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High Activity and Selectivity of Cu/SiO_2 Catalyst for the Direct Synthesis of Indole

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Abstract: Copper supported over silica exhibited very high activity and selectivity for the direct synthesis of indole at atmospheric pressure. Under the reaction temperature of 325°C,the yield of indole could obtain 88%.

Keywords: Cu/SiO_2 catalyst, direct synthesis of indole, aniline, ethylene glycol.

Indole is an important heterocycle material because of its industrial, agricultural and medical applications[1-3]. There are many methods to produce indole[4]. One of the most promising routes, from an industrial point of view, seems to be the direct synthesis from aniline and ethylene glycol[5]. Since it is direct and simple from reactants to indole and utilizes inexpensive starting materials, a low cost process on the industrial scale could be possible. For the direct synthesis of indole, $Co\text{-}Ag/SiO_2\text{-}ZnO$ was regarded as the best and the only catalyst in industry. With this catalyst the yield of indole was 78%[6]. We now report a first example of Cu/SiO_2 catalyst, prepared by impregnation-calcination-reduction, which was very highly active and cheap in the direct synthesis of indole from aniline and ethylene glycol at atmospheric pressure.

Cu/SiO_2 catalysts were prepared by impregnation of SiO_2 (310 m^2/g, 40-60 mesh) with appropriate amounts of aqueous solution of copper nitrate. After impregnating for 24 h at room temperature, the samples were dried at 120°C for 4 h then calcined by temperature programm heating in air from RT to 500°C at a rate of 3°C/min and holding at 500°C for 4 h. Prior to activity tests, the calcined sample (3 mL) was reduced in a mixture gas composed of H_2 (1/2) and N_2 (1/2) at 150°C for 3 h under atmospheric pressure.

The catalytic reactions were carried out under atmospheric pressure in a continuous flow fix-bed glass reactor with inside diameter of 12 mm. The reactor was heated by an electrical furnace equipped with a temperature controller. Liquid reactants were introduced by microsyringe pump. Reactants and products were analyzed by a Shimadzu GC-8A gas chromatograph using OV-17 column. Selectivity of the product was calculated based on the ethylene glycol conversion.

Table 1 showed the catalytic results of Cu/SiO_2 catalysts with different Cu loading. The results indicated that Cu/SiO_2 catalyst has very high activity and selectivity in the

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formation of indole. The activity and selectivity strongly depended on the loading of copper. When the amount of Cu was under 0.680 mmol/g-SiO_2, both the activity and selectivity of the catalyst increased as the amount of Cu increased. However, when the amount of Cu was over 0.680 mmol/g-SiO_2, both decreased as the amount of Cu increased. At Cu loading of 0.680 mmol/g-SiO_2, the activity and selectivity were obtained the maximum value of 88% which were 10 percent higher than those with Co-Ag/SiO_2-ZnO catalyst under the same reaction conditions.

Table 1 The yields and selectivities of indole over Cu/SiO_2 catalyst with different Cu-loading

Cu-loading (mmol/g - SiO_2)	Yield (%)	Selectivity (%)
0.000	4	21
0.375	75	76
0.500	79	79
0.625	84	84
0.680	88	88
0.750	81	81
0.875	75	76
1.000	59	60

Reaction conditions: T = 325°C; aniline/EG mol ratio = 7; SV = 1635 h^{-1}; LHSV = 0.4 h^{-1}.

In summary, Cu/SiO_2 catalyst exhibited very high activity and selectivity for the direct synthesis of indole from aniline and ethylene glycol at atmospheric pressure. Since Cu/SiO_2 catalyst can be easily prepared and is much cheaper than Co-Ag/SiO_2-ZnO catalyst, it would be a promising one for commercial production of indole in the future.

The further study of Cu/SiO_2 catalyst is under way.

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