterogeneous Non-noble Metal Cu/TiO₂ catalyst

Ke Liu,^[a,b] Zhenbo Zhao,^[a] Weiwei Lin,^{*[b,c]} Qiang Liu,^[a,b] Qifan Wu,^[b,c] Ruhui Shi,^[b,c] Chao Zhang,^[b,c] Haiyang Cheng,^[b,c] Masahiko Arai,^[b,c] and Fengyu Zhao^{*[b,c]}

Dedication ((optional))

Abstract: A non-noble heterogeneous catalyst of Cu/TiO2 was prepared for N-methylation of N-methylaniline (MA) with CO₂ and H₂. 5 wt.-% Cu loaded TiO₂ (P25) catalyst exhibited a high performance, with 82% MA conversion and 98% N,N-dimethylaniline (DMA) selectivity under the reaction conditions used (4 MPa H₂, 2 MPa CO₂, 180 °C, 36 h). The Cu/TiO2 catalyst was more effective with respective to the total conversion and the DMA selectivity as compared to 5 wt.-% Cu loaded catalysts on CeO2, ZnO and activated carbon materials. The possible active species of Cu/TiO2 catalyst should be both Cu⁺ and Cu⁰ which contributed to the high activity as the reaction conversion increased linearly with them exposed on the surface of catalyst. Moreover, the reaction pathways involved were studied; it was likely that the reaction took place via an intermediate of formaldehyde that was formed from CO₂ and H₂, as confirmed by in situ diffuse reflectance Fourier-transform infrared spectroscopy, then it reacted with MA to give N-methylformanilide (MFA), and finally MFA was hydrogenated to DMA.

Introduction

of the document.

Carbon dioxide (CO₂) is a renewable, low-cost, abundant, and nontoxic C1 resource and, therefore, the transformation of CO₂ to value-added chemicals has attracted extensive attention in both green and synthetic chemistry fields.^[1] Because of the thermodynamic stability of CO₂, a strong thermodynamic driving power is required for the effective transformation of CO₂. Great efforts have been concentrated on fixation of CO₂ into methanol,

[a]	K. Liu, Prof. Z. Zhao, Q. Liu School of Chemistry and Life Science
	Changebun University of Technology
	Changchun 130012 P. R. China
[b]	K. Liu, Dr W. Lin, Q. Liu, Q. Wu, R. Shi, Dr C. Zhang, Dr. H.
	Cheng, Prof.Dr. M. Arai, Prof. Dr. F. Zhao
	State Key Laboratory of Electroanalytical Chemistry
	Changchun Institute of Applied Chemistry
	Chinese Academy of Sciences
	Changchun, 130022, P. R. China.
	E-mail: linwei@ciac.ac.cn, zhaofy@ciac.ac.cn
[c]	K. Liu, Dr W. Lin, Q. Liu, Q. Wu, R. Shi, Dr C. Zhang, Dr. H.
	Cheng, Prof.Dr. M. Arai, Prof. Dr. F. Zhao
	Jilin Province Key Laboratory of Green Chemistry and Process,
	Changchun Institute of Applied Chemistry.
	Chinese Academy of Sciences
	Changchun, 130022, P. R. China.
	Supporting information for this article is given via a link at the end

mechanism.^[9] This catalyst was also effective in direct synthesis of trimethylamine from N-Methylation of ammonia with CO2 and H₂. ^[10] In addition, Au/Al₂O₃ and Re/TiO₂ catalysts were reported to be active for the N-methylation of aromatic and aliphatic second amines with CO2 and H2, yielding tertiary amines with excellent yields. [11] In addition, supported Cu catalysts were also used in the N-methylation reactions. Shi and co-workers ^[12] applied a simple CuAIO_x catalyst to transform primary and secondary amines into the corresponding N-methyl or N,Ndimethyl products with CO₂ and H₂. In this system, however, a large amount (38 mol%) Cu with respect to amine was required. More recently, Tomishige et al. reported that Cu/CeO₂ catalyst was high efficent for the synthesis of N-methylaniline by Nmethylation of aniline with CO₂ and H₂. ^[13] Cu-based catalysts were widely used for the hydrogenation reactions for its inexpensive price and remarkable

dimethyl ether, higher alcohols, formates, CO, methane, and

light alkanes by using different catalysts. [2] In addition, a

breakthrough development in this area is a new catalytic method

using CO₂ as a carbon source of *N*-methylation reaction.^[3]

Previously Cantat et al. [4] and Beller et al. [5] reported the

methylation of amines with hydrosilanes and CO₂ by

homogeneous catalysts in 2013. Unfortunately, the methods

were not practical due to the use of hydrosilanes as the reducing

agents. At the same time, they reported a possible utilization of

CO₂ as N-methylation reagent. Subsequently, a more practical

method for the direct N-methylation of aromatic amines with CO₂

and H₂ by a homogeneous Ru catalyst of Ru(triphos)(tmm) was

reported by Klankermayer and co-workers. ^[6] Beller et al. ^[7] also

found an improved catalyst with extended scope, in which

aliphatic and aromatic amines as well as primary and secondary

amines were tolerated by an in situ formed homogeneous Ru

catalyst with LiCl or acid additives. However, homogeneous catalysts suffer from problems of catalyst/product separation, reusability, and the necessity of additives (acids, ligands, and salts) in the reaction system. Therefore, high-efficiency

heterogeneous catalysts are required from the view of practical utilization. Shi and co-workers ^[8] reported that Pd/CuZrO_x was

effective for the methylation of amines with CO₂ and H₂ and a

high product yield of about 97% was achieved. Shimizu et al.

utilized Pt-MoO_x/TiO₂ catalyst to transform aliphatic and

aromatic secondary amines to tertiary amines with CO2 and H2

in solvent-free system and proposed a plausible reaction

hydrogenation reactions for its inexpensive price and remarkable hydrogenation activity.^[14] Many years ago, it was demonstrated that Cu catalysts were active in the hydrogenation of CO₂. ^[15] Baiker and co-workers found that active Cu species was mainly present as Cu⁰ over Cu/ZrO₂. ^[16] In contrast, Cu⁺ was proposed

VIANUSCrip

ChemCatChem

to be the active species for Cu/ZnO/SiO₂ catalyst. ^[17] Liu and coworkers reported a direct comparison in the catalytic performances between ZnCu and ZnO/Cu model catalysts for methanol synthesis. ^[18] The results emphasize a synergy of Cu and ZnO at the interface that facilitates methanol synthesis via formate intermediates. Recently, Cu/TiO₂ catalyst was reported to be effective for photocatalytic CO₂ reduction, in which the Cu⁺ and Cu⁰ species formed by H₂-reduction was confirmed to be more active in charge separation than Cu⁺ species alone. ^[19] Cu/TiO₂ was also used in the photocatalytic hydrogenation of CO₂ into CH₄ and the coexistence of Cu⁰ and Cu⁺ was beneficial to enhance the activity by prolonging the lifetime of electrons. ^[20]

Considering the above-mentioned results, we have investigated the feasibility of Cu catalyst for direct N-methylation of N-methylaniline (MA) with CO₂ and H₂. In the present work, TiO₂ (P25) was employed as a support to disperse Cu species and Cu/TiO₂ samples were prepared by deposition-precipitation method and tested for the target reaction in *n*-octane. It is important to note here that Cu/TiO₂ is more effective with respect to the total MA conversion and the DMA selectivity than those Cu catalysts on CeO₂, ZnO, and activated carbon. The bulk and surface properties of Cu/TiO2 catalysts were characterized by XRD, TEM, XPS, and TPR and possible reaction intermediates were examined by controlled reaction runs and in situ high-pressure FTIR for the reaction system in the presence of CO₂ and H₂ under reaction conditions. From those results, discussion was given on Cu species effective for the selective production of DMA from MA and possible reaction pathways concerned.

Results and Discussion

3.1. Catalyst characterization

The BET surface area, pore size and pore volume of 5 wt.-% Cu catalysts on TiO₂ supports pre-calcined at different temperatures were determined by N₂ sorption (as shown in Figure S1). The results obtained with the samples reduced in H₂ at 250 °C were shown in Table S1. The calcination temperature was observed to have a remarkable impact on these textural properties. For example, the BET surface area was 47.4 m²/g for Cu/TiO₂ at 250 °C and it decreased to 42.5, 20.7, and 9.4 m²/g, respectively, by the pre-calcination of TiO₂ support at 600, 700, and 800 °C.

The bulk structure of those catalysts was examined by XRD and Raman spectroscopy measurements. Figure 1 gives the XRD patterns and there is no diffraction peaks of Cu species, probably due to the small metal loading and/or the fine dispersion of Cu species on TiO₂ supports. Figure 1 indicates the presence of anatase and rutile crystal phases in the samples. The relative contents of these two phases changed on the calcination of TiO₂ and were calculated by the following equation (1), where W_R is the weight fraction of rutile phase in the sample and A_A and A_R represent the integral XRD intensities of the anatase (101) at $2\theta = 25.2^{\circ}$ and the rutile (110) at $2\theta = 27.4^{\circ}$ measured, respectively.

$$W_R = \frac{A_R}{0.884A_A + A_R} \tag{1}$$

The results of the relative amounts of anatase and rutile phases estimated are shown in Table S2. W_R was 10% for Cu/TiO₂ sample using un-calcined TiO₂ and it increased to 17%, 85%, and 100% on the calcination at 600, 700, 800 °C, respectively. Such a change of the crystal phase from anatase to rutile with the calcination temperature was also confirmed by Raman spectroscopy (Figure S2).



Figure 1 XRD patterns of Cu/TiO₂-T (Cu loading is 5%) samples using TiO₂ supports pretreated at different calcination temperatures.

The dispersion of Cu particles in those samples was examined by transmission electron microscope (TEM). As shown in Figure 2, Cu was finely dispersed in the form of nanoparticles on the TiO₂ supports. The average Cu particle size was 2.3, 3.6, 4.6 and 6.1 nm for Cu/TiO₂, Cu/TiO₂-600, Cu/TiO₂-700, and Cu/TiO₂-800, respectively. The size of Cu nanoparticles was increased by a factor of 3 on the calcination at 800 °C. The pre-calcination of TiO₂ decreased the degree of Cu dispersion thereon. The reducibility of the above-mentioned Cu/TiO₂-T samples was investigated by H₂-TPR measurements (Figure 3). TiO₂ did not show any reduction peak in the range of temperature range of 50-600 °C $^{[21]}$ and the Cu/TiO₂ samples showed two or more reduction peaks, in which larger or crystallized CuO particles were reduced at higher temperature than that of smaller CuO particles or highly dispersed Cu2+ species. [22] Figure 3 showed two reduction peaks at 114 and 128 °C for Cu/TiO2 and Cu/TiO2-600, in which the former corresponded to the reduction of smaller CuO particles and/or highly dispersed Cu2+ species while the latter to that of larger CuO particles and/or Cu²⁺ species in strong interaction with TiO₂. For Cu/TiO₂-700 and Cu/TiO₂-800 samples, three peaks were observed at around 101, 113, and 158 °C. The first two peaks may be attributable to the highly dispersed copper oxides and the third one presented at a wide range of temperature to the crystalline copper oxides. [23] The large difference between the samples on TiO₂ supports pre-calcined at 600 and 700 °C was in accordance with the differences in the structure of TiO₂ supports

FULL PAPER

WILEY-VCH



Figure 2 TEM images of (a) Cu/TiO_2, (b) Cu/TiO_2-600, (c) Cu/TiO_2-700, (d) Cu/TiO_2-800 samples.

(Figure 1) and in the size of dispersed Cu nanoparticles thereon (Figure 2).Figure 3 shows, however, that all Cu species loaded on those TiO₂ supports could be reduced at a temperature of 250 °C. Thus, for the following activity test in the *N*-methylation of MA with CO₂ and H₂, all the catalysts were reduced at 250 °C.



Figure 3 TPR profiles of Cu/TiO₂-T (Cu loading is 5%) catalysts with the supports calcined at different temperatures.

Furthermore, the chemical state of Cu species exposed on Cu/TiO₂-T samples reduced at 250 °C was examined by XPS measurements (Figure 4). For Cu/TiO₂ (un-calcined), there appeared peaks at binding energies (BE) of 935.7, 955.7 eV and 942.9, 963.7 eV, which were attributed to Cu²⁺ and the shake-up satellite peak of Cu²⁺, respectively, indicating that there was Cu²⁺ species on the surface even after reduction. The difference

in BE between Cu⁺ and Cu⁰ is only 0.1 eV and so these Cu species cannot be distinguished by XPS.^[19] Thus, the peaks at 933.8 and 953.8 eV were assigned to Cu⁰ and/or Cu⁺ species.^[24] The relative amounts of those Cu species and the BE values in the samples examined indicated that the relative amount of Cu⁰ and Cu⁺ decreased with an increase in the calcination temperature of TiO₂ support (Table S3). In addition, Cu⁰ and Cu⁺ was distinguished by using Cu (LMM) Auger photoelectron spectroscopy (Figure S3); A peak at 916.5 eV was ascribed to Cu⁺ and a peak at 921.5 eV to transition state of Cu LMM. ^[25] While, the peak of Cu⁰ at 918.3 eV was not detected due to surface oxidation when the sample exposed to air in the handling. In addition to Cu⁺ and Cu²⁺, some amount of Cu⁰ species might also exist on the surface of Cu nanoparticles of Cu/TiO₂-T catalysts.



Figure 4 XPS results of Cu/TiO₂-T (Cu loading is 5%) with the supports calcined at different temperatures.

3.2 Catalytic performance

The catalytic performances of the Cu/TiO₂ catalysts prepared were investigated for the *N*-methylation of MA with CO₂ and H₂. Under the conditions used, DMA, MFA, aniline (AN), *N*-phenylformamide, *N*,*N*-dimethylcyclohexylamine, and other condensation products were detected to form and the product distribution depended on the catalysts used (Scheme 1).



Scheme 1 N-methylation of N-methylaniline (MA) to N,N-dimethylaniline (DMA) with CO_2 and H_2.

Initially, we compared the catalytic performance of 5 wt.-% Cu catalysts using different support materials, which were loaded and reduced in the same manners as described in Experimental. The results obtained are summarized in Table 1. The most active catalyst was Cu/TiO₂ (P25), giving a conversion

FULL PAPER

WILEY-VCH

of 55.7% and a DMA selectivity of 95.9% (entry 1). When CeO₂, ZnO, and C were used as supports, the conversion and the DMA selectivity became decreased significantly (entries 2 - 4), among which the DMA selectivity was good (81%) with Cu/ZnO catalyst (entry 3). The results indicated that Cu/TiO₂ (P25) was the most efficient catalyst with respect to the total conversion and the DMA selectivity.

Table 1 N-Methylation of N-methylaniline with CO₂ and H₂ over Cu catalysts on various supports.

Entry	Cotoluot a	Conversion	Selectivity (%)			
	Calalysi -	(%)	DMA	MFA	AN	Others ^b
1	Cu/TiO ₂	55.7	95.9	0.1	0.3	3.7
2	Cu/CeO ₂	1.4	38.1	1.1	59.2	1.6
3	Cu/ZnO	9.6	81.0	0.3	13.1	5.6
4	Cu/C	9.6	20.9	0.5	53.0	2.6

Reaction conditions: Catalyst (Cu loading is 5%) 100 mg, MA 1 mmol, n-octane 10 mL, 4 MPa H_2, 2 MPa CO_2, 180 $^\circ\!C$, 8 h.

[a] Reduced in H2 at 250 °C for 2 h. Cu loading 5 wt.-%.

[b] The others were *N*-phenylformamide, *N*,*N*-dimethylcyclohexylamine and condensation products.

The influence of Cu loading on the performance of Cu/TiO₂ (un-calcined) was then studied. The results obtained (Table S4) shows that TiO₂ itself was inactive, the total conversion became increased by loading Cu, and it was maximized at a Cu loading of 5 % in weight in the range of Cu loading up to 15%. In contrast, the selectivity to DMA was large (> 90%) irrespective of the Cu loading. So, a Cu/TiO₂ with 5% loading was used for further experiments. The catalytic performance (activity and selectivity) was examined at different reaction temperatures (Table S5). The total conversion was 20, 56, 52, and 51% and the DMA selectivity was 83, 96, 94, and 86% at 160, 180, 200, and 220 °C, respectively. These results indicate that the optimum reaction temperature was 180 °C.

Table 2 The catalytic performance of Cu/TiO $_2$ catalysts with TiO $_2$ supports precalcined at different temperatures.

Entry	Catalyst ^a	Conversion (%)	Selectivity (%)			
			DMA	MFA	AN	Others ^b
1	Cu/TiO ₂	55.7	95.9	0	0.3	3.8
2	Cu/TiO ₂ -600	51.2	97.0	0	0.4	2.6
3	Cu/TiO ₂ -700	25.4	94.9	3.7	1.4	0
4	Cu/TiO ₂ -800	17.7	94.3	0	4.4	1.3

Reaction conditions: Catalyst (Cu loading is 5%)100 mg, $\it N$ -Methylaniline 1 mmol, n-octane 10 mL, H_2 4 MPa, CO_2 2 MPa, 180°C, 8 h.

[a] Reduced in H₂ at 250 °C for 2 h.

[b] The others were *N*-phenylformamide, *N*,*N*-dimethylcyclohexylamine and condensation products.

Then, the catalytic performance of a series of Cu/TiO_2 samples different in the pre-calcination temperature of TiO_2 was examined, for which the results of structural and surface characterization are given in the above section, and the results

obtained are shown in Table 2. The conversion simply decreased from 56% to 18% with an increase in the calcination temperature up to 800 °C while DMA was produced in a selectivity of > 95% with all these catalysts. As above-mentioned, the size of Cu nanoparticles and the relative fraction of Cu⁺ and Cu⁰ were reduced by the pre-calcination of TiO₂ and the amount of Cu⁺ was even larger than that of Cu⁰. As seen in Figure 5, the total MA conversion increased linearly with the amount of the exposed Cu⁺ and Cu⁰ species, which was estimated by the XPS results (Table S3) and Cu particle size as described in

experimental part. Therefore, the surface Cu⁺ and Cu⁰ species exposed on the catalysts should be the active sites for the

present methylation reaction. 60 MA Conversion (%) Cu/TiO₂ 50 Cu/TiO2-600 40 30 Cu/TiO2-700 20 Cu/TiO2-800 10 0 5 10 15 20 0 Amount of Cu⁺ and Cu⁰ (µmol)

Figure 5 Relation between total conversion and the amount of Cu⁺ and Cu⁰ species exposed on the surface of catalyst.



Figure 6 Variation of MA conversion (\blacksquare), DMA selectivity (\square) and AN selectivity (\bigcirc) with the reaction time in the *N*-methylation of MA over Cu/TiO₂ (Cu loading is 5%). Reaction conditions: Cu/TiO₂ 100 mg, MA 1 mmol, n-octane 10 mL, H₂ 4 MPa, CO₂ 2 MPa, 180°C.

Figure 6 showed the variation of MA conversion and DMA selectivity as a function of reaction time over Cu/TiO₂ (uncalcined) catalyst. The selectivity to DMA was larger than 96%

WILEY-VCH

at an early stage of reaction and this high DMA selectivity remained unchanged during the reaction. A large MA conversion of 82% was achieved with a DMA selectivity of 96%, which is one of the best results reported to date with copper-based catalysts for *N*-methylation reaction.

Finally, the reusability of the most active Cu/TiO₂ catalyst was examined. After the first run, the catalyst was collected from the reaction mixture by centrifugation, washed with ethanol and *n*-octane for several times, and used for the subsequent run. As shown in Figure 7, the conversion was around 55% and the selectivity to DMA was > 97% for the first two runs. However, the conversion decreased to 35% and 29% for the third and fourth runs, respectively. That was, the loss of catalytic activity occurred to some extent during the repeated runs. However, when the spent catalyst used for four runs was thermal treated in air at 450 °C for 4 h followed by reduction in H₂ at 250 °C for 2 h, the MA conversion recovered to 56%, indicating that the spent Cu/TiO₂ could be regenerated through such a simple calcination and reduction process.



Figure 7 Results of repeated reaction runs. Reaction conditions: Cu/TiO₂ (Cu loading is 5%) 100 mg, MA 1 mmol, n-octane 10 mL, H₂ 4 MPa, CO₂ 2 MPa, 180°C, time 8 h. For the fifth run, the spent catalyst used for four times was pretreated in air at 450 °C for 4 h and reduced in H₂ at 250 °C for 2 h.



Figure 8. TEM images of Cu/TiO $_2$ (Cu loading is 5%) after (a) 4 runs and (b) regeneration.

The spent catalyst after used four runs was characterized by ICP, TEM, TGA, and XRD. No leaching of Cu species from the catalyst was detected by ICP but the growth of Cu nanoparticles was observed by TEM, in which the average particle size increased to 3.6 nm from 1.9 nm of the fresh catalyst (Figure 2a, Figure 8a). TGA (Figure S4) indicated a few stage of the reduction of catalyst weight at different temperatures. The first stage below 170 °C was ascribable to the removal of moisture residue and trapped CO2 [26], while the gradual weight decrease at temperatures of 170 to 270 °C to the loss of organic solvent and/or adsorbed substance. A major weight loss occurred between 370 and 570 °C, which should be due to the removal of coke. The deposition of carbon materials was also confirmed by XRD (Figure S5); the spent Cu/TiO₂ catalyst showed diffraction peaks at 20 of 18.1°, 32.1° attributed to carbon deposits. The amount of carbon deposited was about 8 wt.-% to the total weight of the catalyst estimated from TGA. Thus, the factors causing a loss of catalytic activity during recycles should be the deposition of carbon materials, which covered the surface active sites on the Cu particles. As described above, the spent catalyst was regenerated by a simple calcination in air and reduction in H₂, which should remove the carbon deposits from the surface of Cu nanoparticles. The TEM image of regenerated catalyst was shown in Figure 8b. The average particle size decreased to 2.4 nm, close to the fresh one of Cu/TiO₂, which should be ascribed to the removal of the surface carbon deposit during the heat treatment.

Table 3 Results of N-methylation of MA with various carbon sources over Cu/TiQ_2.

Entry	م المانية الم	Conversion	Selectivity (%)			
	Additive	(%)	DMA	MFA	AN	Others ^f
1 ^a	CO ₂	55.7	95.9	0.1	0.3	3.7
2 ^b	HCOOH	95.7	0.9	98.9	0.1	0.1
3°	CH₃OH	31.5	95.8	0	4.2	0
4 ^d	HCHO	69.2	86.3	0	0.3	13.4
5 ^e	CO	14.2	95.1	0	3.8	1.1

Reaction conditions: Catalyst (Cu loading is 5%) 100 mg, MA 1 mmol, *n*octane 10 mL, H_2 4 MPa, 180 °C, 8 h. [a] CO₂ 2 MPa, [b] HCOOH 2 mmol, [c] CH₃OH 16 mmol, [d] HCHO 2 mmol, [e] CO 1 MPa, [f] The others were *N*phenylformamide, *N*,*N*-dimethylcyclohexylamine and condensation products.

3.3 Possible reaction pathways

As described in Scheme 1, MA will transform to DMA through MFA or to AN in the *N*-methylation of MA with CO₂ and H₂. Further control experiments were carried out to explore reaction intermediates and mechanisms involved. Initially several carbon sources were tested, including HCOOH, CH₃OH, HCHO, and CO that were possible species produced from CO₂ and H₂ during the reaction. ^[2e, 27] Table 3 gives the results of *N*-methylation reactions using these compounds over the most active Cu/TiO₂ catalyst, with which a MA conversion of 56% and a DMA selectivity of 96% were obtained in the presence of CO₂ and H₂ (entry 1). When HCOOH was used instead of CO₂, the MA conversion was increased to 96% but MFA was exclusively produced in a selectivity of 99% (entry 2). CH₃OH gave a

WILEY-VCH

smaller conversion of 32% with a high DMA selectivity of 96% (entry 3) similar to that with CO₂ (entry 1), and medium conversion (69%) and DMA selectivity (86%) were obtained with HCHO (entry 4), while a small conversion (14%) and a high DMA selectivity (95%) with CO (entry 6). Those results indicate that CH₃OH and/or HCHO should be intermediate formed in the target reaction with CO₂ and H₂.

Next, an intermediate of MFA (Scheme 1) was used as a starting reactant, with which control reactions were conducted in the absence or presence of different methyl reagents under the same conditions as used for the above-mentioned reactions with MA. The results obtained are shown in Table 4. With no methyl reagent, a MFA conversion of 96% was obtained and DMA and MA were produced in comparable amounts (entry 1). When 2 MPa CO₂ was added, the product selectivity was significantly changed and DMA was obtained in a selectivity of 80% being larger by a factor of 4 compared to MA (entry 2). As described above, the reaction with MA gave a larger DMA selectivity of 96% (Table 1). Therefore, it is assumed for the target methylation reaction of MA that MFA was produced from MA and some fraction of MFA molecules produced converted back to MA: however, the rate of MFA transformation to DMA is faster than that to MA (Table 4) and so MFA can finally change to DMA after repeated transformation between MFA and AM during the course of reaction. When either HCOOH or CH₃OH was used, the major product was MA with a selectivity of 79% (entry 3) or 70% (entry 4). In contrast, for the case of HCHO, DMA was exclusively obtained in a selectivity of 93% at a 100% conversion (entry 5). The results of Tables 3 and 4 indicate that HCHO is a possible intermediate and it is of significance in the selective N-methylation of MA to DMA compared to CH₃OH.

Table 4 Results of hydrogenation of MFA with di	ifferent carbon sources
over Cu/TiO ₂ catalyst.	

Entry	additiva	Conversion				
	auuilive	(%)	DMA	MA	AN	Others ^e
1	-	95.7	48.5	51.2	0.3	0
2 ^a	CO ₂	100	79.5	19.4	0	1.1
3 ^b	HCOOH	83.3	20.2	78.6	1.2	0
4 ^c	CH₃OH	100	28.6	70.0	0.3	1.1
5 ^d	HCHO	100	92.9	6.5	0.1	0.5

Reaction conditions: Catalyst (Cu loading is 5%) 100 mg, MFA 1 mmol, *n*-octane 10 mL, H₂ 4 MPa, 180 °C, 8 h. [a] CO_2 2 MPa, [b] HCOOH 2 mmol, [c] CH₃OH 16 mmol, [d] HCHO 2 mmol, [e] The others were *N*phenylformamide, *N*,*N*-dimethylcyclohexylamine and condensation products.

Furthermore, FTIR was used to examine intermediate species formed from CO₂ and H₂ on Cu/TiO₂ (Cu loading is 5%) catalyst under the reaction conditions. The Cu/TiO₂ catalyst was exposed to CO₂ and H₂ at 180 °C for 4 h in the reactor and then subjected to FTIR measurement. Figure S6 gives a FTIR spectrum collected, indicating absorption bands at 2935 and 2861 cm⁻¹ assignable to CHO* species. The bands at 1648 and 1446 cm⁻¹ correspond to the carbonyl vibration and C-H stretching in the CHO group, respectively. ^[28] It is suggested that the CHO* species are generated on Cu/TiO₂ catalyst during the process.

Besides, the catalyst was also subjected to in-situ ATR-FTIR to further examine the existence of intermediate species. As shown in Figure 9, there appeared three new bands at 1677, 1109 and 990 cm⁻¹ at 43 min, and these bands became intense with time, which are assigned to the carbonyl (C=O) vibration of HCHO as they are similar to the spectrum of pure HCHO (Figure S6). Therefore, it was more likely that CHO* species was the main reaction intermediate in the N-methylation reaction. Based on the above results, the reaction pathways were proposed, as shown in Scheme 2. First, CO2 reacts with H2 to form CHO* species on the surface of Cu⁺ and Cu⁰ active species, CHO* species formed reacts with MA to yield intermediate MFA, and then MFA was hydrogenated to DMA, which was in agreement with the case of the reaction with homogeneous copper catalyst ^[27c]. In the present catalysis system, the Cu⁺ and Cu⁰ are active species, as the reaction conversion increased linearly with the amount of Cu⁺ and Cu⁰ species exposed on the surface of catalyst (Figure 5).



Figure 9 In-situ ATR-FTIR spectra recorded at different times in H_2 and CO_2 atmosphere over Cu/TiO₂. Conditions: Cu/TiO₂ (Cu loading is 5%) 50 mg, CO₂ 2 MPa, H_2 4 MPa, n-octane 4.4 mL, 180 °C.



Scheme 2 Possible reaction pathways for N-methylation of MA with CO₂ and H₂ over Cu/TiO₂ catalyst (Cu loading is 5%).

Conclusions

In summary, a non-noble metal catalyst of Cu/TiO_2 is effective for the heterogeneous *N*-methylation of MA with CO_2 and H_2 .

Under the optimum reaction conditions, the desired product of DMA was obtained in a high selectivity of 96% at 82% conversion. It is likely that CO₂ reacts with H₂ to form CHO* species, CHO* formed reacts with MA to give intermediate MFA, and finally MFA is hydrogenated to DMA. These processes occur on the active species of Cu⁺ and Cu⁰. While, the deactivated catalyst can be recovered by a simple heat treatment of calcination at 450 °C in air and reduction at 250 °C in hydrogen, through which the activity of the regenerated Cu/TiO₂ is similar to its original activity.

Experimental Section

2.1. Preparation of catalysts

All chemicals used in this work were analytic grade and used without further purification. A commercial TiO₂ (P25) (Acros) was selected as support and a Cu/TiO2 catalyst with Cu 5 wt.-% loading was prepared by deposition-precipitation method. The support TiO₂ powder and a certain amount of $Cu(NO_3)_2$ ·3H₂O were dissolved in 100 mL of deionized water while stirring and the suspension was put into a water bath at 50 °C. Then, a Na2CO3 solution was added dropwise into the suspension until the pH value became to 9.5. The mixture was aged for 2 h and the precipitate obtained was filtered and washed with deionized water and ethanol several times, followed by drying at 80 °C overnight and calcination in static air at 350 °C for 4 h. The Cu/TiO₂ catalysts with different Cu loadings of 1, 3. 10. and 15 wt.-% were also prepared, and they are herein named as 1%Cu/TiO₂, for example. For comparison, several catalysts with 5% Cu supported on other supports of ZnO (Aladdin), CeO_2 (Sinopharm Chemical Reagent Co., Ltd.) and active carbon (Sigmaaldrich) were prepared by the same procedures described above, and they are named as Cu/ZnO, Cu/CeO₂ and Cu/AC, respectively. In addition, the TiO₂ (P25) powder was calcined at different temperatures (600, 700, 800 °C) in air for 4 h and these calcined TiO₂ materials were also used as supports for 5 wt.-% Cu catalysts. These catalysts are denoted as Cu/TiO2-T, where T stands for the TiO₂ calcination temperature. If no otherwise specified, Cu/TiO₂ stands for a catalyst with Cu loading of 5% in weight. All the catalyst samples were reduced in H₂ at 250 °C for 2 h prior to characterization and reaction runs.

2.2. Characterization of catalysts

Powder X-ray diffraction (XRD) was performed using a Bruker D8 Advance X-ray diffractometer with a Cu K source at 40 kV and 40 mA for a 20 range from 10 $^{\circ}$ to 90 $^{\circ}$ with a scan speed of 4 $^{\circ}/min.$ Transmission electron microscopy (TEM) was carried out on a JEOL JEM-2010 instrument at an accelerating voltage of 187 kV. Temperature programmed reduction (TPR) profiles were measured on Micromeritics AutoChem II 2920. For TPR, a catalyst sample (50 mg) was pretreated in Ar at 120 °C for 1 h to remove physically adsorbed H₂O and other impurities. After cooling to 50 °C, the sample was flushed in Ar for an additional 0.5 h and then heated to 800 °C at a rate of 10 °C min⁻¹ in a flow of 10% H_2/Ar (30 mL min⁻¹). Nitrogen adsorption-desorption experiments were conducted with a Micromeritics ASAP 2020 surface area and porosity analyzer. X-ray photoelectron spectroscopy (XPS) measurements were carried on VG Microtech 3000 Multilab equipped with an Al Ka X-ray exciting source (1486.6 eV). The C1s peak at 248.6 eV (accuracy within ±0.3 eV) was used as reference. XPSPEAK fitting software was used for the deconvolution of overlapped XPS peaks. Visible Raman spectra were recorded on a Jobin–Yvon U1000 scanning double monochromator with a spectral resolution of 4 cm⁻¹. The line at 514 nm from a DPSS 532 Model 200 532-nm single-frequency laser was used as excitation source. Thermo-Gravimetric Analysis (TGA) measurements were performed on a TA-Q50 system under air atmosphere at a heating rate of 10 °C min⁻¹. Thermograms were recorded in the temperature range of 50 to 800 °C.

In order to examine possible intermediate species produced from CO2 and H2, Fourier-transform infrared (FTIR) spectra of Cu/TiO₂ pretreated with CO₂ and H₂ were recorded at room temperature with a NICOLET iS50 infrared spectrometer in the region of 400-4000 cm⁻¹. A Cu/TiO₂ sample was exposed to CO₂ (2 MPa) and H₂ (4 MPa) at 180 °C for 4 h in a 50 mL stainless steel autoclave reactor, the gases were vented to ambient pressure, the catalyst was put into the infrared instrument, and then the FTIR spectra were collected. In addition, in-situ total reflectance Fouriertransform infrared spectroscopy (ATR-FTIR) measurements were performed in a 22 mL high-pressure cell with a transparent diamond prism window on the bottom plate using a Nicolet iS50 spectrometer equipped with a MCT detector. First, a background spectrum was collected under air and 4.4 mL octane, and 50 mg Cu/TiO₂ were added to the cell. It was sealed and flushed with H₂ a few times and introduced with 4 MPa H₂ and 2 MPa CO₂. Then, FTIR spectra were collected for a period of 2 h while stirring.

2.3. Activity test

N-methylation of N-methylaniline (MA) with CO₂ and H₂ was performed in a 50 mL stainless steel autoclave reactor at 180 °C. Prior to the catalytic test, all the catalysts were reduced in a quartz tube with a H₂ flow (30 mL min⁻¹) at 250 °C for 2 h. Measured amounts of MA (1 mmol), solvent (n-octane 10 mL) and catalyst (100 mg) were added into the reactor and it was sealed and flushed with 1 MPa H₂ at least three times to remove the air. The reactor was then heated to 180 °C and pressurized with 4 MPa H₂ and 2 MPa CO₂. The reaction was started under stirring. After the reaction finished, the reactor was cooled and the gas mixture was then vented to ambient pressure. The liquid products obtained were analyzed by gas chromatograph (Shimadzu GC-2010, Rtx-5 capillary column) using a flame ionization detector and identified by gas chromatography/mass spectrometry (GC/MS, Agilent 5890). The conversion and selectivity to N,N-dimethylaniline (DMA) were calculated using the following equations.

MA conversion (%) =
$$\left(1 - \frac{\text{Amount of MA unreacted}}{\text{Initial amount of MA}}\right) \times 100$$
 (2)

 $DMA \text{ selectivity (\%)} = \frac{Amount \text{ of } DMA \text{ produced}}{Total \text{ amount of all products}} \times 100 \quad (3)$

The catalyst reusability was also examined. The catalyst was collected by centrifugation after the first run, washed with ethanol and then n-octane several times each, and reused for the next run under the same reaction conditions as described above.

In order to exmaine the active species, the ralation between total conversion and the amount of Cu⁺ and Cu⁰ species exposed on the surface of catalyst was examined, The amount of Cu⁺ and Cu⁰ species was calculated based on the Cu particle size and XPS results. The Cu dispersion (D) was calculated from the following equation: $D = 6(v_m/a_m)/d$. The calculation method was obtained from the hand book of heterogeneous catalysis, v_m = the volume of a Cu

FULL PAPER

atom, a_m = the area of a Cu atom, where v_m and a_m is 11.83 Å³ and 6.85 Å², respectively. The average diameter (*d*) of Cu particles was determined by TEM. Moles of the exposed of Cu⁰ and Cu⁺ was calcuated by [(the mole of Cu used) × (the dispersion **D**) × (the relative amount of Cu⁺ and Cu⁰)]. The relative amount of Cu⁺ and Cu⁰ species was calculated by (Cu⁺ + Cu⁰)/(Cu²⁺ + Cu⁺ + Cu⁰) from the XPS results (Table S3).

Acknowledgements

The authors gratefully acknowledge the financial support from the National Key Research and Development Program of China (2016YFA0602900), Natural Science Fund Council of China (NSFC 21603212, 21672204), and Chinese Academy of Sciences President's International Fellowship Initiative (2018VCA0012).

Keywords: *N*-Methylation • *N*-methylaniline • CO₂ • Copper • Heterogeneous catalysis

- a) M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* 2014, *114*, 1709-1742; b) S. G. Jadhav, P. D. Vaidya, B. M. Bhanage, J. B. Joshi, *Chem. Eng. Res. Des.* 2014, *92*, 2557-2567; c) R. Sun, Y. Xu, J. Liu, J. Mu, S. Ji, *Sci. China-Chem* 2018, *48*, 547-561.
- [2] a) Z. H. He, Q. L. Qian, J. Ma, Q. L. Meng, H. C. Zhou, J. L. Song, Z. M. Liu, B. X. Han, *Angew. Chem. Int. Ed.* 2016, *55*, 737-741; b) P. Gao, S. G. Li, X. N. Bu, S. S. Dang, Z. Y. Liu, H. Wang, L. S. Zhong, M. H. Qiu, C. G. Yang, J. Cai, W. Wei, Y. H. Sun, *Nat. Chem.* 2017, *9*, 1019-1024; c) X. H. Zhou, T. M. Su, Y. X. Jiang, Z. Z. Qin, H. B. Ji, Z. H. Guo, *Chem. Eng. Sci.* 2016, *153*, 10-20; d) G. A. Filonenko, W. L. Vrijburg, E. J. M. Hensen, E. A. Pidko, *J. Catal.* 2016, *343*, 97-105; e) A. Alvarez, A. Bansode, A. Urakawa, A. V. Bavykina, T. A. Wezendonk, M. Makkee, J. Gascon, F. Kapteijn, *Chem. Rev.* 2017; f) A. Behr, K. Nowakowski, in *CO2 Chemistry, Vol.* 66 (Eds.: M. Aresta, R. V. Eldik), Elsevier Academic Press Inc, San Diego, 2014, pp. 223-258; g) G. Centi, S. Perathoner, *Catal. Today* 2009, *148*, 191-205; h) B. Liu, S. S. Geng, J. Zheng, X. L. Jia, F. Jiang, X. H. Liu, *Chemcatchem* 2018, *10*, 4718-4732.
- a) A. Tlili, E. Blondiaux, X. Frogneux, T. Cantat, *Green Chem.* 2015, *17*, 157-168. b) K. Beydoun, K. Thenert, E. S. Streng, S. Brosinski, W. Leitner, J. Klankermayer, *ChemCatChem* 2016, *8*, 135-138.
- [4] O. Jacquet, X. Frogneux, C. D. Gomes, T. Cantat, Chem. Sci. 2013, 4, 2127-2131
- [5] Y. H. Li, X. J. Fang, K. Junge, M. Beller, Angew. Chem. Int. Ed. 2013, 52, 9568-9571.
- [6] K. Beydoun, G. Ghattas, K. Thenert, J. Klankermayer, W. Leitner, Angew. Chem. Int. Ed. 2014, 53, 11010-11014.
- [7] Y. H. Li, I. Sorribes, T. Yan, K. Junge, M. Beller, Angew. Chem. Int. Ed. 2013, 52, 12156-12160.
- [8] X. J. Cui, Y. Zhang, Y. Q. Deng, F. Shi, Chem. Commun. 2014, 50, 13521-13524.

- [9] K. Kon, S. Siddiki, W. Onodera, K. Shimizu, Chem.-Eur. J. 2014, 20, 6264-6267.
- [10] T. Toyao, S. Siddiki, K. Ishihara, K. Kon, W. Onodera, K. Shimizu, *Chem. Lett.* **2017**, *46*, 68-70.
- [11] a) X. L. Du, G. Tang, H. L. Bao, Z. Jiang, X. H. Zhong, D. S. Su, J. Q. Wang, *ChemSusChem* **2015**, *8*, 3489-3496; b) G. Tang, H. L. Bao, C. Jin, X. H. Zhong, X. L. Du, *RSC Adv.* **2015**, *5*, 99678-99687; c) T. Toyao, S. Siddiki, Y. Morita, T. Kamachi, A. S. Touchy, W. Onodera, K. Kon, S. Furukawa, H. Ariga, K. Asakura, K. Yoshizawa, K. I. Shimizu, *Chem. Eur. J.* **2017**, *23*, 14848-14859.
- [12] X. Cui, X. Dai, Y. Zhang, Y. Deng, F. Shi, Chem. Sci. 2014, 5, 649-655.
- [13] M. Tamura, A. Miura, Y. Gu, Y. Nakagawa, K. Tomishige, *Chem. Lett.* 2017, 46, 1243-1246.
- [14] L. F. Chen, P. J. Guo, M. H. Qiao, S. R. Yan, H. X. Li, W. Shen, H. L. Xu, K. N. Fan, *J. Catal.* **2008**, *257*, 172-180.
- [15] a) M. Behrens, F. Studt, I. Kasatkin, S. Kuhl, M. Havecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B. L. Kniep, M. Tovar, R. W. Fischer, J. K. Norskov, R. Schlogl, *Science* **2012**, *336*, 893-897; b) F. Studt, M. Behrens, E. L. Kunkes, N. Thomas, S. Zander, A. Tarasov, J. Schumann, E. Frei, J. B. Varley, F. Abild-Pedersen, J. K. Norskov, R. Schlogl, *Chemcatchem* **2015**, *7*, 1105-1111.
- [16] R. A. Koeppel, A. Baiker, A. Wokaun, Appl. Catal. A-Gen. 1992, 84, 77-102.
- [17] W. P. A. Jansen, J. Beckers, J. C. Van der Heuvel, A. W. D. Van der Gon, A. Bliek, H. H. Brongersma, *J. Catal.* **2002**, *210*, 229-236.
- [18] S. Kattel, P. J. Ramirez, J. G. Chen, J. A. Rodriguez, P. Liu, *Science* 2017, 355, 1296-1299.
- [19] L. J. Liu, F. Gao, H. L. Zhao, Y. Li, Appl. Catal. B-Environ. 2013, 134, 349-358.
- [20] B. R. Chen, V. H. Nguyen, J. C. S. Wu, R. Martin, K. Koci, *Phys. Chem. Chem. Phys.* 2016, *18*, 4942-4951.
- [21] M. L. Lan, B. Zhang, H. Y. Cheng, X. R. Li, Q. F. Wu, Z. Ying, Y. X. Zhu, Y. Li, X. Meng, F. Y. Zhao, *Mol. Catal.* **2017**, *43*2, 23-30.
- [22] a) W. P. Dow, Y. P. Wang, T. J. Huang, *J. Catal.* **1996**, *160*, 155-170; b)
 G. Fierro, M. LoJacono, M. Inversi, P. Porta, F. Cioci, R. Lavecchia,
 Appl. Catal. A: Gen. **1996**, *137*, 327-348; c) J.-N. Nian, S.-A. Chen, C. C. Tsai, H. Teng, *J. Phys.Chem. B* **2006**, *110*, 25817-25824; d) F. S.
 Delk, A. Vavere, *J. Catal.* **1984**, *85*, 380-388.
- [23] X. F. Yu, N. Z. Wu, Y. C. Xie, Y. Q. Tang, J. Mater. Chem. 2000, 10, 1629-1634.
- [24] R. Morrish, A. J. Muscat, *Chem. Mater.* **2009**, *21*, 3865-3870.
- [25] N. Boreriboon, X. Jiang, C. Song, P. Prasassarakich, J. CO2 Util. 2018, 25, 330-337.
- [26] S. Luo, L. Barrio, N.-P. Thuy-Duong, D. Vovchok, A. C. Johnston-Peck, W. Xu, E. A. Stach, J. A. Rodriguez, S. D. Senanayake, *J. Phys. Chem. C* 2017, *121*, 6635-6642.
- [27] a) F. L. Chan, G. Altinkaya, N. Fung, A. Tanksale, *Catal. Today* 2018, 309, 242-247; b) X.F. Liu, X.Y. Li, L.N. He, *Eur. J. Org. Chem.* 2019, 2019, 2437-2447. c) X. D. Li, S. M. Xia, K. H. Chen, X. F. Liu, H. R. Li, L. N. He, Green Chem. 2018, 20, 4853-4858.
- [28] M. C. Arevalo, J. L. Rodriguez, A. M. Castro-Luna, E. Pastor, *Electrochim. Acta* **2006**, *51*, 5365-5375.

WILEY-VCH

Entry for the Table of Contents

FULL PAPER



A non-noble metal catalyst of Cu/TiO_2 is effective for the heterogeneous *N*-methylation of *N*-methylaniline with CO_2 and H_2 , in which CHO^{*} is formed as methyl reagent, and it reacts with *N*-methylaniline to produce intermediate *N*-methylformanilide followed by its hydrogenation to *N*,*N*-dimethylaniline.

Ke Liu, Zhenbo Zhao, Weiwei Lin,* Qiang Liu, Qifan Wu, Ruhui Shi, Chao Zhang, Haiyang Cheng, Masahiko Arai, and Fengyu Zhao*

Page No. – Page No.

N-methylation of *N*-methylaniline with Carbon Dioxide and Molecular Hydrogen over a Heterogeneous Nonnoble Metal Cu/TiO₂ catalyst

