Lewis acid double metal cyanide catalysts for hydroamination of phenylacetylene†

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Double metal cyanides (DMCs) are highly active recyclable heterogeneous catalysts for hydroamination of phenylacetylene with 4-isopropylaniline. The best hydroamination yields are obtained with Zn–Co DMCs, especially if the particle size is decreased by a reverse emulsion synthesis technique.

Hydroamination, the direct addition of an amine to a carbon–carbon unsaturated bond, is an attractive atom economical route to amines, imines and enamines.1 The reaction is thermodynamically feasible but high activation barriers exist, even for the energetically more favourable alkynes.2 Homogeneous catalysts have been extensively investigated, but only few heterogeneous catalysts have been found.1,3–5 Especially with industrial applications in mind a heterogeneous system offers a huge advantage in terms of product work-up. Double metal cyanides (DMCs) are industrially applied solid catalysts for huge advantage in terms of product work-up. Double metal cyanides (DMCs) are industrially applied solid catalysts for the ring opening polymerization (ROP) of epoxides producing polyether–polyols.6–8 They were also reported as catalysts for ring opening reactions and for transesterifications.9–15 In the present work, DMCs were found to be highly active hydroamination catalysts, giving a 99% yield of the Markovnikov addition product. The reaction rate could be further improved with a nanosized Zn–Co DMC prepared by a reverse emulsion technique.

DMCs combine two transition metals in their structure and can be considered as analogues of Prussian blue (Fe₄[Fe(CN)₆]₃·1·4H₂O). This framework of Feᴵᴵ–CN–Feᴵᴵ bridges is based on a face-centered cubic unit cell.12 In this study, a standard DMC material was synthesized by addition of a water-soluble metal cyanide, K₃[Co(CN)₆], to an excess amount of ZnCl₂ or another water-soluble metal salt.† As a complexing agent (CA) tert-butanol was used; poly(tetramethylene ether) glycol (PTMEG) was added as the co-complexing agent (co-CA). The co-CA may act as a protecting agent and thus affect the particle size;12 in epoxide polymerization reactions, the introduction of such CA and co-CA into the catalyst matrix makes the DMCs more active.12 In order to assess the effect of particle size, nanosized DMCs (NDMCs) were prepared by a reverse emulsion synthesis procedure in which Igepal CA-520 (poly(oxyethylene)-(4-isooctylphenyl)ether) is used as an emulsifier to stabilize the formation of water droplets in the dispersion medium.16

The structure of the Zn–Co DMC materials was characterized by powder X-ray diffraction (PXRD) (Fig. 1 (left) and Fig. S1 in ESI†), which proved the presence of the cubic lattice structure in all Zn–Co DMCs. The principal reflections of a simulated pattern, based on the crystal structure of the pure Zn–Co Prussian blue analogue Zn₃[Co(CN)₆]·1·2H₂O, are all readily recognized in the experimental patterns (Fig. 1c, left).17 When comparing the PXRD of the standard Zn–Co DMC and the Zn–Co NDMC, it is clear that even for the nanosized material, the DMC structure is retained (Fig. 1a and b, left).

Fig. 1 PXRD of standard Zn–Co DMC (a), nanosized Zn–Co DMC (b) and simulated pattern (c) (left); difference IR spectrum of adsorbed pyridine on standard Zn–Co DMC (right).

† Electronic supplementary information (ESI) available. See DOI: 10.1039/c0cc05335j
The unique nature of the zinc site in the Zn-Co DMC derived from ZnCl₂ is further underscored by a comparison with other Zn catalysts. The Zn source was altered from ZnCl₂ to ZnSO₄·7H₂O (entry 10) or Zn(CF₃SO₃)₂ (entry 11). Much lower activities, however, were found with the sulfate anion and the triflate anion. This is in agreement with results in the literature for polymerization reactions catalyzed with DMCs. When the catalytic activity of ZnCl₂ as such was tested, no hydroamination product was formed, even after 24 h (entry 12). This illustrates the special character of the Zn-sites in Zn-Co DMCs: the activity is not due to mere deposition of Zn salts on a solid support. The Co cyanide salt K₃[Co(CN)₆] was tested as well under the same conditions and showed no hydroamination activity.

In the literature, Zn⁺⁺ ion exchanged zeolite H-beta (Zn-beta) has been proposed as a hydroamination catalyst. Here, Zn Lewis acid sites are combined with Brønsted acid sites of the parent zeolite material. Zn-beta (50% of sites exchanged) was compared with the DMC for the test reaction. The zeolite catalyst was activated at 200 °C under vacuum overnight. After 24 h, a 71% yield of the Markovnikov hydroamination product was found (entry 13). Even after rigorous water exclusion, some acetophenone byproduct was formed (14%), lowering the selectivity significantly. The purely Lewis acid Zn-Co DMCs are in contrast highly selective and active towards the hydroamination product; less stringent activation conditions are needed to avoid acetophenone formation.

The stability of the Zn-Co-DMC-PTMEG catalyst was investigated with a hot filtration test. A sample was taken from the stirred reaction mixture after 2 h at 110 °C and filtered without cooling the reaction mixture. The resulting filtrate showed no further catalytic activity after 4 h at the reaction temperature (Fig. S8, ESI†). Zn-Co-DMC-PTMEG

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Yield—3 hᵇ</th>
<th>Yield—24 hᵇ</th>
</tr>
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<tbody>
<tr>
<td>1 Zn–Fe(III)-DMC-PTMEG</td>
<td>0%</td>
<td>1%</td>
</tr>
<tr>
<td>2 Zn–Fe(III)-DMC-PTMEG²</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>3 Cu–Fe(III)-DMC-PTMEG²</td>
<td>0%</td>
<td>5%</td>
</tr>
<tr>
<td>4 Cu–Co-DMC-PTMEG²</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>5 Zn-Co-DMC-PTMEG²</td>
<td>33%</td>
<td>92%</td>
</tr>
<tr>
<td>6 Zn-Co-DMC-PEG²</td>
<td>0%</td>
<td>18%</td>
</tr>
<tr>
<td>7 Zn-Co-DMC-P123²</td>
<td>8%</td>
<td>67%</td>
</tr>
<tr>
<td>8 Zn-Co-DMC-PTMEG³</td>
<td>21%</td>
<td>79%</td>
</tr>
<tr>
<td>9 Zn-Co-DMC-pure²</td>
<td>13%</td>
<td>40%</td>
</tr>
<tr>
<td>10 Zn-(SO₄)₂-Co-DMC-PTMEG⁴</td>
<td>0%</td>
<td>8%</td>
</tr>
<tr>
<td>11 Zn-(CF₃SO₃)₂-Co-DMC-PTMEG⁵</td>
<td>7%</td>
<td>28%</td>
</tr>
<tr>
<td>12 ZnCl₂⁶</td>
<td>0%</td>
<td>0%</td>
</tr>
<tr>
<td>13 Zn-beta²</td>
<td>7%</td>
<td>71%</td>
</tr>
<tr>
<td>14 Zn-Co-DMC-PTMEG⁴</td>
<td>48%</td>
<td>99%</td>
</tr>
<tr>
<td>15 Zn-Co-NDMC-Igepal⁶</td>
<td>46%</td>
<td>96%</td>
</tr>
<tr>
<td>16 Zn-Co-NDMC-Igepal⁴</td>
<td>57%</td>
<td>99%</td>
</tr>
</tbody>
</table>

ᵇ Reaction conditions: 0.5 mmol of alkyn, 1.0 mmol of amine, 50 mg of catalyst in toluene (1 ml) at 110 °C. Determined by GC. ᶜ PTMEG poly(tetramethylene ether) glycol, PEG polyethylene glycol, P123 Pluronic as co-block polymer, Igepal CA-520. ᵈ No co-CA used. ᵉ No CA nor co-CA. ᶠ ZnSO₄·7H₂O instead of ZnCl₂. ᵍ Zn(CF₃SO₃)₂ instead of ZnCl₂. ʰ 5 mol% ZnCl₂. ᵢ 50% of the cation exchange capacity (CEC) of H-beta zeolite exchanged with Zn(CH₃CO₂)₂, activated overnight under vacuum at 200 °C. ｊ 1 mol of alkyn and 0.5 mmol of amine. ⁹ Isolated yield: 88%.
(conditions of entry 5) was also found to be a recyclable catalyst. After 3 runs, the high yield of hydroamination product was intact: a 92% yield of the imine was found in the third run. Thus, Zn-Co-DMC-PTMEG is a stable, efficient and recyclable hydroamination catalyst. The amine/alkyne ratio was altered in a reaction with Zn-Co-DMC-PTMEG. The highest yield was obtained with 0.5 mmol amine and 1 mmol alkyl. After 3 hours 48% of the hydroamination product was formed, and after 24 hours, 99% yield based on amine was obtained (entry 14).

Nitrogen adsorption measurements were performed on Zn-Co-DMC-PTMEG. A typical Type 1 adsorption isotherm was recorded, characteristic of microporous materials (Fig. S9, ES†). The micropore radius of Prussian blue analogues is small.17,24 We estimated the pore size by the Horvath–Kawazoe model as < 4.6 Å. It can therefore be safely assumed that most of the catalysis takes place at the outer surface of the DMC material. In that case, one expects an activity increase as the outer surface of the material is increased. Therefore, nanosized DMC particles were prepared by a reverse emulsion synthesis, using various neutral or ionic emulsifying agents. Best results were obtained with Igepal® CA-520. At a 2 : 1 amine : alkynyl ratio, the initial rate with the NDMC was more than 40% higher than with the standard DMC (entries 5 and 15, after 3 h). When an excess amine was used, the hydroamination yield amounted to 57% already after 3 h (entries 14 and 16). The emulsifier also acts as a co-CA in this synthesis, since it is incorporated into the structure in the same way as PTMEG;16 an oxygen atom of the emulsifier is coordinated to a Zn atom in the DMC structure. A nitrogen adsorption isotherm of the Zn-Co NDMC (Fig. S9, ES†) was also recorded. A large increase in the outer surface area can be seen between the standard and reverse emulsion prepared DMC (21 m^2 g^{-1} and 170 m^2 g^{-1}), confirming a smaller particle size. Thus the rate of hydroamination can be improved by lowering the size of the catalyst particles by the reverse emulsion method, indicating that the outer surface area is indeed important for the catalytic activity.

In conclusion, DMCs were uncovered as a group of new Lewis acid hydroamination catalysts. These materials show the possibility of fine-tuning the activity by modifying many parameters of the synthesis procedure. Here, the combination of Zn and Co was found to be the most active one. Lowering the size by a reverse emulsion synthesis offers new methods of even further enhancing the catalytic activity. First experiments with alkylamines and aliphatic alkynes also show promising results. We are currently expanding the substrate scope for hydroaminations with DMC catalysts.

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Notes and references

1) Synthesis of standard DMCs:12 10 mmol of the metal salt (ZnCl_2, ZnSO_4·7H_2O, Zn(CF_3SO_2)_2 or CuCl_2·H_2O) were dissolved in 100 ml of deionized water, together with 1 mmol of the co-complexing agent, poly(tetramethylene ether)glycol (PTMEG, 1000 g mol^{-1}), polyethylene glycol (PEG, 2000 g mol^{-1}) or Pluronic® P123 (P123, 5750 g mol^{-1}). This solution was vigorously stirred at 80 °C. Next, a solution of 1 mmol metal cyanide salt (K_3[Co(CN)_6], K_3[Fe(CN)_6] or K_3[Fe(CN)_6]·3H_2O) in deionized water (10 ml) was added dropwise. The stirring was continued for 30 min. 25 ml of the complexing agent tert-butanol (tBuOH) was added and the resulting mixture was stirred for an additional 3 hours at 80 °C. The solids were centrifuged and washed with a 1 : 1 mixture of tBuOH and deionized water. The resulting catalyst was then dried at 60 °C overnight, followed by drying at 80 °C under vacuum for 8 hours. Synthesis of nanosized Zn-Co DMC (reverse emulsion method):16 10 g of Igepal® CA-520, 7.7 ml of tBuOH and 109 ml of cyclohexane were mixed with a mechanical stirrer (300 rpm) at room temperature. A solution of 10 mmol ZnCl_2 in 2 ml of deionized water was added dropwise. Next, a solution of 2 mmol K_3[Co(CN)_6] in 2 ml of water was added dropwise as well. The resulting mixture was stirred for 1 hour at room temperature. The formed catalyst particles were centrifuged and washed with tBuOH. The particles were dried overnight at 60 °C and afterwards dried under vacuum at 80 °C.


4116 | Chem. Commun., 2011, 47, 4114–4116

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