

# A highly dispersed Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15 nanocatalyst: Preparation, characterization and the catalytic application in direct synthesis of dimethyl carbonate

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## ABSTRACT

A highly dispersed Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15 nanocatalyst was prepared by incipient wetness impregnation. It was noteworthy that SBA-15 should be modified by ethylene glycol (EG) before the impregnation. The results of BET and TEM investigations indicated that Cu-Ni nanoparticles uniformly dispersed on the internal pore surface. Besides, the catalyst prepared by treated SBA-15 exhibited higher catalytic activity than that obtained from non-treated SBA-15 in direct synthesis of dimethyl carbonate. The high catalytic activity of Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15-EG nanocatalyst could be attributed to the excellent dispersion of active metal nanoparticles and strong interaction between the metal particles and the surface of our carrier.

**Keywords:** Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15, nanoparticles, dispersion, ethylene glycol, dimethyl carbonate

## 1 INTRODUCTION

Dimethyl carbonate (DMC) is an environmentally benign chemical of wide versatility as well as a non-toxic substitute for dimethyl sulfide and phosgene, which are toxic and corrosive as methylation or carbonylating agents [1-3]. Moreover, due to its high oxygen content and reduced environmental impact, DMC can also be used as an oxygenating fuel additive [4]. Up to date, some catalysts have been reported to be effective for one-step synthesis of DMC from CH<sub>3</sub>OH and CO<sub>2</sub>, including CeO<sub>2</sub>[5], Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>[6]. Bian et al explored bimetallic Cu-Ni active phases supported on carbonaceous materials, including graphite oxide (GO)[7], thermally expanded graphite[8], and so on.

Mesoporous silica SBA-15 has attracted significant attention in catalysis due to its highly ordered hexagonal structure with narrow pore size distribution, thick pore wall, high surface areas[9]. SBA-15 has been successfully applied as a support to prepare supported metal catalysts[10]. It is considered that improving the dispersion of supported active component and increasing the thermal

stability of the catalyst are in favor of catalytic reaction. Nevertheless, Conventional impregnation method cannot assure the incorporation of active species into the support mesopores. The unsatisfactory dispersion of active centers also cause the confusion on the heterogeneity of the impregnated catalysts. It is believed that the nature of the support seriously affects the properties of catalysts via modulating the interaction between the supported active components and support to reduce metal aggregation.

In the present work, SBA-15 was modified by ethylene glycol (EG) at room temperature before impregnation of metal precursors. The main goal is to explore the influence of the modified SBA-15 on the dispersion of supported Cu-Ni nanoparticles and the interaction between the supported metal species and support.

## 2 EXPERIMENTAL

### 2.1 Preparation

The mesoporous silica SBA-15 was synthesized according to a hydrothermal method [9]. SBA-15 was treated with ethylene glycol (EG) before the impregnation of metal precursors, for 1 h at room temperature by incipient wetness impregnation method. The samples were dried in air at 373 K for 12 h. The catalyst was prepared by two sequential steps where in the first one the impregnation was carried out by aqueous solution of Zr(NO<sub>3</sub>)<sub>2</sub>·5H<sub>2</sub>O and Ce(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O with molar ratio (Ce/Zr=1) to obtain Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15 with 10% Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> loading at the end. The Cu-Ni was introduced in the second step by using aqueous solutions of Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O with 15% Cu-Ni loading. After that, the sample was dried over night at 373 K, following calcination at 773 K for 4 h and reduction in a 5% H<sub>2</sub>/N<sub>2</sub> flow at 773K for 3 h. This catalyst was marked as Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15-EG. As comparison, Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15 was also prepared by the same method using non-pretreated SBA-15. For characterization of reduced catalysts, the catalysts were passivated by 99% nitrogen at room temperature to protect the reduced copper-nickel after reduction.

## 2.2 Characterization

X-ray diffraction (XRD) analysis was performed using an X-ray diffraction apparatus (XRD-7000) with Cu K $\alpha$  (40 kV, 40 mA) radiation, TEM images of the passivated catalysts were determined by a TecnaiG<sup>2</sup>-F20S-TWIN microscope, Temperature-programmed reduction (TPR) experiments were carried out in a quartz tube reactor using 0.2 g calcined catalysts, The textural properties of the support and Cu-Ni supported catalysts were measured by N<sub>2</sub> sorption at liquid N<sub>2</sub> temperature, using a gas sorption analyzer NOVA2000e.

The synthesis of DMC was carried out in a stainless steel autoclave reactor with an inner volume of 100 mL equipped with a stirrer and an electric heater. In a typical reaction sequence. 8 g CH<sub>3</sub>OH and 1 g of catalyst was introduced into the autoclave, then the reactor was purged with carbon dioxide. After pressurizing the autoclave to a certain pressure with CO<sub>2</sub>, the reactor was heated and stirred constantly. The products were cooled to room temperature. Then the gas was collected in a gas bag, and an inner standard (benzene, 1 g) was added into the liquid. Products in both the gas and liquid phases were analyzed by gas chromatograph (GC) equipped with TCD detector and FID detector. The separation column packing is Porapak Q for TCD-GC and SE-54 for FID-GC.

## 3 RESULTS AND DISCUSSION

The N<sub>2</sub> adsorption-desorption isotherms of SBA-15 support and those corresponding to bimetallic Cu-Ni catalysts are shown in Figure 1. As-synthesized SBA-15 displayed a typical Type IV isotherm according to the BDDT classification and standard H1 type hysteresis loop by IUPAC classification which is associated with porous materials consisting of well-defined cylindrical channels. SBA-15 exhibited a sharp step increase in nitrogen uptake at relative pressures of 0.6-0.8, arising from the capillary condensation of nitrogen inside the primary mesopores with a uniform pore diameter. The broad hysteresis loop is caused by the presence of a uniform array of mesopores connected by micropores, thus hampering the filling and emptying of the accessible volume [11]. The isotherms of Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15 and Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15-EG catalysts are similar to that of the SBA-15 support. The results indicate that the mesoporous structure of our SBA-15 was hold in all of our fresh catalysts even after impregnation. However, the sharp inflection shifts toward lower relative pressures, suggesting that the formation of Cu-Ni phases have already dispersed in the internal pore surface and the hexagonally ordered structure of SBA-15 has been partly destroyed in the samples.

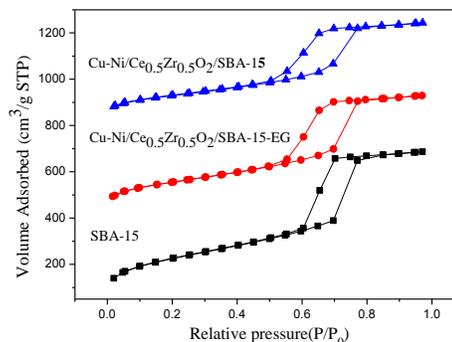


Figure 1: N<sub>2</sub> adsorption-desorption isotherms of the support and the fresh catalysts

The high stability of as-synthesized SBA-15 was further confirmed by small-angle XRD patterns. Low angle patterns evidence the presence of an ordered mesoporous structure before and after incorporating the different active phases to the support (Figure 2). All of the blank substrate and activated supported catalysts show remarkable peaks for the mesoporous silica (100), (110) and (200) planes, indicating a high degree of hexagonal mesoscopic organization. When Cu-Ni is loaded onto SBA-15, the d<sub>100</sub> peak shifts to higher angle, and the d<sub>100</sub>, d<sub>110</sub>, and d<sub>200</sub> peaks attenuate in intensity. This is consistent with previous reports in the literature[12]. It is possible that mostly dispersed Cu-Ni are embedded into the channel of SBA-15. In this case, the d-spacing of the 100 plane is decreased resulting in the shift of the d<sub>100</sub> peak to higher angle. The XRD patterns of Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15-EG catalyst are essentially identical to that of Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15 catalyst.

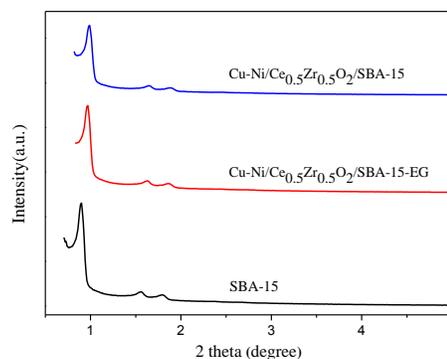


Figure 2: Low angle XRD patterns of the fresh catalysts

The wide-angle XRD patterns of various fresh catalysts are displayed in Figure 3. For the two typical diffraction peaks at 43.57  $^{\circ}$  (111), 51.13  $^{\circ}$  (200) could be assigned to diffraction of metal phase Cu, Ni and cubic phase Cu and Ni alloy. XRD results indicates that alloy phase Cu-Ni were

partly formed in reduction and activation process. The fresh Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15 catalyst, prepared by non pretreated SBA-15, exhibits sharp and strong Cu-Ni alloy peaks. There was no Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> diffraction peak for the samples, reflecting a uniform dispersion of Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> species on the surface of catalysts. Nevertheless, The Cu-Ni alloy peaks of Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15-EG catalyst were broad and weak, indicating the more highly dispersed Cu-Ni nanoparticles at the carrier surface. And it demonstrated that employing EG pretreated SBA-15 was favorable for the dispersion of Cu-Ni nanoparticles. It is also observed a well-ordered hexagonal array of cylindrical channels in accordance with low angle XRD patterns and the N<sub>2</sub> adsorption-desorption isotherms.

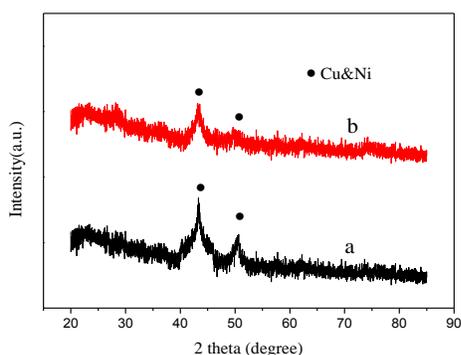


Figure 3: X-ray diffraction patterns of catalysts: (a) Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15, (b) Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15-EG

TEM images of Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15 are presented in Figure 4(a). The places with darker contrast could be assigned to the presence of copper-nickel particles with different dispersion. The small dark spots in the image could be ascribed to copper-nickel particles embedded into the mesostructured support, hence the growth of those particles were limited by silica walls. The larger dark areas over the channels most likely corresponded to the copper-nickel agglomerates on the external surface without the limitation of pores. These particles were present in a wide distribution of sizes. On the other hand, the morphology of Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15-EG was characterized by TEM. As shown in Figure 4(b), the long-range ordered structure was preserved, which was in agreement with the N<sub>2</sub> adsorption-desorption results. It is proved that indicate the pretreated SBA-15 by EG extremely enhanced the dispersion of species where no particles agglomerations were noticed at the external surface of the SBA-15 grains. The Cu-Ni particles were obviously smaller in Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15-EG than in Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15.

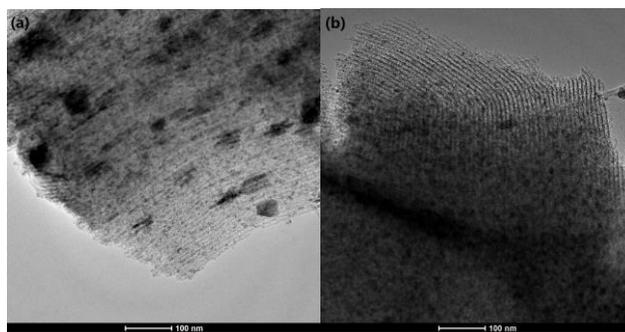


Figure 4: TEM images of the fresh catalysts: (a) Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15, (b) Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15-EG

The reduction performance of various catalysts was determined by temperature-programmed reduction (TPR). As shown in Figure 5, Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15 catalyst typically show one reduction zone between 473 and 533K. The sample profile corresponds to the reduction of CuO and NiO particles with weak metal-support interaction. Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15-EG catalyst presents two reduction zones. We consider that the reduction at low below than 573K could be ascribed to CuO and NiO particles with lower metal-support interaction. On the other hand, The catalyst show a broader peak at 673-873K, and can be attributed to Cu-Ni species on the pore wall surface and a highly stable Cu-Ni phase with strong interaction with the support. Thus, the shift of the reduction profile of the SBA-15 supported sample towards higher temperatures for the modified SBA-15 catalyst indicates that the modified silica support increased Cu-Ni phase and the support interaction, contributing to the decreased reducibility and the increased dispersion of supported copper-nickel. Moreover, the stronger metal-support interaction in promoted sample agrees with the smaller crystallites sizes found in the catalyst.

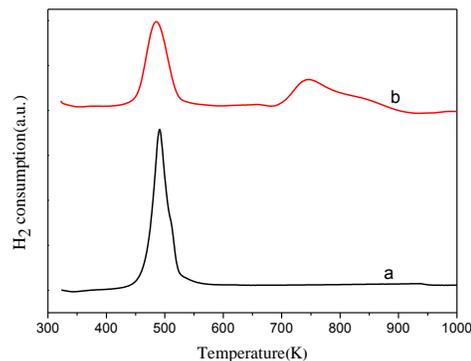


Figure 5: The H<sub>2</sub>-TPR profiles for different catalysts: (a) Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15, (b) Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15-EG

The activity test for Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15 and Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15-EG catalysts in direct synthesis of

DMC from CH<sub>3</sub>OH and CO<sub>2</sub> is illustrated in Figure 6. Catalytic reaction was carried out at different temperatures in a range of 363-413 K. From Figure 6, it could be seen that when the reaction temperature increased, the conversion of CH<sub>3</sub>OH over Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15 and Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15-EG catalysts remarkably increased from 363 to 393 K, and then decreased again when temperature went up to 413 K. Under the same reaction conditions, Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15 catalyst has lower conversion of CH<sub>3</sub>OH. Increasingly, The catalyst prepared by ethylene glycol (EG) can improve the conversion of CH<sub>3</sub>OH. Especially, at low reaction temperature (363-393 K), the conversion of CH<sub>3</sub>OH has an obvious increase. It is reported that the activation of CO<sub>2</sub> is structure sensitive and small particle size promotes its activation. Therefore, the Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15-EG catalyst exhibited higher activity in direct synthesis of dimethyl carbonate due to its higher dispersion of supported copper-nickel.

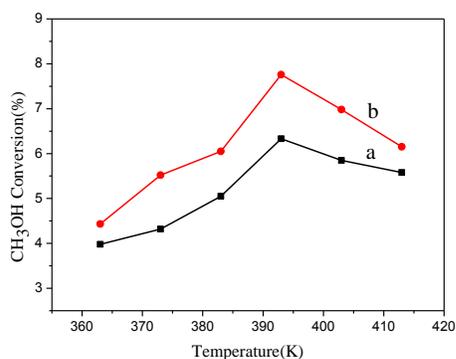


Figure 6: The conversion of CH<sub>3</sub>OH of various catalysts: (a) Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15, (b) Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15-EG (reaction condition: catalyst weight, 1.0 g; CH<sub>3</sub>OH, 8 g; reaction pressure, 8.0 MPa)

## 4 CONCLUSION

In a word, EG pretreated SBA-15 was employed to prepare the Cu-Ni supported catalyst, which exhibited higher activity and excellent stability in direct synthesis of dimethyl carbonate. Since the EG pretreatment significantly modified the surface properties of SBA-15 support, The smaller Cu-Ni particle size and strong metal-support interaction formed more active sites and reduced copper-nickel sintering, contributing to high activity and excellent stability of Cu-Ni/Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub>/SBA-15-EG catalyst in direct synthesis of dimethyl carbonate.

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## REFERENCES

- [1] Y. Ono, Catalysis in the production and reactions of dimethyl carbonate, an environmentally benign building block, *Appl. Catal. A: General*, 155,133-166, 1997.
- [2] E. Leino, P. Maki-Arvela, V. Eta, Conventional synthesis methods of shortchain dialkylcarbonates and novel production technology via direct route from alcohol and waste CO<sub>2</sub>, *Appl. Catal. A: General*, 383,1-13, 2010.
- [3] D. Delledonne, F. Rivetti, U. Romano, Developments in the production and application of dimethylcarbonate, *Appl. Catal. A: General*, 221, 241-251, 2001.
- [4] M. A. Pacheco, C. L. Marshall, Review of dimethyl carbonate (DMC) Manufacture and its characteristics as a fuel additive. *Energy Fuel*, 11, 2-29, 1997.
- [5] M. Aresta, A. Dibenedetto, C. Pastore, A. Angelini, B. Aresta, I. Papai, Influence of Al<sub>2</sub>O<sub>3</sub> on the performance of CeO<sub>2</sub> used as catalyst in the direct carboxylation of methanol to dimethylcarbonate and the elucidation of the reaction mechanism. *J. Catal.* 269, 44-52, 2010.
- [6] Z.F. Zhang, Z.T. Liu, Z.W. Liu, J. Lu, DMC Formation over Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> Prepared by Complex-decomposition Method, *Catal. Lett.* 129, 428-436, 2009.
- [7] J. Bian, M. Xiao, S.J. Wang, X.J. Wang, Y.X. Lu, Y.Z. Meng, Highly effective synthesis of dimethyl carbonate from methanol and carbon dioxide using a novel copper-nickel/graphite bimetallic nanocomposite catalyst, *Chem. Eng. J.* 147, 287-296, 2009.
- [8] J. Bian, M. Xiao, S.J. Wang, Y.X. Lu, Y.Z. Meng, Novel application of thermally expanded graphite as the support of catalysts for direct synthesis of DMC from CH<sub>3</sub>OH and CO<sub>2</sub>, *J. Colloid Interface Sci.* 334, 50-57, 2009.
- [9] D. Zhao, J. Feng, Q. Huo, N. Melosh, G.H. Frederickson, B.F. Chmelka, Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores, *Science*, 279, 548-52, 1998.
- [10] A. Ungureanu, B. Dragoi, A. Chiriac, Composition-Dependent Morphostructural Properties of Ni-Cu Oxide Nanoparticles Confined within the Channels of Ordered Mesoporous SBA-15 Silica. *Appl. Mater. Interfaces*, 5, 3010-3025, 2013.
- [11] H.L. Zhang, C.J. Tang, F. G, L. Dong, Direct synthesis, characterization and catalytic performance of bimetallic Fe-Mo-SBA-15 materials in selective catalytic reduction of NO with NH<sub>3</sub>, *Micropor. Mesopor. Mater.* 151,44-55, 2012.
- [12] L.B. Sun, J.H. Kou, Y. Chun, J. Yang, F.N. Gu, Y. Wang, New attempt at directly generating superbasicity on mesoporous silica SBA-15. *Inorg Chem*, 47, 4199-4208, 2008.