Novel Heterogeneous Route for the Coupling of Phenylethyne by a Catalyst derived from Cu–Mg–Al Hydrotalcite

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Cu–Mg–Al hydroxycarbonate, derived from Cu–Mg–Al hydrotalcite, affords yields of >80% for the heterogeneous coupling of phenylethyne to 1,4-diphenylbuta-1,3-diyne in the presence of sodium hydroxide and oxygen.

Substituted 1,4-diphenylbuta-1,3-diynes are an important class of liquid crystals for IR and long-wavelength application.[1] They are generally synthesised by coupling the corresponding phenylethynes.[2] The two most widely used syntheses are: (*i*) oxidative homocoupling reactions in a usually basic medium containing copper salts (*i.e.* Glaser and Eglington reactions)[2] and (*ii*) heterocoupling reactions of a terminal alkyne with a haloalkyne (*i.e.* Chodkiewicz–Cadiot).[2] Although the mechanism of the former has been discussed controversially,[3,4] it is assumed that the deprotonation of the alkynes is the rate-determining step. The rate of the reaction is therefore increased by the amount and strength of the base used in the reaction. Furthermore, copper ions are able to form an alkyne complex which facilitates the abstraction of the alkyne proton. In recent years, considerable effort has been devoted to the solid-state chemistry and catalytic use of hydrotalcite-like materials: a class of anionic, basic clays.[5] Hydrotalcite-like compounds are layered mixed hydroxides with the general formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}(A)^{n-}_{x/n}\cdot m\ H_2O$. Their structure consists of brucite-like layers $[Mg(OH)_2]$, in which divalent cations are partially substituted by trivalent cations resulting in a net positive charge. The excessive charge is balanced by interlayer anions, usually carbonate, associated with variable amounts of water. This type of structure can be built up with many different cations and offers a pronounced versatility in elemental composition and catalytic functionality.

Here, we report on a novel reaction system for the coupling of phenylethynes which consists of a copper-containing hydrotalcite-derived catalyst, oxygen, and sodium hydroxide, thus offering a heterogeneous alternative to the conventional homogeneous reactions.

The Cu–Mg–Al hydrotalcite-derived catalyst was prepared by coprecipitation at 333 ± 2 K. A solution of Na_2CO_3 (0.75 mol l^{-1}) was continuously added to a 1.5 l reaction vessel containing a solution of $Cu(NO_3)_2$, $Mg(NO_3)_2$ and $Al(NO_3)_3$ (final pH = 9.6). The molar ratio Cu : Mg : Al was 5 : 5 : 4. The precipitate was filtered off, washed with water, and dried at 363 K for 48 h. The dried sample was finally calcined *in vacuo* at 673 K for 4 h. The uncalcined sample showed the typical hydrotalcite-like XRD pattern,[6] whereas the calcined sample was X-ray amorphous. The specific surface area (S_{BET}), specific adsorption pore volume (V_p), and mean pore diameter ($d_p = 4\ V_p/S_{BET}$) of the calcined catalyst were determined by nitrogen physisorption at 77 K resulting in $S_{BET} = 84\ m^2\ g^{-1}$, $V_p = 0.69\ cm^3\ g^{-1}$, and $d_p = 30$ nm, respectively. The final copper content amounted to 36 mass%.

The phenylethyne coupling was carried out in a 100 ml stainless steel autoclave equipped with a 50 ml glass liner and a PTFE lid. The reaction mixture consisted of phenylethyne (2 g), calcined catalyst (≤ 180 μm; 50 mg), and different amounts of dry sodium hydroxide dissolved in 25 ml of *n*-butanol ([NaOH] = 0.05–0.4 mol l^{-1}). The autoclave was pressurised with initial oxygen pressures of 0.5–2 MPa, and subsequently heated to 333 K. After a reaction time of 1 h at a stirring speed of 1000 rpm, conversion and selectivity were determined by GC analysis. The catalytic results were independent of the amount of catalyst (≤ 100 mg), particle size (≤ 315 μm), and stirring speed (≥ 750 rpm), indicating the absence of mass transfer effects. Conversions were reproducible to within ±2% and selectivities to within ±5%.

A rise in the concentration of sodium hydroxide caused a prominent increase in the conversion of phenylethyne, whereas the selectivity to 1,4-diphenylbuta-1,3-diyne decreased slightly (Fig. 1). Without sodium hydroxide no conversion of phenylethyne was observed. Consequently, the intrinsic basicity of the hydrotalcite-like compound was not sufficient for deprotonation of phenylethyne. The decrease in selectivity to 1,4-diphenylbuta-1,3-diyne is attributed to the formation of by-

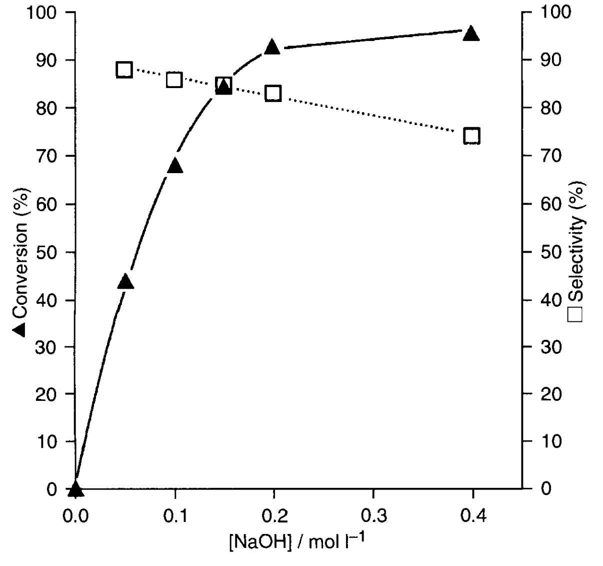

Fig. 1 Influence of sodium hydroxide concentration on conversion of phenylethyne (▲) and selectivity to 1,4-phenylbuta-1,3-diyne (□)

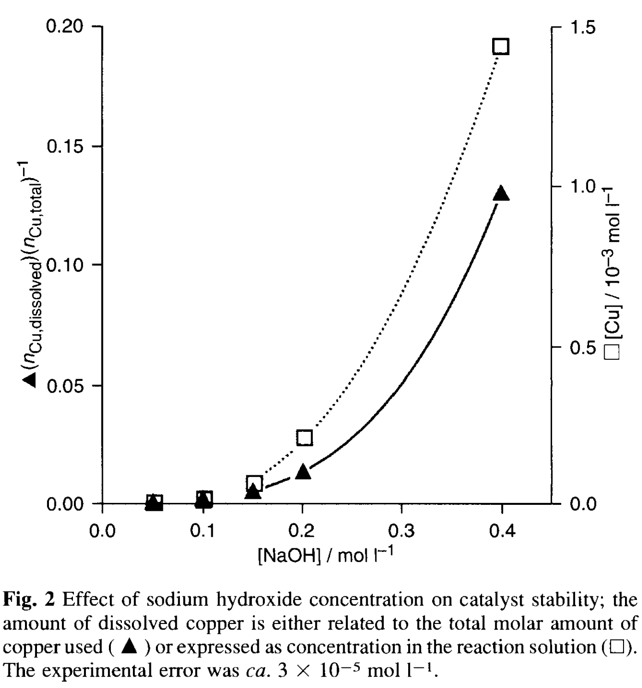

Fig. 2 Effect of sodium hydroxide concentration on catalyst stability; the amount of dissolved copper is either related to the total molar amount of copper used (▲) or expressed as concentration in the reaction solution (□). The experimental error was *ca.* 3×10^{-5} mol l^{-1}.

products originating from polymerisation and isomerisation, such as butyl phenylacetate, which was identified by GC–MS analysis.

As to the chemical stability of the catalyst, very small amounts of insoluble, yellow copper(I) phenylethynide were formed; 0.2 mg at 1 MPa of O_2 and 0.1 mol l^{-1} NaOH.[7] This compound withstood the oxidative reaction conditions and contributed *ca.* 1% to the overall conversion of phenylethyne. The amount of copper dissolved in the reaction medium was determined by atomic absorption spectroscopy and depended significantly on the sodium hydroxide concentration (Fig. 2).† Up to a concentration of *ca.* 0.15 mol l^{-1} NaOH, the fraction of dissolved copper remained negligibly low; higher concentrations, however, led to a marked rise in the formation of soluble copper hydroxide species.[8] In contrast to copper(I) phenylethynide, the amount of copper dissolved in 0.1 mol l^{-1} NaOH did not result in a detectable contribution to the catalytic activity.

The influence of the initial oxygen pressure is illustrated in Fig. 3. An increase in oxygen pressure from 0.5 to 1 MPa caused a prominent rise in conversion; from 1 to 2 MPa the slope decreased. This behaviour is expected because of the enhanced reoxidation of $\mathrm{Cu^{I}}$ to $\mathrm{Cu^{II}}$ and thus provides corroborative evidence for the participation of $\mathrm{Cu^{II}}$ ions in the deprotonation of phenylethyne, *i.e.* the rate-determining step. In contrast to the conversion of phenylethyne, the selectivity to 1,4-diphenylbuta-1,3-diyne is almost unaffected by increasing the oxygen pressure up to 2 MPa.

In conclusion, a novel route for the heterogeneous coupling of phenylethyne by Cu–Mg–Al hydroxycarbonate, leading to yields of 1,4-diphenylbuta-1,3-diyne comparable with those achieved in conventional homogeneous reaction systems, is described. Sodium hydroxide concentration and oxygen pressure are crucial parameters influencing the conversion of phenylethyne in this reaction. Further optimisation of this novel catalytic route is presently being studied in our laboratory.

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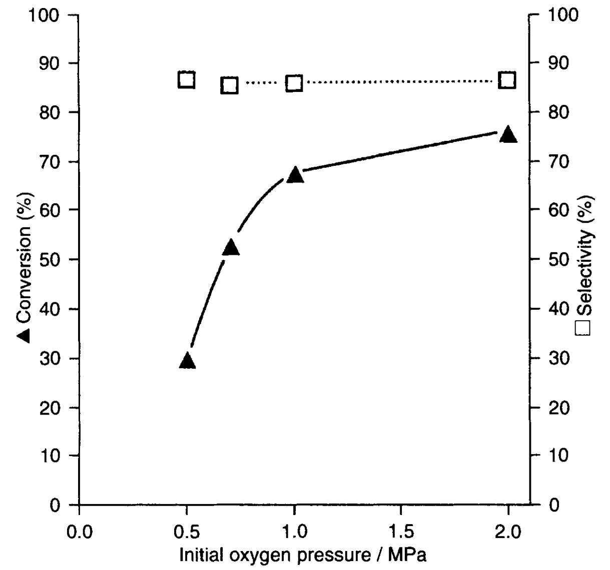

Fig. 3 Influence of initial oxygen pressure on conversion of phenylethyne (▲) and selectivity to 1,4-phenylbuta-1,3-diyne (□)

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† For 0.1 mol l^{-1} NaOH and 1 MPa O_2, aluminium was not detectable in the reaction solution by atomic absorption spectroscopy, *i.e.* [Al] $< 2 \times 10^{-5}$ mol l^{-1}.

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