Modified Mg–Al hydrotalcite: a highly active heterogeneous base catalyst for cyanoethylation of alcohols

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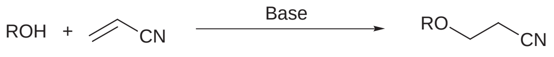
Modified Mg–Al hydrotalcite (Mg : Al = 3 : 1) prepared by thermal decarbonation followed by rehydration of a conventional Mg–Al hydrotalcite is found to be a highly active, reusable and air stable catalyst for cyanoethylation of alcohols.

Cyanoethylation of alcohols is a widely used reaction for the synthesis of drug intermediates and organic compounds of industrial interest.[1] Acrylonitrile undergoes cyanoethylation with a number of monohydric alcohols to give alkoxypropionitriles which, after hydrogenation, give industrially important amines. The reaction is catalysed by homogeneous base catalysts such as alkali hydroxides[2] and alkoxides[3] and tetraalkyl ammonium hydroxide. However, these catalysts need to be neutralised before purification of the product, resulting in the generation of waste, loss of catalyst and reduced product yields. Alternatively, use of anion exchange resins as heterogeneous catalyst have also been reported.[4,5] Recently, Hattori and Kabashima[6] reported use of alkaline earth oxides, hydroxides and alumina supported KF and potassium hydroxide supported on alumina as heterogeneous catalysts for this reaction. High activities were reported for high temperature activated MgO catalyst (800 °C *in vacuo*). The general reaction scheme for cyanoethylation of alcohols is shown in Scheme 1.



Scheme 1

Previously we had reported that modified hydrotalcite, prepared by thermally decarbonating the conventional Mg–Al hydrotalcite followed by controlled rehydration, is highly active for aldol and Knoevenagel condensation reactions.[7,8] The high activity of this catalyst is attributed to the presence of a large number of OH^- groups, generated during rehydration of the thermally activated hydrotalcite, which act as Brönsted basic sites. The use of modified hydrotalcites as heterogeneous Brönsted basic catalysts instead of homogeneous catalysts such as alkali hydroxides and alkoxides has a number of advantages, *viz.* ease of separation, reusability, no waste, and higher activities and selectivities (depending on the reaction).

In continuation of our above mentioned work here we report that the modified hydrotalcites having formula $[Mg_{(1-x)}Al_x(OH)_2](OH)_x{\cdot}yH_2O$ show unprecedented high activity for the cyanoethylation of alcohols with acrylonitrile. The activity of this catalyst is the highest so far reported in the literature for any heterogeneous catalyst. The catalysts were found to be reusable without significant loss in activity. The other interesting aspect of this work is that these catalysts were found to be active even after exposure to air in this reaction, a rare phenomena for a solid basic catalyst.

Mg–Al hydrotalcites having Mg : Al = 3 : 1 was synthesised using the procedure reported by Miyata *et al.*[9] The presence of pure hydrotalcite structure was confirmed by powder X-ray diffraction. The preparation of modified hydrotalcite includes activation of the hydrotalcite in carbon dioxide free N_2 at 450 °C, followed by cooling and hydrating the material in a flow of nitrogen saturated with water at room temperature in a controlled fashion.

The catalytic reactions were carried out using 10 ml of alcohol and 4 mmol of acrylonitrile. The catalyst after rehydration was transferred to the reactor containing the alcohol followed by addition of acrylonitrile. The samples were analysed by gas-liquid chromatography.

Table 1 shows a comparison of the modified hydrotalcites rehydrated for different periods of time with fresh and calcined hydrotalcites and MgO (from the results of Hattori[6]) for the reaction of acrylonitrile with MeOH in which methoxypropionitrile is the only product. The modified hydrotalcites are much more active than MgO, which also needs a very high activation temperature (800 °C *in vacuo*). The hydrotalcite as such shows only marginal activity as it contains very few basic sites. It is interesting to note that even though the calcined hydrotalcite has a high Lewis basicity, it is only marginally active. This shows that this reaction is catalysed by weak Brönsted basic sites (OH^- sites).

Similar to our earlier results for the aldol condensation reaction,[7] for cyanoethylation the catalytic activity also depends upon the rehydration time. In the present case optimum activity is observed for the catalyst rehydrated for 6 h (catalyst = 0.1 g, water saturated N_2 flow = 80 ml min^{-1}).

The reusability of the catalyst was studied by using the same catalyst after allowing the catalyst to settle, decanting the supernatanat reaction mixture and continuing the reaction by introducing fresh reactants (acrylonitrile and MeOH). The results are sumarised in Table 2. The catalyst was found to be reusable without appreciable loss in activity.

The study was further extended to other monohydric alcohols such as EtOH, Pr^iOH, BuOH and Bu^tOH. The results are summarised in Table 3. Except for Bu^tOH, the catalysts are found to be highly active for all the alcohols, which is in agreement with the results for the homogeneous catalyst. The selectivity for the corresponding alkoxypropionitrile was 100%,

Table 1 Comparison of various catalysts for cyanoethylation of acrylonitrile with MeOH[a]

Catalyst	Conditions for activation of the catalyst	t/min	Conversion of acrylonitrile (%)
Mg–Al Hydrotalcite	used as was	120	2.5
Mg–Al Hydrotalcite	N_2 flow at 450 °C	120	20
Modified Mg–Al Hydrotalcite	N_2 at 450 °C rehydration for 3 h in wet N_2 at room temp.	90	98
Modified Mg–Al Hydrotalcite	N_2 at 450 °C rehydration for 6 h in wet N_2 at room temp.	45	99.8
Modified Mg–Al Hydrotalcite	N_2 at 450 °C rehydration for 12 h in wet N_2 at room temp.	45	100
MgO[b]	800 °C *in vacuo*	120	98.7

[a] Reaction conditions: acrylonitrile (0.04 mol), MeOH (10 ml), 50 °C, Catalyst (0.1 g). [b] Results from ref. 6.

Table 2 Reusability of modified Mg Al hydrotalcite catalyst (rehydrated for 6 h) for cyanoethylation of acrylonitrile with MeOH[a]

Cycle	Conversion (%)
1	99.8
2	98.0
3	96.0

[a] Reaction conditions as in Table 1.

Table 3 Cyanoethylation of various monohydric alcohols with acrylonitrile over modified Mg–Al hydrotalcite (rehydrated for 6 h)[a]

Alcohol	t/min	Conversion of acrylonitrile (%)
EtOH	25	100
$\mathrm{Pr^iOH}$	90	95.6
BuOH	20	100
$\mathrm{Bu^tOH}$	120	10

[a] Reaction conditions as in Table 1.

except for $\mathrm{Pr^iOH}$, in which case the selectivity for β-isopropoxypropionitrile was 80%.

Normally, solid basic catalysts are highly sensitive to air and loose their activity due to carbonation when exposed, preventing them from being used industrially. To check this an experiment was carried out to see if the catalyst remained active when exposed to air. To our surprise we found that the modified hydrotalcite catalyst, even after exposure to air (1 h), showed the same activity as a sample not exposed (100% conversion in 45 min). This result makes this catalyst attractive for practical use.

In summary we have shown that modified Mg–Al hydrotalcite is a highly active, reusable and air stable catalyst for cyanoethylation of monohydric alcohols.

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Notes and References

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