Catalysis Letters 25 (1994) 365–370

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

M.H.W. Burgers and H. van Bekkum

Laboratory of Organic Chemistry and Catalysis, Delft University of Technology,
Julianalaan 136, 2628 BL Delft, The Netherlands

Received 1 October 1993; accepted 23 December 1993

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 CO_2, 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 N_2) to 98–100% (using CO_2) 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

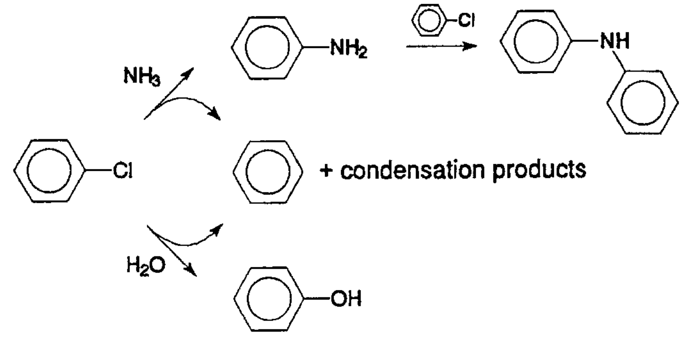

Fig. 1. Reaction scheme of the nucleophilic substitution of chlorobenzene with ammonia or water.

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 $(MeO)CO_2^-Na^+$ or $(OMe)_2RCO^-Na^+$ – 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, was used for each run. Reactions were performed at atmospheric pressure, downflow, in a borosilicate glass tube (i.d. 7 mm) heated by a fluidised bed oven. The catalysts were pretreated with ammonia/nitrogen at 400°C, to accomplish the reduction of Cu^{2+} to Cu^{+} [11], as Cu^{+} is presumed to be the actual catalyst [1]. During the reactions, the feed gas (33.4 ml/min) contained 16.5 vol% water or ammonia and 0.84 vol% chlorobenzene, giving a WHSV (20°C) of 0.078 h^{-1} $g_{chlorobenzene}/g_{cat}$. Ammonium chloride produced as a side product during aminations was removed by a rapid temperature drop of the product gas to 250°C. Quantitative analysis was performed by on-line GC, product identification by GC-MS.

3. Results and discussion

3.1. SUBSTITUTION OF CHLOROBENZENE WITH AMMONIA

Investigating the Cu-Y catalysed chlorobenzene amination, we varied the carbon dioxide content in the carrier gas. Adding limited amounts of CO_2 to the carrier gas only had limited influence. However, using pure CO_2 as carrier gas, a significant aniline selectivity change was observed, as shown in fig. 2. In all tests, the conversion after 0.5 h on stream was 70 ± 10%, but because of the significant catalyst deactivation of Cu-Y [3] this conversion decreased. Using pure CO_2, the activity dropped faster than with pure N_2: 50% conversion was reached after 3.2 h for CO_2 versus 5–6 h for pure N_2. However, these data can only be seen as an indication, as quantitative measurements in CO_2 experiments were hindered by a condensation product in the reactor offgas. This product could not be identified by

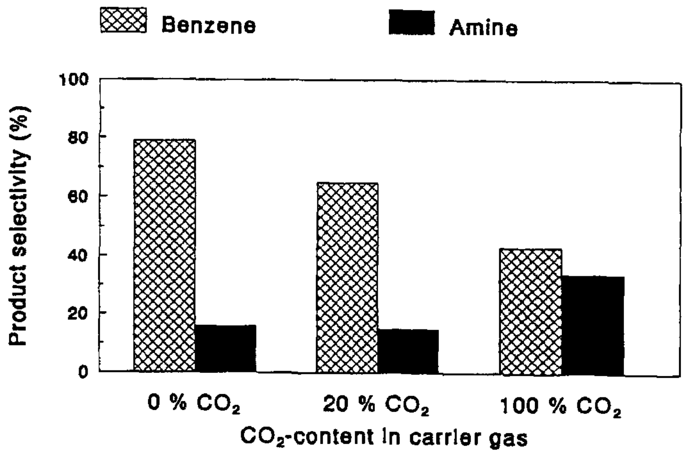

Fig. 2. Benzene and amine (aniline/diphenylamine) selectivity in the substitution of chlorobenzene with ammonia, catalysed by Cu-Y at 400°C, at 50% conversion (reached after 5.0, 6.1 and 3.2 h on stream, respectively).

GCMS – apart from a little aniline – so we presume it to be a carbon dioxide/ammonia/hydrogen chloride condensation product.

The selectivity pattern at 50% chlorobenzene conversion, shown in fig. 2, shows that the formation of benzene is significantly lower with CO_2, leading to an increase in amine selectivity from 16% with N_2 to 38% with CO_2.

As it was shown that the formation of benzene can also be suppressed to less than 5% by using other copper-exchanged zeolites (e.g. copper mordenite) [3], application of carbon dioxide as carrier gas may not be very important in the chlorobenzene amination. However, in preliminary experiments with substituted aromatics (e.g. chlorotoluene) the reduction is a far more serious problem; in this field, application of carbon dioxide might lead to selectivity improvements which cannot be obtained with catalyst variation.

3.2. SUBSTITUTION OF CHLOROBENZENE WITH WATER

Investigating the Cu-mordenite catalysed chlorobenzene hydrolysis, we compared results of pure N_2 with pure CO_2 as the carrier gas. The results, depicted in fig. 3, show that the conversion under CO_2 tends to be higher in the first state of the reaction, but steady-state conversions seem to be comparable. As in the substitution with ammonia, the benzene formation is decreased significantly: the phenol selectivity is increased from 90% with N_2 to 98–100% with CO_2. Increasing the reaction temperature (conversions and selectivities are shown in fig. 4) it is shown that even at 450°C the phenol selectivity remains >95% with CO_2, while a temperature increase usually increases the reduction rate significantly.

Thus, the CO_2 method shows a way to obtain phenol with higher selectivities.

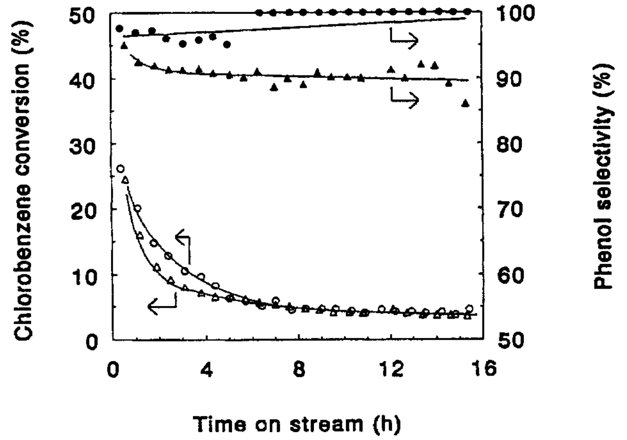

Fig. 3. Chlorobenzene conversion (○) and phenol selectivity (●) in the $PhCl/H_2O$ reaction with CO_2 as carrier gas at 400°C, catalysed by Cu-mordenite. Data with N_2 as carrier gas ((△) and (▲), respectively) are given for comparison.

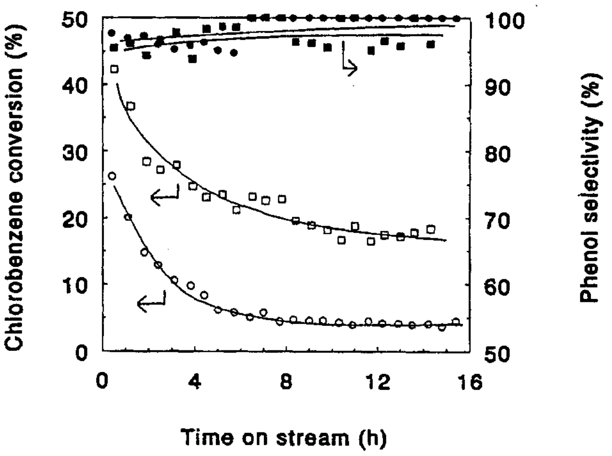

Fig. 4. Chlorobenzene conversion and phenol selectivity in the PhCl/H_2O reaction with CO_2 as carrier gas at 400°C ((○) and (●), respectively), and at 450°C ((□) and (■) respectively).

Again, like in the amination reactions, the low reduction rate observed might be especially important when substituted chloroaromatics, suffering even more from reduction, are to be converted.

In the liquid phase halobenzene substitution, it was proposed that the stabilisation of Cu^+ in solution is responsible for the enhanced selectivity [7,10]. We have proposed in the vapour-phase chlorobenzene/ammonia substitution that the reduction of Cu^+ to Cu^0 plays a role in the benzene formation [3]. Therefore, it is likely that nucleophile/carbon dioxide adducts – like NH_2COOH in the case of ammonia – are formed under reaction conditions, acting as a stabilizing agent for Cu^+ and thereby decreasing the benzene formation rate. Besides, if the reduction of Cu^+ to Cu^0 still takes place, another CO_2 effect might be the rapid reoxidation of Cu^0: this process, in which CO_2 is converted to CO, has been shown to take place on copper-containing silica/alumina [12]. Mechanistic investigations are to be performed to investigate which of these phenomena plays a major role in the selectivity improvement of CO_2 in vapour-phase nucleophilic substitutions.

4. Conclusion

Application of carbon dioxide as a carrier gas in vapour phase nucleophilic substitutions of chlorobenzene – instead of the usual nitrogen – leads to significantly increased selectivities. Both in amination and hydrolysis reactions, a decrease in chlorobenzene reduction, the most important side reaction, was observed. The key factor might be formation of a Cu^+-stabilizing carbon dioxide/nucleophile condensation product; another effect might be a rapid reoxidation of the Cu^0 which might otherwise lead to unwanted side reactions. A combination of these phenomena cannot be excluded.

Acknowledgement

This work was financially supported by the Dutch Innovation Orientated Research Program on Catalysis.

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