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Continuous synthesis of $N$-ethylethylenediamine over supported Cu–Zn–La catalysts

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A series of Cu-based catalysts were prepared and employed in the $N$-ethylation of ethylenediamine with ethanol in a fixed-bed reactor. Satisfying results were obtained using Cu–Zn–La/Al$_2$O$_3$ as a catalyst. In addition, Cu–Zn–La/SiO$_2$, Cu–Zn–La/Al$_2$O$_3$ and Cu–Zn–La/HZSM-5 were characterized by the Brunauer–Emmett–Teller method (BET), H$_2$-temperature program reduction (H$_2$-TPR), X-ray diffraction (XRD), transmission electron microscopic measurements (TEM) and NH$_3$-temperature programmed desorption (NH$_3$-TPD) in order to investigate the influence of supports on their catalytic performance. It was found that both the BET surface area and the acidity of the support are key factors in the catalytic performance. Moreover, reaction parameters including temperature, hydrogen pressure and liquid hourly space velocity were optimized. Under optimal conditions, a 73.3% conversion of ethylenediamine and a 71.2% selectivity of $N$-ethylethylenediamine were achieved. Finally, the lifetime of the catalysts was evaluated and the reaction proceeded continuously for over 200 h.

Keywords: $N$-ethylation, $N$-ethylethylenediamine, Cu–Zn–La catalysts

Introduction

It is known that $N$-ethylethylenediamine (EEDA) always serves as one of the most important building blocks and is widely employed in the synthesis of some antibacterials including piperacillin, cepoperazone and cefbuperazone (Bernady & Mogolesko, 1980; Tahara et al., 1983). Therefore, the synthetic method of EEDA has been intensively studied. Generally, $N$-alkylated amines can be synthesized from amines and alkylhalides with stoichiometric amounts of inorganic bases (Buchwald et al., 2006; Salvatore et al., 2002). Though this nucleophilic substitution proceeds smoothly, it always suffers from poor selectivity and serious environmental contamination. By contrast, $N$-alkylation of amines with alcohols provides a greener method yielding $N$-alkylated amines (Ishida et al., 2012). Recently, Chen et al. (2010) investigated $N$-alkylation with $\gamma$-Al$_2$O$_3$ as the catalyst. However, the rigorous reaction conditions were still an obstacle. Also some noble metals have been employed for the $N$-alkylation of amines with alcohols. For example, Michlik and Kempe (2010) and Hamid et al. (2009) reported $N$-alkylation with iridium and ruthenium complexes, respectively. Meanwhile, silver has been applied in this reaction by Liu et al. (2012). However, all of these catalysts were expensive and non-recoverable. In addition, Yamakawa et al. (2004) studied $N$-alkylation of ethylenediamine (EDA) over CuO–ZnO/Al$_2$O$_3$. Similarly, Wang et al. (2007) employed Cu–Zn–Al for the synthesis of EEDA observing catalyst deactivation. In this work, Cu–Zn–La/Al$_2$O$_3$ was selected for the synthesis of EEDA and satisfying EDA conversion and EEDA selectivity were obtained. Moreover, this catalyst was able to continuously operate for 200 h without any deactivation offering thus tremendous potential for large-scale productions. Besides, the influence of different supports including

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SiO$_2$, Al$_2$O$_3$ and HZSM-5 on this N-alkylation process was investigated using the Brunauer–Emmett–Teller method (BET), H$_2$-temperature program reduction (H$_2$-TPR), X-ray diffraction (XRD), X-ray diffraction (XRD), transmission electron microscopic measurements (TEM) and NH$_3$-temperature programmed desorption (NH$_3$-TPD). It was found that the BET surface area and the acidity of the support both play an important role in the catalytic performance of Cu–Zn–La/Al$_2$O$_3$.

**Experimental**

All catalysts were prepared using the conventional coprecipitation–kneading method (Wang et al., 2007; Song et al., 2015). A metal nitrate aqueous solution and a sodium carbonate aqueous solution were simultaneously added dropwise to distilled water at 353 K under mechanical stirring. During this process, pH of the system was maintained at approximately 8. When the addition was finished, the precipitate was aged for an hour, filtered, washed with distilled water, dried and pulverized. The powder was calcined at 623 K for 3 h and then kneaded vigorously with a certain amount of supports. After drying in air for 6 h at 383 K, the catalysts were calcined at 823 K for 4 h and then reduced before use.

Textural properties of supports and the corresponding supported catalysts were studied by N$_2$ adsorption and desorption experiments using a NOVA 2000e analyzer (Quantachrome, USA). XRD of the experimental samples was measured on a Rigaka D/max 2500 X-ray diffractometer with Cu K$_\alpha$ radiation (40 kV, 100 mA) in the scan range of 10–90°. The H$_2$-TPR measurements were recorded on a Micromeritics 2910 (USA) apparatus equipped with a thermal conductivity detector (TCD) at the heating rate of the samples of 10°C min$^{-1}$ from ambient temperature to 900°C in a mixture of 5 vol. % of H$_2$ in N$_2$. TEM analysis of the samples was performed using a JEOL electron microscope (JEM-2010, Japan) operated at 200 keV. NH$_3$-TPD was carried out on a TP-5000 instrument (Beijing Tianpu Instrumnet and Technology, China) with TCD.

N-ethylation of EDA was performed in a fixed-bed tubular reactor (i.d. = 15 mm; length = 660 mm), which was charged with catalyst (40.0 mL). The mixture of EDA and ethanol (1 : 5 mole ratio of EDA to ethanol) was injected at the flow rate of 0.3 mL min$^{-1}$ with the help of a syringe pump. The reaction temperature was controlled by a PID cascade controller and the hydrogen pressure in the reaction system was set with help of a hydrogen regulator. After reaching a steady state of the reaction system, the reaction mixture was collected each hour and analyzed by gas chromatography (SE-30 capillary column; Lanzhou Institute of Chemical Physics, China): 60 m × 0.25 mm, 0.2 µm film thickness). Composition of the reaction mixture was confirmed by GC–MS (HP-1 capillary column: 30 m × 0.25 mm, 0.2 µm film thickness).

**Results and discussion**

N-ethylation of EDA to EEDA is a very complicated reaction. Except for the target product, many by-products including N-ethyl products of EEDA, piperazine (PIP) and its derivatives are also produced (Fig. 1).

Thus, it is very hard to improve the conversion of EDA with high selectivity of EEDA. Based on our preliminary work (Sun et al., 2012; Wu et al., 2012), Cu-based catalysts were employed in this reaction.

Table 1 clearly indicates that Cu–Zn/Al$_2$O$_3$ and Cu–La/Al$_2$O$_3$ both exhibited better catalytic performance than Cu/Al$_2$O$_3$. The catalytic performance of Cu–Zn–La/Al$_2$O$_3$ was optimal. When Cu–Zn–La/Al$_2$O$_3$ was employed in this reaction, a 73.3 % conversion of EDA and a 71.2 % selectivity of EEDA