Nanoplatelet-based reconstructed hydrotalcites: towards more efficient solid base catalysts in aldol condensations†

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Rehydration of Mg–Al hydrotalcite in the liquid phase using ultrasounds or a high stirring speed leads to nanoplatelets with surface areas of 400 m^2 g^{-1}, displaying catalytic activities in aldol condensations up to 8 times higher than the best catalytic system reported in the literature.

Activated Mg–Al hydrotalcites (HTs) are efficient heterogeneous catalysts in a number of base-catalysed reactions, among others the self and cross-aldol condensation of aldehydes and ketones, Knoevenagel and Claisen-Schmidt condensation, and Michael addition.[1] These processes are important in the pharmaceutical and fragrance industries where HTs are progressively replacing the classically applied and less environmental friendly liquid bases such as NaOH.[2] The activity of these layered materials originates from the presence of basic hydroxyl ions of Brønsted character in the interlayer space.[3] The as-synthesised Mg–Al hydrotalcite is typically activated by thermal decomposition into a high surface area mixed oxide and then reconstructed by rehydration in contact with water vapour or immersed in liquid water under decarbonated atmosphere. This ultimately converts the starting hydroxycarbonate ($Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$) into the active topotactic hydroxide hydrate ($Mg_6Al_2(OH)_{18}\cdot 4.5H_2O$).

The rehydration conditions of calcined HTs strongly influence the properties and performance of the final catalyst in aldol condensations. Roelofs *et al.*[4] showed that rehydration in vapour phase leads to a lower crystallinity and surface area than rehydration by immersion in liquid water (57 *vs.* 200 m^2 g^{-1}). Figueras *et al.*[5] observed a similar effect, and the surface area of the mixed oxide decreased to 20 m^2 g^{-1} after rehydration in vapour phase. This originated a decreased activity in isophorone isomerisation, which was attributed to the lower accessibility of the basic sites in meixnerite. Despite numerous studies, conclusive relationships between the rehydration procedure and (i) the surface area, (ii) the number and nature of the active OH-groups, and (iii) the activity of the activated HTs in aldol condensations have not been derived. This fundamental understanding is essential for obtaining more efficient catalysts.

Herein, we have identified relevant activity-directing factors associated with the rehydration method of Mg–Al hydrotalcite in the condensation between citral and acetone or MEK, to yield pseudoionones (PS). Novel approaches to maximise the accessibility of active sites by synthesis of nanoplatelet-based activated hydrotalcites leads to outstanding activities, up to 8 times higher than the best catalytic system reported to date.

As described below‡ and shown in Table 1, the synthesised Mg–Al hydrotalcite (Mg/Al = 3/1) was calcined and rehydrated in gas (HT_{RG}) or liquid phases (HT_{RL}). Liquid-phase rehydration was carried out under stirring in water at different conditions or in 1 : 1 mixtures of water and ethanol ($HT_{RL\text{-}ET}$). Besides, ultrasound irradiation was applied as an alternative to stirring, leading to $HT_{RL\text{-}US}$. Table 1 compares the BET surface areas of the differently rehydrated samples. Rehydration in liquid phase at 100 rpm leads to a surface area of 203 m^2 g^{-1}, remarkably higher than in the gas-phase rehydrated sample (15 m^2 g^{-1}). The surface area of HT_{RL} is practically doubled upon increasing the stirring speed from 100 to 700 rpm, reaching 374 m^2 g^{-1}. A slight increase in surface area was observed when the rehydration time was increased from 1 to 6 h or using ethanol, reaching surface areas around 400 m^2 g^{-1}.

The FE-SEM micrographs of two representative rehydrated samples are shown in Fig. 1. HT_{RG} is built of thicker aggregates, while $HT_{RL700\text{-}A}$ presents a more exfoliated morphology. The degree of exfoliation of the HT_{RL} samples increases with the stirring speed or conducting longer treatments. Sonication causes cavitation in aqueous media, where the formation, growth, and collapse of microbubbles occurs.[6] So, the use of ultrasounds should stimulate exfoliation of hydrotalcite particles during rehydration, as confirmed by the surface area of $HT_{RL\text{-}US}$ in Table 1 (440 m^2 g^{-1}).

Strikingly, the surface areas of the reconstructed HT_{RL} samples are significantly higher than that of HT_C, and to the best of our knowledge, the highest reported in the literature for rehydrated HT.

The basic properties of the rehydrated samples were studied by temperature-programmed desorption (TPD) using different probe molecules, including CO_2, CH_3CN, and CH_3NO_2.†

The CO_2 TPD profiles for HT_{RG} and HT_{RL500} samples (see Fig. 2) are very similar (see supplementary information for other

Table 1 BET surface area of differently rehydrated hydrotalcites

Catalyst	Time/h	Stirring speed/rpm	$S_{BET}/m^2\ g^{-1}$
HT_C	—	—	210
HT_{RG}	15	—	15
HT_{RL100}	1	100	203
HT_{RL500}	1	500	270
$HT_{RL700\text{-}A}$	1	700	374
$HT_{RL700\text{-}B}$	6	700	401
$HT_{RL\text{-}ET}$	1	700	404
$HT_{RL\text{-}US}$	0.083	—	440

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† Electronic Supplementary Information (ESI) available: XRD and TPD of CH_3CN and CH_3NO_2 for rehydrated Mg–Al mixed oxides. See http://www.rsc.org/suppdata/cc/b4/b417322h/
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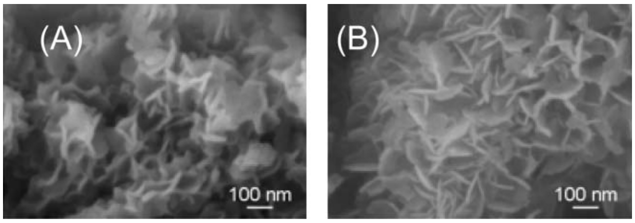

Fig. 1 FE-SEM image of (A) HT_{RG}, (B) $HT_{RL700\text{-}A}$.

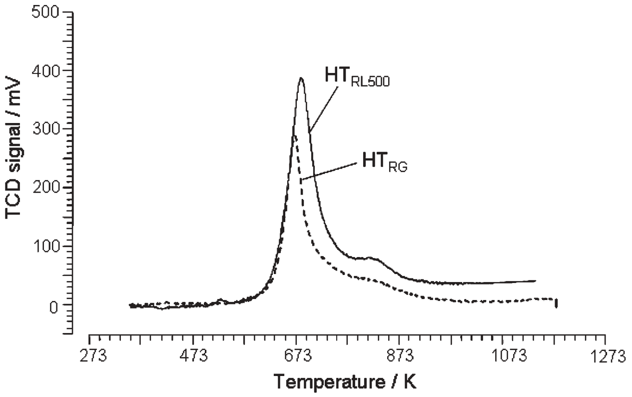

Fig. 2 CO_2 uptake during temperature-programmed desorption over HT_{RG} and HT_{RL500}. CO_2 adsorption at 353 K for 1 h.

probe molecules†), indicating that the nature of the resulting basic hydroxyl groups does not depend on the rehydration method. First peak, which decomposes at temperatures around 700 K, is attributed to the contribution of mainly bicarbonate species, on the catalyst surface, while the smaller peak above 800 K is due to carbonate species.

The total number of hydroxyls in the reconstructed hydrotalcites can be determined from thermogravimetric analysis (see Table 2) and depends on the rehydration process. The HT_{RG} sample shows the highest amount of total OH^- groups (3251 μmol $g_{cat}{}^{-1}$), while the $HT_{RL\text{-}US}$ sample shows the lowest amount (2250 μmol $g_{cat}{}^{-1}$). This could be explained by the different rehydration time (15 h and 5 min, respectively) that produces different reconstruction degree (see supplementary data).† As concluded from the uptake of CO_2 during TPD experiments (see Table 2), the number of probed OH^- groups in the samples is in the range of 438 up to 972 μmol $g_{cat}{}^{-1}$, rather similar in contrast with the BET surface values (between 15 and 440 m^2 g^{-1}). Comparison of the TGA with the CO_2 uptake enables to conclude that the number of basic sites probed by CO_2 is estimated at only 13, 28.5, 31 and 32%, for HT_{RG}, HT_{RL500}, $HT_{RL700\text{-}B}$ and $HT_{RL\text{-}US}$, respectively.

Table 2 Characterisation measurements of rehydrated hydrotalcites

Catalyst	Crystallite size (001)/Å	Total OH^-/[a] μmol $g_{cat}{}^{-1}$	Probed OH^-/[b] μmol $g_{cat}{}^{-1}$
HT_{RG}	141	3251	438
HT_{RL500}	71	2826	804
$HT_{RL700\text{-}B}$	—	3137	972
$HT_{RL\text{-}US}$	49	2250	720

[a] By TGA. [b] By TPD of CO_2.

The latter observation already evidences that a large fraction of OH^- groups in the HTs are unreachable by CO_2, due to diffusion limitations in the interlayer space. Obviously, the results with CO_2 should be dramatically aggravated in the condensation of ketones, which are considerably bulkier. Accordingly, a decisive factor to maximise the catalytic performance of reconstructed HT in aldol condensations should be mainly directed towards securing an improved accessibility of the basic groups to the reactants. Then, the formation of smaller platelets in the liquid-phase rehydrated samples using ultrasounds or vigorous mechanical stirring, increases the number of external OH^- groups near the edges of the layers, which are obviously the most accessible. Additionally, the crystallite size (expressed as average thickness) of the different rehydrated samples has been calculated from the integral breadth (β) of the (001) reflection in the XRD patterns, according to the Scherrer equation. The results are summarised in Table 2 where it can be seen that vigorous stirring and ultrasounds produce the exfoliation of the sample, obtaining small crystallites. In concordance with this reasoning, a linear correlation has been obtained between the surface area and the initial reaction rate in the aldol reactions between citral–acetone or citral–MEK (Fig. 3). The lower activity of HT_{RG} can be attributed to the low surface area, resulting from the collapse of the platelets into larger particles upon gas-phase rehydration. Contrarily, the higher surface areas and thinner platelets of the HT_{RL} samples automatically derive in a larger number of exposed OH^-, and particularly those located at the edges of the platelets are readily accessible. The limited diffusion of reactants in the interlayer space of reconstructed hydrotalcites was originally proposed by Roelofs *et al.*,[4] who suggested that only 5% of the hydroxyl ions of the rehydrated samples were active enough to carry out the aldol condensation of citral with acetone. This was concluded from the preparation of samples with different platelet size using different ageing conditions.

In the present work, we have minimised diffusion limitations by the synthesis and stabilisation of nanoplatelets. For the aldol condensation of citral–acetone, rehydration in liquid phase provides different well-exfoliated catalysts, either by increasing the stirring speed or the time of rehydration. Initial reaction rates between 5×10^{-3} and 8×10^{-3} mol min^{-1} $g_{cat}{}^{-1}$ are obtained, which are higher than the best activity reported so far (1×10^{-3} mol min^{-1} $g_{cat}{}^{-1}$).[7] This is represented in Fig. 3 by a black square, which corresponds to a Mg–Al hydrotalcite calcined at 723 K and rehydrated by direct addition of decarbonated water at room temperature.[7] Indeed, the surface area of this rehydrated sample fits well to the obtained correlation. The aldol condensation of citral–MEK is somewhat slower due to the different acidic character of the α-H in the MEK molecule and its bigger size. However, an enhanced catalytic activity is observed when increasing the stirring speed or using ultrasounds in the rehydration step. In all cases, the selectivity to pseudoionone products is higher than 95% and no loss of activity is detected upon three consecutive runs at 1 h of reaction (conversion higher than 93%).

In summary, our results confirm that only hydroxyl groups in the edges of the platelets, *i.e.* at the entrances of the interlayer space are mainly responsible for the observed activity. This leads to a dramatic underutilization of the active sites through the interlayer

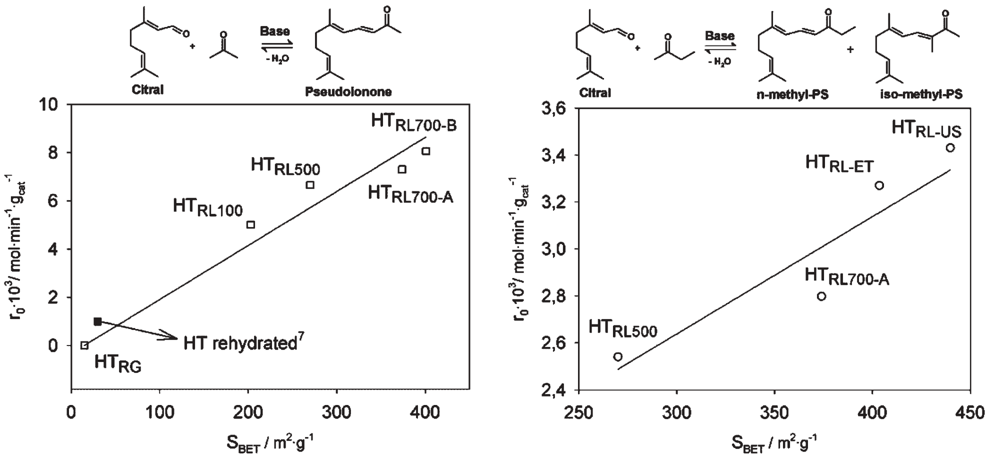

Fig. 3 Initial reaction rate *vs.* surface area of differently rehydrated hydrotalcites in the aldol condensation of citral–acetone and citral–MEK.

space. Liquid-phase rehydration generally leads to catalysts with higher surface areas and thinner platelets as compared to gas-phase rehydration. The nature of the basic sites does not depend on the rehydration conditions, as evidenced by TPD with different probe molecules. A relatively simple and cheap method to further overcome the limited accessibility of OH^- groups in the interlayer of liquid-phase reconstructed hydrotalcites has been established, by using a higher stirring speed or ultrasounds during rehydration. These protocols lead to materials with surface areas up to 440 $m^2 g^{-1}$, due to the high degree of exfoliation of the HT platelets. The linear correlation between the surface area of the rehydrated hydrotalcite and the catalytic performance in Fig. 3 is useful to predict initial activities of rehydrated hydrotalcites by knowing their surface area. Some of our materials display nearly one order of magnitude higher activities than the most active systems reported to date in the literature.

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Notes and references

‡ Mg–Al (Mg/Al = 3/1) hydrotalcite was prepared by coprecipitation at constant pH, thermally decomposed in air at 723 K for 15 h (HT_C), and rehydrated both in gas and liquid phases. A gas-phase sample was obtained under an argon flow saturated with water (15 h at 40 ml min^{-1}). Rehydration in liquid phase was performed in decarbonated water (1 g in 100 ml of water) at RT using (i) mechanical stirring at different times (1 or 6 h) and stirring speed (100, 500, and 700 rpm) or (ii) sonication (5 min). After that, the samples were filtered, washed with ethanol and dried under Ar. The samples were characterized by N_2 adsorption, SEM, and TPD with different probe molecules (CO_2, CH_3CN, CH_3NO_2). The condensation reactions were carried out at 333 K with a ratio ketone/citral = 4.4. Samples were taken at regular time periods and analysed by gas chromatography. Tetradecane was used as internal standard.

1 D. Tichit, M. N. Bennani, F. Figueras, R. Tessier and J. Kervennal, *Appl. Clay Sci.*, 1998, **13**, 401; K. K. Rao, M. Gravelle, J. Sanchez Valente and F. Figueras, *J. Catal.*, 1998, **173**, 115; M. L. Kantam, B. M. Choudary, Ch. Venkat Reddy, K. K. Rao and F. Figueras, *Chem. Commun.*, 1998, **9**, 1033; M. J. Climent, A. Corma, S. Iborra and J. Primo, *J. Catal.*, 1995, **151**, 60; A. Guida, M. H. Lhouty, D. Tichit, F. Figueras and P. Geneste, *Appl. Catal. A*, 1997, **164**, 251; B. M. Choudary, M. L. Kantam, Ch. Venkat Reddy, K. K. Rao and F. Figueras, *J. Mol. Catal. A*, 1999, **146**, 279.
2 P. S. Gradeff, US Patent, 1974, 3,840,601.
3 M. J. Climent, A. Corma, S. Iborra and A. Velty, *Catal. Lett.*, 2002, **79**, 157.
4 J. C. A. A. Roelofs, A. J. van Dillen and K. P. de Jong, *Catal. Today*, 2000, **60**, 297; J. C. A. A. Roelofs, D. J. Lensveld, A. J. van Dillen and K. P. de Jong, *J. Catal.*, 2001, **203**, 184.
5 F. Figueras, J. Lopez, J. Sanchez-Valente, T. T. H. Vu, J.-M. Clacens and J. Palomeque, *J. Catal.*, 2002, **211**, 144.
6 F. Cataldo, *Ultrason. Sonochem.*, 2000, **7**, 35.
7 M. J. Climent, A. Corma, S. Iborra, K. Epping and A. Velty, *J. Catal.*, 2004, **225**, 316; M. J. Climent, A. Corma, S. Iborra and A. Velty, *J. Catal.*, 2004, **221**, 474.