Meerwein–Ponndorf–Verley reduction of carbonyl compounds catalysed by Mg–Al hydrotalcite

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Properly activated Mg–Al hydrotalcite (Mg : Al = 3 : 1) is found to be a highly active, selective and regenerable heterogeneous catalyst for Meerwein–Ponndorf–Verley reduction of carbonyl compounds in the liquid phase.

The reduction of carbonyl compounds is one of the most widely practised operations in the synthetic organic, fine and perfumery chemical industries. Of particular importance is selective reduction of carbonyl groups in the presence of other functional groups. New methods, new catalysts and new reagents which offer greater activity, selectivity and reusability are constantly being sought.

The Meerwein–Ponndorf–Verley (MPV) reduction of aldehydes and ketones is one such reaction when high selectivities are obtained using metal alkoxides as catalysts, such as $Al(OPr^i)_3$ and $La(OPr^i)_3$.[1] However, the metal alkoxide catalysts are homogeneous, create problems during separation and are not reusable. Hence, reusable heterogeneous catalysts will have a distinct advantage if they can match the performance of homogeneous catalysts. In this regard, Posner *et al.*[2] were first to report the use of Al_2O_3 as a catalyst. However, a large amount of catalyst needed to be used (1–2 g Al_2O per mmol substrate) to achieve high conversions. Recently, Van Bekkum[3] showed that properly activated zeolite β was a highly active and stereoselective catalyst for the reduction of 4-*tert*-butylcyclohexanone to *cis*-4-*tert*-butylcyclohexanol. However, the use of zeolite β has limitations due to its pore size (7.4 × 6.5 Å). Kaspar *et al.*[4] have reported the use of MgO as a moderately selective catalyst for the reduction of α,β-unsaturated ketones in a fixed bed reactor using vapour phase conditions. In a fundamental study Ivanov *et al.*[5] have shown that MPV reductions can be catalysed by both basic and acid sites. Niyama *et al.*[6] reported that catalysts having adequate acidity and basicity show high activity in this reaction.

Here we report that properly activated Mg–Al hydrotalcite having a Mg/Al ratio of 3 : 1 is a highly active, selective and regenerable catalyst for MPV reduction of carbonyl compounds in the liquid phase. The high activity of these catalysts is attributed to the presence of both strongly basic and mildly acidic sites.

Mg–Al hydrotalcites having different ratios were synthesised using the procedure reported by Miyata *et al.*[7] The presence of pure hydrotalcite structure was confirmed by PWXRD. The catalysts activated in N_2 upto 550 °C showed a MgO pattern by X-ray diffraction indicating the formation of a solid solution of Al in MgO. The catalytic test was carried out using propan-2-ol as the hydrogen donor at 82 °C. The catalyst was pre-treated in N_2 at the desired temperature and carefully transferred to the reactor containing propan-2-ol without exposure to air, after which the substrate was introduced. Periodically withdrawn samples were analysed by gas-liquid chromatography.

The preliminary testing of hydrotalcites having different Mg/Al ratios and different calcination temperatures was carried out for the reduction of 4-*tert*-butylcyclohexanone to 4-*tert*-butylcyclohexanol. The hydrotalcite having a Mg : Al ratio of 3 : 1, calcined at 450 °C, was found to be the most active (Table 1). Hence all further studies were carried out using this catalyst.

Table 1 Effect of Mg : Al ratio and calcination temperature on the activity of Mg–Al hydrotalcites for MPV reduction of 4-*tert*-butylcyclohexanone[a]

Mg : Al ratio	Activation temperature/°C	Initial rate/$10^{4\,b}$
2 : 1	450	0.27
3 : 1	350	0.85
3 : 1	450	4.12
3 : 1	550	2.22
5 : 1	450	0.73
3 : 1[c]	450	4.09

[a] Reaction conditions: 4-*tert*-butylcyclohexanone (13 mmol), propan-2-ol (10 ml), catalyst (0.15 g) activated in N_2, reaction temperature 82 °C; [b] In mol per min per g catalyst. [c] Catalyst regenerated after one use in N_2 at 450 °C.

To allow comparison with the results reported by Van Bekkum[3] the same reaction was carried out using similar conditions on a reduced scale. Under these conditions, even with a lower catalyst loading (0.075 g instead of 0.1 g), 98% conversion was reached within 4 h with selectivity for alcohol greater than 95% (Fig. 1) (*trans* to *cis* alcohol ratio: 85 : 15). This shows that the activity of the catalyst prepared from hydrotalcite precursor is substantially higher than that reported for alumina, silica–alumina and Y-zeolite.[3]

The reusability of the catalyst was checked *via* solid separated by filtration and reactivated in N_2 at 450 °C. The reused catalyst showed similar activity to a fresh sample (Table 1).

The study was extended to the reduction of some industrially important unsaturated carbonyl compounds, such as cinnamaldehyde, citral and citronellal, to the corresponding unsaturated alcohols, which are high value perfumery chemicals. The results are summarised in Table 2. As can be seen, the catalyst is both active and highly selective.

The higher selectivities obtained are rather unexpected as hydrotalcites are strongly basic and one would have expected the aldol condensation reaction to be predominant. However, as we have already shown in our previous publication, the aldol

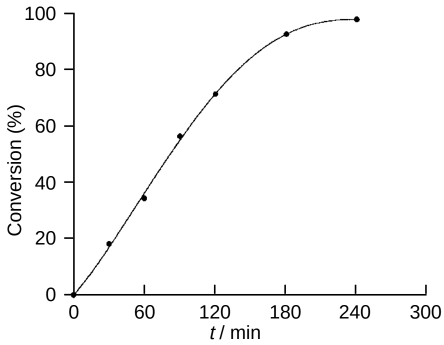

Fig. 1 Conversion *versus* time plot for reduction of 4-*tert*-butylcyclohexanone using Mg–Al hydrotalcite (Mg : Al = 3 : 1). Reaction conditions: same as Table 1 except 4-*tert*-butylcyclohexanone (1 mmol) catalyst (0.075 g) activated in N_2 at 450 °C.

Table 2 MPV reduction of unsaturated aldehydes to unsaturated alcohols over Mg–Al hydrotalcite (Mg : Al = 3 : 1)[a]

Aldehyde	t/h	Conversion (%)	Selectivity for unsaturated alcohol (%)
Citronellal	4	90	95[b]
Cinnamaldehyde	5	75	92[c]
Citral	5	83	70[d]

[a] Reaction conditions: aldehyde (1 mmol) catalyst (0.14 g) activated in N_2 at 450 °C, propan-2-ol (10 ml), T = 82 °C, stirring speed = 900 rpm. [b] Citronellol. [c] Cinnamyl alcohol. [d] Nerol + geraniol.

condensation reaction is catalysed by Brönsted bases (OH^- groups) and calcined hydrotalcites, which are Lewis bases, do not catalyse this reaction.[8] As we have used catalysts activated in N_2 at 450 °C having only Lewis basicity, they do not give aldol products under the mild reaction conditions used; this is consistent with the previous work.

The high activity of calcined hydrotalcites probably comes from the synergetic effect of strong Lewis basicity and mild acidity, as shown in Fig. 2. This mechanism agrees with that proposed by Ivanov *et al.*[5] based on *in situ* IR experiments.

In summary, we have shown that properly activated Mg–Al hydrotalcite (Mg : Al = 3 : 1) is a highly active, selective and regenerable catalyst for Meerwein–Ponndorf–Verley reduction of carbonyl compounds under liquid phase conditions.

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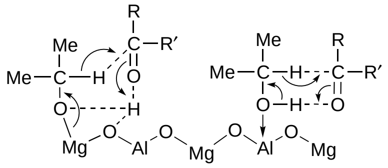

Fig. 2 Proposed mechanism of the MPV reduction over Mg–Al hydrotalcite

Notes and References

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