Selectivity enhancing effects of carbon dioxide in vapour-phase nucleophilic chlorobenzene substitutions, catalysed by copper-containing zeolites

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The nucleophilic substitutions of chlorobenzene with ammonia and water, leading to aniline and phenol respectively, were investigated using copper-exchanged zeolites. In these reactions, the performance of carbon dioxide as a carrier gas was compared with that of nitrogen. The conversions were slightly influenced; the substitution selectivity, however, increased rapidly with CO2, as the reduction to benzene was decreased substantially. In amination experiments, the benzene formation was decreased by a factor 2-3 with copper-Y. In hydrolysis experiments, the phenol selectivity increased from 85-90% (using N2) to 98-100% (using CO2) with copper mordenite at 400°C.

Keywords: nucleophilic aromatic substitution; copper mordenite; copper-Y; carbon dioxide; phenol formation; aniline formation

1. Introduction

Nucleophilic aromatic substitutions form an important group of processes in the synthesis of various organic intermediates and fine chemicals. In general, these processes are performed in the liquid phase, batchwise, with dissolved copper salts as catalysts [1]. It is of interest, however, to investigate heterogeneous catalysis, as a better catalyst recycle can be achieved. Therefore, the substitution of chlorobenzene with ammonia to form aniline has been studied using various copper-containing materials [2,3]. Copper-exchanged silica/alumina showed almost no aniline formation, while copper-exchanged zeolites gave better substitution results. The actual selectivity pattern (see fig. 1) was highly dependent on the type of zeolite applied: reduction to benzene was an important side process, and in some systems heavier condensation products were formed. With Cu-mordenite and Cu-ZSM-5 aniline was formed with a selectivity of 90-95%; with Cu-Y, however, aniline formation could be as low as 10%, with 50-75% reduction towards benzene [3].

More attention has been given to the substitution of chlorobenzene with water
to form phenol. This reaction can also be performed with high selectivity using metal-exchanged zeolites: both copper-containing ZSM-5 [4,5] and nickel-containing ZSM-5 [6] were found to be successful.

Recently, it was reported that in copper-catalysed liquid phase reactions, addition of dimethylformamide [7], carbon dioxide [8,9] or various alkyl esters [10] increased yields in the substitution of bromoaromatics with sodium methoxide, as the reduction to the corresponding aromatic is suppressed. It was presumed that these compounds form an adduct with the methoxide anion – like $(\text{MeO})\text{CO}_2^-\text{Na}^+$ or $(\text{OMe})_2\text{RCO}^-\text{Na}^+$ – thereby decreasing the Cu$^+$ reduction and acting as a co-catalyst.

We have investigated the effects of carbon dioxide as carrier gas in vapour-phase nucleophilic aromatic substitutions. In the chlorobenzene substitution with ammonia, the catalytic behaviour of Cu-Y was tested, as the high benzene formation of this catalyst gives good opportunity for comparison. To investigate the CO$_2$ effects in the chlorobenzene substitution with water, the catalytic properties of Cu-mordenite were tested.

2. Experimental

Sodium mordenite (Na-MOR), silicon/aluminium ratio of 6.3 ± 0.2, was obtained from PQ zeolites (coded CBV-10A); it was exchanged twice with 20 mM aqueous copper(II) nitrate at 75°C for 8 h. The material obtained had a Cu$^{2+}$/Al ratio of 0.3, as measured with AAS/AES elemental analysis, giving a copper content of 3.3 (±0.3) wt% based on moisture-saturated material. Sodium-Y (Na-Y), silicon/aluminium ratio 2.5 ± 0.1, was obtained from Akzo Chemical Division; it was exchanged once with aqueous 10 mM copper(II) nitrate at 75°C for 8 h, giving a Cu$^{2+}$/Al ratio of 0.15 and a copper content of 3.2 (±0.3) wt%.

The catalysts were pelletised, crushed and sieved; the fraction with a diameter between 0.7 and 1.0 mm was collected. 1.00 g of material, stored under ambient,