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Fast catalytic conversion of diethylene glycol to morpholine over thermally stable Zn promoted Cu-NiO/Al_2O_3 catalyst prepared *via* combustion approach

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ABSTRACT

Highly active and thermally stable M-Cu-NiO/Al_2O_3 catalysts (M represents Al/La/Mg/Zn) were prepared by combustion method and applied in diethylene glycol (DEG) conversion to morpholine (Mp). Copper species preserved relatively small crystallite size (19 nm), high dispersion (40.3%) and high surface area (272 m^2/g) in M-Cu-NiO/Al_2O_3 catalysts. High dispersion and intimate contact of copper with Al and La/Mg/Zn synergistically enhanced DEG conversion and Mp selectivity. Addition of promoter *i.e.* La, Mg, or Zn facilitated the formation of surface defects and isolated species to inhibit migration and aggregation of Cu moities during calcination as well as in high temperature DEG conversion reaction. Compared to other catalysts, Zn-Cu-NiO/Al_2O_3 combusted catalyst exhibited the highest DEG conversion of 99% (55% higher than impregnated catlayst) and Mp selectivity (95%), even at a high DEG space velocity of 0.8 mL g^{-1} h^{-1}. Moreover, Zn-Cu-NiO/Al_2O_3 exhibited excellent thermal stability *i.e.* less than 2% decrease in initial DEG conversion after 80 h of reaction. The catalysts followed an overall activity order of: Zn-Cu-NiO/Al_2O_3 > Mg-Cu-NiO/Al_2O_3 > La-Cu-NiO/Al_2O_3. The catalysts were characterized by XRD, BET surface area, SEM and XPS techniques. The present study, credited to its cost-effective nature, simplicity of operation and high efficiency, can be effectively applied for DEG conversion to Mp on industrial level.

1. Introduction

Morpholine (Mp) as a typical heterocyclic compound has great industrial importance and a wide range of applications [1]. It can be functionalized as a kind of chemical intermediate in drug/pesticide discovery [2,3], and rubber and textile industries [4]. Besides these applications, Mp shows good biodegradability, which has attracted considerable interest in the field of catalysis and antioxidant applications [5,6].

Over the last two decades, a number of concise and inventive methods have been proposed to synthesize Mp and its derivatives [2], among which catalytic amination of vapor phase diethylene glycol (DEG) is the most widely practiced [7,8]. As this process is catalytic, development of novel catalyst and its structural design are the critical factors which can affect activity as well as selectivity of the process. In this connection, Cu(Ni)-based colloidal catalysts have gained considerable attention in amination of alcohol recently [9–12] attributed to their low cost and high resistance to poisoning. Cu and Ni based catalysts have been reported with superior selectivity towards C—O bond cleavage than C—C bonds *via* hydrogenolysis reaction [13,14]. However, some bi/ternary Cu-Ni based catalysts have been found to exhibit low activity and thermal stability due to poor dispersion of Cu/Ni species [15] and aggregation of Cu(Ni)O crystallites at high temperature for H_2 production (> 200 °C) [16,17]. Thus, in case of catalytic Mp synthesis, the dispersion of active species and thermal stability with high anti-sintering ability in catalysts [18,19] are crucial factors and hot research points which require considerable attention.

Many attempts have been made to design new methods for catalyst synthesis with better dispersion of active species and enhanced thermal stability. Zhao et al. [15] and Avgouropoulos et al. [20] applied combustion approach for the synthesis of Ni-Al_2O_3 and CuO-CeO_2 catalysts with a significantly smaller crystal size of Cu or Ni than that prepared by impregnation technique, which resulted in 10–15 % increased CO conversion. Similarly, the incorporation of an extra promoter can also

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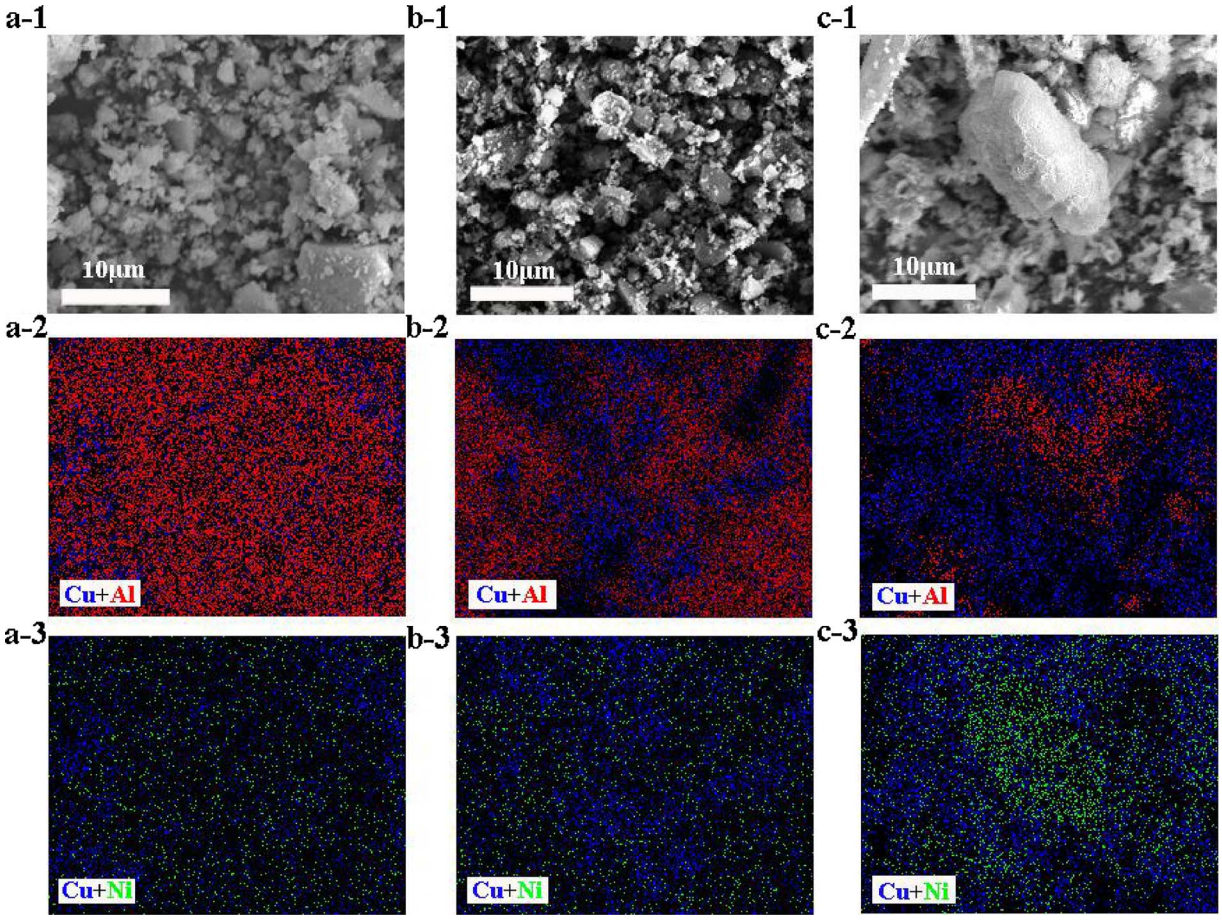

Fig. 1. SEM images and elemental mappings of: (a: CS-Al_1-Zn, b: CS-Al_1 and c: IS-Al_1-Zn) (a1–c1) SEM images of the as-prepared catalysts; (a2–c2) Overlay of binary metal elemental maps of Cu (blue) and Al (red); (a3–c3) Overlay of binary metal elemental maps of Cu (blue) and Ni (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

enhance the dispersion of active species and thermal stability. Hu et al. [21] studied that addition of Mn to Cu/Al_2O_3 catalysts can give rise to high dispersion of Cu nanoparticles, a large number of surface defects and exceptional catalytic hydrogenation performance in dimethyl succinate to γ-butyrolactone with stability enduring up to 100 h. Papavasiliou et al. [22] reported that 0.05% of ZnO doped into $CuO\text{-}CeO_2$ catalysts led to significantly smaller crystal size of CeO_2 than parent catalyst, which increased CO conversion from 38 to 51% in steam reforming of methanol. Similarly, few reports based on the conversion of DEG to Mp over supported Ni and Cu based catalysts can be found (Table S1), most of which suffer either from low DEG conversion or Mp selectivity.

Up to the authors' knowledge, no reports on the incorporation of Al, La, Mg and Zn to $Cu\text{-}NiO/Al_2O_3$ used for the conversion of DEG to Mp can be found. Thus, in this work, a series of $Cu\text{-}NiO/Al_2O_3$ catalysts promoted by oxides of Al, La, Mg, and Zn were synthesized *via* combustion approach and tested in DEG conversion to Mp with high activity, thermal stability and selectivity. Rapid synthesis process and homogeneous mixing resulted in high dispersion of active species in catalytic samples. The physicochemical properties of catalysts were characterized by X-Ray diffraction (XRD), N_2O titration experiments, N_2 adsorption/desorption, hydrogen temperature programmed reduction (H_2-TPR), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). Furthermore, effects of preparation methods, Cu/Al ratio, and liquid hour space velocity (LHSV) on gas phase DEG conversion and Mp selectivity over promoter-loaded $Cu\text{-}NiO/Al_2O_3$ catalysts were systematically investigated. Thermal stability performance and durability test of the catalysts were investigated using temperature-swing reaction.

2. Experimental

2.1. Materials and reagents

Different metal nitrate salts *i.e.* ($Cu(NO)_2{\cdot}3H_2O$, $Ni(NO_3)_3.6H_2O$, Al $(NO_3)_3.9H_2O$, $La(NO_3)_3.6H_2O$, $Zn(NO_3)_2.6H_2O$ and Mg $(NO_3)_2.6H_2O$, > 99.0%, AR) were purchased from Guangdong Guanghua Sci-Tech Co. Ltd. Al_2O_3, Ethylene glycol ($C_2H_6O_2$, ≥99.0%) and DEG ($C_4H_{10}O_3$, ≥99.0%) were purchased from Sinopharm Chemical Reagents Co. Ltd. All other solvents and reagents were obtained from commercial sources and used without further purification.

2.2. Catalyst preparation

The $M\text{-}Cu\text{-}NiO/Al_2O_3$ catalysts were prepared by combustion method [15]. Firstly, $Cu(NO_3)_2.3H_2O$, $Ni(NO_3)_2.6H_2O$ and Al $(NO_3)_3.9H_2O$ were dissolved in deionized water with Cu:Ni:Al molar ratio of 5:1:x (x = 0, 1, 4 and 10), and Cu, Ni, Al as 10, 1.8 and 0.84 wt.% of the support. The mixture was moderately stirred at 293 K till dissolution, to which 2 wt.% promoter specie (Mg, La, or Zn) was added using their respective nitrate precursors. 6 g pre-calcined Al_2O_3 (particle size of 180–325 μm) at 973 K, was added to this mixture followed by the addition of 5 mL ethylene glycol under constant stirring. The resulting mixture was kept in an ultrasound bath at 47 kHz with a power of 30 W for 1 h. The mixture was calcined in muffle furnace at 773 K for 5 h at a heating rate of 5 K/min.