

The Investigation of the Efficient Catalytic Methylation or Formylation of Amines with CO₂

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Abstract: Conversion of abundant CO₂ into methylamine and formamide has been attempted on ordinary hydrogenation catalysts, such as Pt, Ru, Rh, Ir, Pd, Cu, Co, Ni. The high catalytic performance of amines methylation or formylation with CO₂ was obtained on Cu-base or Au-base nanocatalysts, respectively. The reaction conditions, including temperature, pressure, concentration, were optimized. Combined with various characterization results, the conversion and selectivity to different products could be ascribe to electronic effect and acid-base properties of catalysts surface. The methylation or formylation with CO₂ provide a renewable pathway for the production of methylamine and formamide.

Keywords: CO₂, nanocatalysts, amines, methylation, formylation.

1. Introduction (11-point boldface)

Energy crisis and resource shortage have been to the two of the biggest problems in our world. People have been paying more and more attention on the conversion of carbon dioxide to fuels and chemicals. It is extremely important that the coupling of carbon dioxide and functional compounds in both basic research and industry application, because carbon dioxide is a C₁ resource which is abundant, renewable and nontoxic. The methylation or formylation amines with carbon dioxide and hydrogen created new approaches for the production of some highly valuable chemicals. In alternative approach would be to first generate hydrogen via a photo-electrochemical process or an electrochemical process using electrical power from photovoltaic cells or wind turbines. Then, the hydrogen were used in a heterogeneously catalysis process to reduce CO₂ to methanol, a sustainable source of fuel and chemical products would be established.

In this abstract, common hydrogenation catalyst which catalyze the methylation or formylation of amines with carbon dioxide, such as Pt, Ru, Rh, Ir, Pd, Cu, Co, Ni and so on, were invested to compare their catalysis effect.

2. Experimental (or Theoretical)

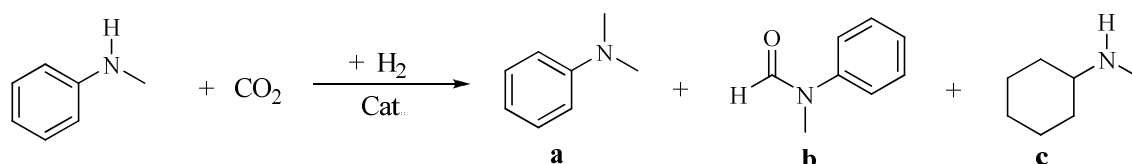
The catalysts with 10 wt% Cu, Ni, Co supported over different oxides (Al₂O₃, MgO, TiO₂, ZrO₂, CeO₂ and ZnO) as well as Cu-Al₂O₃ with Cu loadings from 2 to 40 wt%, were prepared by co-precipitation (CP) method. The catalysts with 5 wt% Pt, Pd, Ru, Rh, Ir supported over Al₂O₃, 5 wt% Au supported over different oxides (Al₂O₃, MgO, TiO₂, ZrO₂, CeO₂ and ZnO) as well as Au-MgO with Au loadings from 1 to 10 wt%, were prepared by impregnation (IM) method.

The catalysts were characterized with XRD, BET, XPS, FT-IR, Raman, H₂-TPR, CO₂/NH₃-TPD, pyridine-IR and some in situ experience.

The methylamine and formamide of N-methylaniline with CO₂ reactions were carried out in a stainless steel autoclave reactor (100 mL) at a stirring speed of 800 r/min. Prior to each reaction, the calcined catalyst sample was reduced at 623 K in H₂ atmosphere at a flow of 40 mL/min for 3 h.

3. Results and discussion

Table 1. Conversion and selectivity of methylamine and formamide over various catalysts.



Entry	Catalysts	Conversion / %	Selectivity / %			
			a	b	c	Others
1	5Pt-Al ₂ O ₃	1.5	39.5	57.9	-	2.6
2	5Pd-Al ₂ O ₃	34.9	1.6	-	96.9	1.5
3	5Ru-Al ₂ O ₃	33.6	1.7	-	94.4	3.9
4	5Rh-Al ₂ O ₃	2.6	0.9	81.3	-	17.8
5	5Au-Al ₂ O ₃	7.5	3.3	90.3	-	6.4
6	5Ir-Al ₂ O ₃	5.7	2.8	76.1	-	21.1
7	10Ni-Al ₂ O ₃	10.8	10.7	27.6	52.7	8.9
8	10Co-Al ₂ O ₃	1.3	92.8	-	-	7.2
9	10Cu-Al ₂ O ₃	18.2	37.6	54.8	-	7.6

Reaction conditions: 3.0 g N-methylaniline, 27 g 1,4-dioxane, 0.1 g Cu or 0.01 g Au, 2 MPa H₂ + 2 MPa CO₂, 433 K, 8 h. Others include some undetermined products.

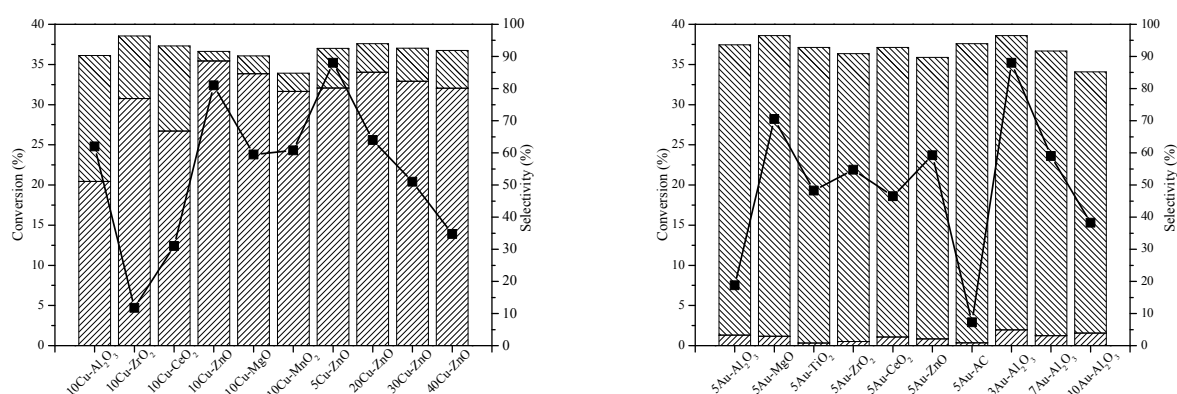


Figure 1. Catalytic performance of methylamine over Cu-base catalysts and formamide over Au-base catalysts.

Reaction conditions: 3.0 g N-methylaniline, 27 g 1,4-dioxane, 0.1 g Cu or 0.01 g Au, 2.0 MPa CO₂ + 2.0 MPa H₂, 180 °C for Au-base catalysts or 200 °C for Cu-base catalyst, 8 h.

4. Conclusions

The methylation and formylation of N-methylaniline with CO₂ over catalysts containing Pt, Ru, Rh, Ir, Pd, Cu, Co, Ni or Au were investigated. The excellent performance of methylation or formylation of N-methylaniline with CO₂ was achieved over Cu-ZnO or Au-MgO catalysts, separately. The experiment results indicate that the methylation of N-methylaniline with CO₂ can be efficiently catalyzed by the Cu-ZnO catalyst with 10 wt% Cu loading at 200 °C, while the formylation of N-methylaniline with CO₂ can be efficiently catalyzed by the Au-MgO catalyst with 5 wt% Au loading at 180 °C. The selectivity for methylation and formylation of amines with CO₂ could be influenced by the change of reaction parameters. The efficient catalytic methylation and formylation are significant for the CO₂ conversion.

References

1. Aresta M, Dibenedetto A, Angelini A., *Chem. Rev.*, 114 (2014) 1709.
2. Y. Li, X. Cui, K. Dong, K. Junge, M. Beller, *ACS Catal.*, 7 (2017) 1077.
3. Preti, D.; Resta, C.; Squarcialupi, S.; Fachinetti, G., *Angew. Chem. Int. Ed.*, 50 (2011) 12551.
4. Filonenko, G. A.; Vrijburg, W. L.; Hensen, E. J. M.; Pidko, E. A., *J. Catal.*, 343 (2016) 97.
5. Wang, Y.; Zhang, J.; Chen, H.; Zhang, Z.; Zhang, C.; Li, M.; Wang, F., *Green Chem.*, 19 (2017) 88.