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Hydrotalcite reconstructed by *in situ* rehydration as a highly active solid base catalyst and its application in aldol condensations†

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Reconstructed hydrotalcite is a highly active heterogeneous base catalyst for a wide variety of reactions. Herein, we report a procedure to effectively prepare the reconstructed hydrotalcite. Mg–Al mixed oxide, which originates from hydrotalcite, is added directly to the aqueous-phase reaction system of the aldol condensation without the protection of an inert gas. Under the reaction conditions, the reconstructed hydrotalcite is *in-situ* generated, and is used as a catalyst for then aldol condensation as soon as it forms, resulting in the elimination of the deactivation of reconstructed hydrotalcite. The experimental results showed that the *in-situ* reconstructed hydrotalcite had higher catalytic activity and water tolerance. The work provides a simple and effective method for reconstructed hydrotalcite.

Introduction

Hydrotalcite, with a general formula of $[\mathrm{Mg}_{(1-x)}\mathrm{Al}_x(\mathrm{OH})_2](\mathrm{CO}_3)_{x/2}{}^{2-}\cdot n\mathrm{H_2O}$, is a class of double layered anionic clay having brucite-like $Mg(OH)_2$ layers, where magnesium cations are octahedrally-coordinated with hydroxyl ions and share edges to form brucite-like layers. When a magnesium cation is replaced by an aluminum cation, a positive charge is generated in the layer, which is balanced by an anion, such as carbonate or hydroxyl, located between the layers. Water molecules can also be present in the interlayer space. In recent years, hydrotalcite-like compounds have been used in numerous fields.[1,2] Hydrotalcite-like compounds are solid bases, and the basicity of hydrotalcite-like compounds can be easily tuned by changing the nature and the ratios of the M^{2+}/M^{3+} metals or by introducing a suitable anion in the interlayer region.[3] Based on their unique basic properties, hydrotalcite-like compounds have been widely used as catalysts or catalyst precursors in organic reactions.[4] The thermal decomposition of Mg–Al hydrotalcite yields a high surface area Mg–Al mixed oxide [hereafter indicated as Mg(Al)O], which presumably exposes strong Lewis base sites.[5] Interestingly, the calcined hydrotalcites (mixed oxides) can be reconstructed back to the original lamellar structure upon contact with water, due to the memory effect.[4,6] During the rehydration, the brucite-like layers are reformed and the charge-compensating carbonate anions are replaced by hydroxyl anions, thus forming Brønsted base sites. The reconstructed Mg–Al hydrotalcite with Brønsted base sites exhibits higher catalytic activity than the decomposed Mg–Al hydrotalcite with Lewis base sites in a variety of reactions, such as self- and cross-aldol condensations of aldehydes and ketones,[7–10] Knoevenagel and Claisen–Schmidt condensations,[11–13] Michael additions,[14] and the transesterification of tributyrin with methanol.[15]

The catalytic performance of reconstructed hydrotalcite is closely related to the rehydration procedure.[2,16] There are two rehydration procedures, gas-phase rehydration and liquid-phase rehydration, for reconstructed hydrotalcite. Gas-phase rehydration was carried out by treating the calcined sample in an N_2 or argon flow saturated with water at room temperature for 24 h to yield rehydrated hydrotalcite.[17] Liquid-phase rehydration was carried out by directly immersing the calcined hydrotalcite in decarbonated water at room temperature for about 5 h. After the rehydration process, the sample was filtered, washed with ethanol, and dried under argon to yield the rehydrated hydrotalcite.[2] The rehydration processes performed to date are complex and time-consuming. On the other hand, Abelló *et al.* found that the poisoning of the active Brønsted basic centers in the rehydrated hydrotalcite by CO_2 was very fast (50% activity loss after 1 h exposure to ambient conditions).[17] This means that the rehydrated hydrotalcite, which was prepared through a complex and time-consuming process, could sharply lose its activity when exposure to ambient conditions. Therefore, extreme care was taken to avoid contact of the rehydrated hydrotalcite with air using an inert gas atmosphere in all operations during preparation,

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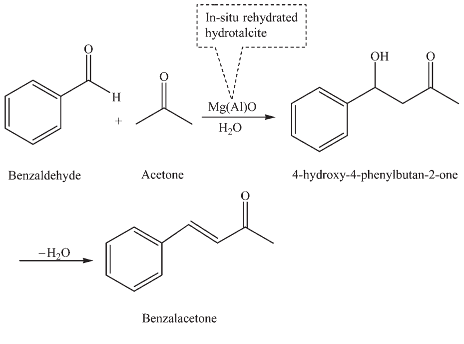
processing, storage, and use of the solid.[11–17] The disadvantage in terms of the rehydration method may limit the implementation of the rehydrated hydrotalcite catalyst in organic reactions.[17]

The development of more efficient, safer, and environmentally friendly chemical technologies is a major requirement of humanity. The aim of this work was to seek one method which could avoid the disadvantage of rehydrated hydrotacite resulting from the conventional preparation method. In this work, Mg(Al)O, originating from hydrotalcite, was directly added into the aqueous-phase reaction system of an aldol condensation without the protection of an inert gas (Scheme 1). The structure of the catalyst before and after reaction was determined. The results showed that the reconstructed hydrotalcite was *in-situ* generated under the reaction conditions. The aldol condensation of benzaldehyde with acetone was carried out to study the catalytic activity of the *in-situ* rehydrated hydrotalcite. On the basis of the structure and activity of the catalyst, we explored the possibility of *in-situ* reconstructing hydrotalcite in the presence of a reaction solution. The experimental results demonstrated that the reconstructed hydrotalcite, formed by *in situ* rehydration, exhibited a higher catalytic activity than the reconstructed hydrotalcite formed by the conventional preparation method. Furthermore, the *in-situ* rehydration method for preparing reconstructed hydrotalcite was simple and time-saving, and the obtained solid base catalyst was water tolerant.

Experimental section

Preparation of Mg–Al hydrotalcites

Mg–Al hydrotalcite with Mg^{2+}/Al^{3+}atomic ratios of 2, 3 and 4 were prepared using a standard aqueous co-precipitation method at constant pH and temperature.[18] An aqueous solution (166 ml) of the metal nitrates in the desired Mg^{2+}/Al^{3+} molar ratio, with a total concentration of 1.5 M, was mixed slowly with an alkaline solution of Na_2CO_3/NaOH with continuous stirring. The molar quantity of Na_2CO_3 employed was twice that of Al^{3+}. The pH value of the mixture was kept constant, typically at values between 9 and 10, by adjusting the rate of addition of the alkaline solution. The temperature was maintained at 25 °C, which resulted in the formation of a heavy slurry, and the mixture was aged at 60 °C for 18 h with stirring, to enhance the selective formation of the precipitated hydrotalcite phase. The slurry was then cooled to 25 °C, filtered, and washed with water until the pH value of the filtrate was near 7. The precipitate was dried at 90 °C for 16 h. The resulting materials were hydrotalcites. The hydrotalcites were labeled as HT-*X*, where *X* corresponds to the Mg/Al molar ratio. For example, HT-2 corresponds to hydrotalcite with Mg/Al molar ratio of 2.



Scheme 1 The aldol condensation of benzaldehyde with acetone catalyzed by *in-situ* redydrated hydrotalcite.

Preparation of mixed oxides and single oxide

The Mg–Al hydrotalcite as-prepared, was calcined at 500 °C for 5 h in static air to generate Mg(Al)O. The generated Mg(Al)O samples were denoted Mg(Al)O-*X*, where *X* corresponds to the Mg/Al molar ratio.

A reference MgO catalyst was prepared by the thermal decomposition of $Mg(OH)_2$ using the same decomposition procedure as Mg(Al)O samples. The $Mg(OH)_2$ precursors were obtained by precipitation using aqueous NaOH from the corresponding aqueous nitrate salt solutions. The γ-Al_2O_3 used was a commercial sample (Alfa Aesar, S_{BET} = 220 m^2 g^{-1}). It was activated at 500 °C for 5 h in static air before the reaction test.

Preparation of rehydrated hydrotalcite by the conventional method

The structure of rehydrated hydrotalcite was affected by the rehydration conditions, such as the rehydration reagent, stirring speed, washing reagent.[2,11,19–21] To compare the activities of the rehydrated hydrotalcite catalyst prepared by the *in-situ* rehydration method with that by the conventional method, typical conventional methods of preparing rehydrated hydrotalcite were employed according to the procedure described in the literature.[2,11,19–21] In this work, four rehydration methods were used. Their difference is in the property of the rehydration reagent and washing reagent, details are shown below. The Mg–Al hydrotalcite was calcined at 500 °C for 5 h in static air to form the corresponding Mg(Al)O. The Mg(Al)O was immersed in decarbonated water at room temperature for 1 h. After the rehydration process, the sample was filtered, and dried at 60 °C under N_2 to yield rehydrated hydrotalcite by the first method. The obtained rehydrated hydrotalcite was denoted HT-R. The second method and the third method were similar to that of the first method, with a difference in rehydration reagent. The rehydration reagent of the second method was ethanol solution (v/v, 1:1), while the rehydration reagent of the third method was acetone solution (v/v, 1 : 1). The rehydrated hydrotalcite by the second and third method were denoted HT-RE and HT-RA, respectively. These three methods did not contain a washing step, while the fourth method was subjected to an extra washing step using acetone. The procedure of the fourth method was similar to that of the third method. The rehydrated hydrotalcite by the fourth method was denoted HT-RAA.

Catalyst characterization

X-ray diffraction patterns were recorded using a D/Max-3C X-ray powder diffractometer (Rigaku Co., Japan), using a Cu Kα source fitted with an Inel CPS 120 hemispherical detector. The elemental compositions of the catalysts were determined using energy dispersive X-ray spectroscopy (EDS). The results of the elemental analyses are shown in Table S1 (ESI†). Infrared transmission spectra were recorded in the range of 400–4000 cm^{-1} by a FTIR spectrometer (Bruker Tensor 27, Germany). The KBr pellet technique was applied for determining the IR spectra of the samples.

The surface area and pore characteristics of the catalysts were determined using a Micromeritics ASAP 2020 instrument. The sample was degassed at different temperatures (100 °C for hydrotalcite, 250 °C for oxide) for 4 h in N_2 prior to surface area measurements. Nitrogen adsorption and desorption isotherms were measured at −196 °C, and the specific surface areas of the catalysts were determined by applying the BET (Brunauer–Emmett–Teller) method to the nitrogen adsorption data obtained in the relative pressure range from 0.06 to 0.30. Total pore volumes were estimated from the amount of nitrogen adsorbed at a relative pressure of 0.995. Pore volume and pore size distributions were obtained from analysis of the desorption branches of the nitrogen isotherms using the BJH (Barrett–Joyner–Halenda) method.

Reaction procedure

The reaction was carried out in a round bottom glass flask equipped with a vertical condenser under vigorous stirring. Typical reactions were performed with 0.02 mol of benzaldehyde, 0.1 mol of acetone and 0.1 mol of de-ionized and decarbonated water [mole ratio of benzaldehyde/acetone/water (hereafter denoted B/A/W) was 1 : 5 : 5] using 0.4245 g of Mg(Al)O catalyst at 65 °C for the specified time (3 h). The reaction products were analyzed by gas chromatography (Shimadzu GC-2014) using a flame ionization (FID) detector and an Rtx-wax column (30 m × 0.32 mm × 0.5 um). Decane was used as the internal standard. The reaction products were characterized by GC-MS (Shimadzu GCMS-QP2010UItra).

Results and discussion

BET surface area and pore size

Table 1 shows the nitrogen physisorption data of hydrotalcite and Mg(Al)O. The surface area of hydrotalcite was in the range of 35–78 $m^2\ g^{-1}$ (Table 1, entries 1–3). The Mg(Al)O, originaing from hydrotalcite, showed a higher surface area, which was in the range of 168–215 $m^2\ g^{-1}$ (Table 1, entries 4–6). Table 2 shows the nitrogen physisorption data of the rehydrated hydrotalcite samples. The surface area of HT-R was 23 $m^2\ g^{-1}$ (Table 2, entry 1), which was lower than other rehydrated hydrotalcites. The surface area of HT-RE (Table 2, entry 2) and HT-RA (Table 2, entry 3) was *circa* 80 $m^2\ g^{-1}$, which was similar to that of *in-situ* rehydrated HT-3 (Table 2, entry 5). HT-RAA (Table 2, entry 4) had the largest surface area (130 $m^2\ g^{-1}$). Besides, the pore diameter of the samples were in the range of 10–42 nm, suggesting that all the samples are mesoporous materials irrespective of the nature of the sample (*i.e.*, whether it was hydrotalcite or oxide).

Effect of water and acetone amount

In the tested system, water may work as both the rehydrating agent to *in-situ* reconstruct hydrotalcite and the solvent of the aldol condensation between benzaldehyde and acetone; acetone was both solvent and reactant. Therefore, their amount may affect the *in-situ* formation and activity of rehydrated hydrotalcite. For the three variables (amount of water, acetone as well as benzaldehyde), we studied the effect of one variable by keeping the ratio of the other two variables constant. The weights of Mg(Al)O and benzaldehyde were kept constant during the whole process.

Effect of water amount when the ratio of B/A was constant

The effect of the water amount was studied when the ratio of B/A was set constantly as 1 : 5 (Fig. 1). The results showed that benzaldehyde conversion and benzalacetone yield increased with water amount and reached a maximum when the ratio of B/A/W was 1 : 5 : 5. Above a 1 : 5 : 5 ratio of B/A/W, the conversion and yield remained constant at the maximum and did not change with further increasing the amount of water. This suggests that an amount of water that was equal to or greater that of acetone, was favored to obtain a maximum yield when the ratio of B/A was 1 : 5.

Effect of acetone amount when the ratio of B/W was constant

The effect of the amount of acetone was studied when the ratio of B/W was set constantly as 1 : 5 (Fig. 2). As shown in Fig. 2, the maximum conversion and yield was obtained when the amount of acetone and water was equal. When the amount of acetone was lower than that of water, the conversion was high (>90%) and the yield was higher than 40%. However, both the conversion and yield decreased sharply when the amount of acetone was higher than that of water.

Table 1 Nitrogen physisorption data of hydrotalcite as-synthesized and Mg(Al)O

Entry	Sample	Surface area[a] ($m^2\ g^{-1}$)	Pore diameter[b] (nm)	Pore volume[b] ($cm^3\ g^{-1}$)
1	HT-2	78	28	0.66
2	HT-3	67	19	0.47
3	HT-4	35	15	0.22
4	Mg(Al)O-2	199	27	0.87
5	Mg(Al)O-3	168	13	0.64
6	Mg(Al)O-4	215	10	0.53

[a] Calculated by the BET method. [b] Calculated by the BJH method from the desorption isotherm.

Table 2 Nitrogen physisorption data of rehydrated hydrotalcite samples and their catalytic activities

Entry		1	2	3	4	5
Rehydrated HT		HT-R	HT-RE	HT-RA	HT-RAA	*In-situ* rehydrated HT-3
Rehydration conditions	Rehydration reagent	H_2O	H_2O + ethanol (1 : 1)	H_2O + acetone (1 : 1)	H_2O + acetone (1 : 1)	*In-situ* rehydration
	Washing reagent	No	No	No	Acetone	
Surface area[a] ($m^2\ g^{-1}$)		23	75	80	130	82
Pore diameter[b] (nm)		14	9	10	12	42
Pore volume[b] ($cm^3\ g^{-1}$)		0.18	0.38	0.24	0.52	0.14
Conversion of benzaldehyde (%)		28	32	30	25	97
Yield of benzalacetone (%)		12	16	13	11	77
Selectivity to benzalacetone (%)		43	50	43	44	81

[a] Calculated by the BET method. [b] Calculated by the BJH method from the desorption isotherm.

Cooperative effect of water and acetone amount when the ratio of acetone to water was constant

Since Fig. 1 and Fig. 2 indicate that when the amount of water is equal to or greater than the amount of acetone both high conversion and yield can be achieved, the cooperative effect of the amount of water and acetone was studied under the conditions of 1 : 1 A/W molar ratio. As shown in Fig. 3, the conversion of benzaldehyde could reach nearly 100% when the ratio of B/A/W was as low as 1 : 1 : 1. It was maintained near 100% as the ratio increased to 1 : 5 : 5. Above a 1 : 5 : 5 B/A/W ratio, the conversion of benzaldehyde declined. It decreased to 70% when the ratio of B/A/W was 1 : 15 : 15. The variation of benzalacetone yield with respect to the B/A/W ratio was different to that of benzaldehyde conversion. The benzalacetone yield was 42% when the ratio of B/A/W was 1 : 1 : 1 and went to a maximum as the ratio of B/A/W was 1 : 5 : 5. Above a 1 : 5 : 5 B/A/W ratio, the benzalacetone yield declined. Therefore, the optimum ratio of B/A/W was 1 : 5 : 5.

The low benzalacetone yield under the ratio of 1 : 1 : 1 may be attributed to the formation of the by-product dibenzalacetone. For a ratio of 1 : 1 : 1, the amount of acetone was low. A low amount of acetone may increase the formation of dibenzalacetone, formed by further reaction of benzaldehyde with benzalacetone.[10,22]The formation of dibenzalacetone decreased the yield of benzalacetone.

XRD patterns of *in-situ* rehydrated HT-3

Fig. 4 presents the X-ray diffraction patterns of as-synthesized HT-3, Mg(Al)O-3, and *in-situ* rehydrated HT-3. The as-synthesized HT-3 sample presented a pure hydrotalcite phase, characterized by diffraction peaks at 11.4°, 23.0° and 34.9° (Fig. 4a). Calcination of hydrotalcite at 500 °C gave a uniform

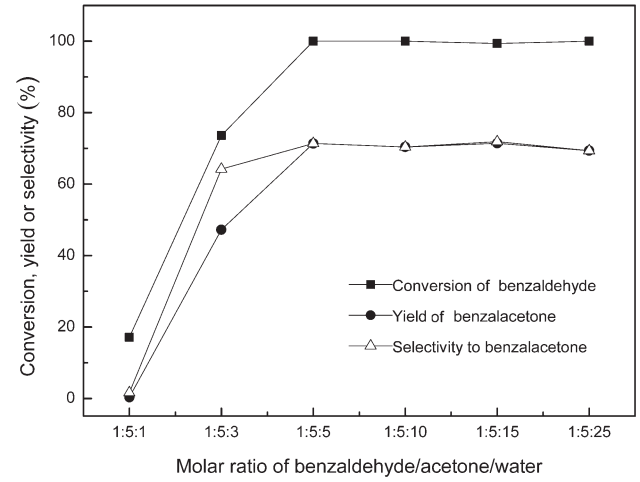


Fig. 1 Effect of water amount on the activity of rehydrated hydrotalcite. Reaction conditions: benzaldehyde (0.02 mol), ratio of benzaldehyde to acetone (1 : 5), reaction temperature (65 °C), Mg(Al)O-3 catalyst amount (0.4245 g), reaction time (3 h).

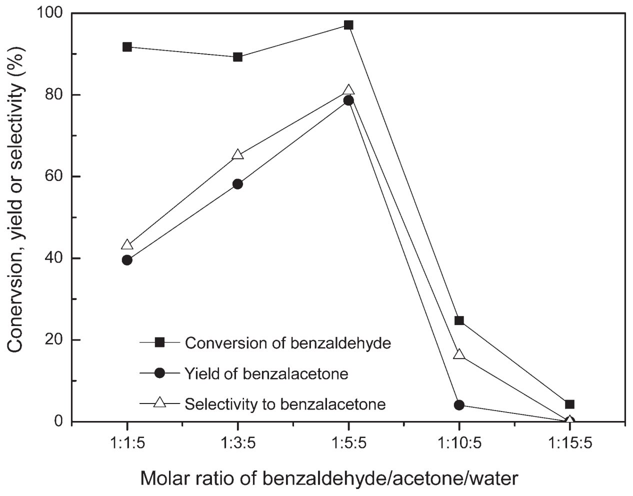


Fig. 2 Effect of acetone amount on activity of rehydrated hydrotalcite. Reaction conditions: benzaldehyde (0.02 mol), ratio of benzaldehyde/water (1 : 5), reaction temperature (65 °C), Mg(Al)O-3 catalyst amount (0.4245 g), reaction time (3 h).

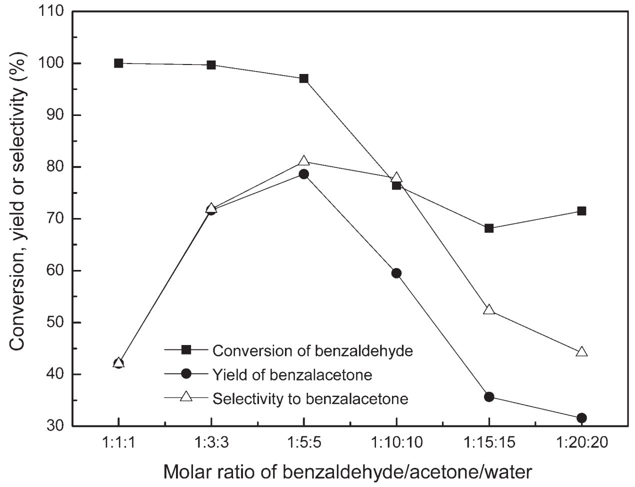


Fig. 3 The cooperative effect of the amount of water and acetone when the ratio of acetone to water was constantly 1 : 1. Reaction conditions: benzaldehyde (0.02 mol), reaction temperature (65 °C), Mg(Al)O-3 catalyst amount (0.4245 g), reaction time (3 h).

mixed oxide phase Mg(Al)O, with diffraction lines very similar to that of MgO (Fig. 4b).[2,7] Under B/A/W ratios of 1 : 5 : 5 (Fig. 4c) and 1 : 1 : 1 (Fig. 4d), where the amount of water was equal to that of acetone, the *in-situ* rehydrated sample showed the typical X-ray diffractograms of hydrotalcite. Furthermore, under a B/A/W ratio of 1 : 1 : 5, where the amount of water was more than that of acetone, the *in-situ* rehydrated sample showed the typical X-ray diffractograms of hydrotalcite (Fig. 4e). The results demonstrated that HT-3 could be successfully *in-situ* reconstructed if the amount of water was equal to or greater than the amount of acetone.

In contrast, the structure of the *in-situ* rehydrated sample was affected by the absolute amount of water when the relative concentration ratio of W/A was less than 1. Under a 1 : 5 : 1 B/A/W ratio, where the amount of water was lower and far less than that of acetone, the *in-situ* rehydrated sample still kept the structure of Mg(Al)O and did not show the typical X-ray diffractograms of hydrotalcite (Fig. 4f). However, under a B/A/W ratio of 1 : 15 : 5, where the absolute amount of water was high and far less than that of acetone, the *in-situ* rehydrated sample showed the typical X-ray diffractograms of hydrotalcite (Fig. 4g). This indicates that, even if the relative concentration ratio of water/acetone was less than 1, HT-3 could be *in-situ* reconstructed if the absolute amount of water was enough.

Combining the results of activity and structure, it was found that the amount of water, equal to or greater than acetone, favors the maximum yield and the formation of *in-situ* reconstructed hydrotalcite. Whereas when the amount of water was less than acetone, the maximum yield and the formation of *in-situ* reconstructed hydrotalcite was disfavored. Furthermore, when the water amount was less than acetone, it showed low activity even if hydrotalcite was successfully *in-situ* reconstructed. This indicated that the amount of water affected both the formation of rehydrated hydrotalcite and the activity of the *in-situ* reconstructed hydrotalcite.

XRD patterns of *in-situ* rehydrated HT-2 and HT-4

The Mg/Al ratio of hydrotalcite may affect its *in-situ* rehydration, so the XRD patterns of *in-situ* rehydrated hydrotalcite with different of Mg/Al ratios were tested. Fig. 5 presents the X-ray diffraction patterns of *in-situ* rehydrated HT-2 and HT-4 under a 1 : 5 : 5 B/A/W ratio. Both the *in-situ* rehydrated HT-2 and HT-4 showed the typical X-ray diffractograms of hydrotalcite, which showed that HT-2 and HT-4 could also be successfully *in-situ* reconstructed under a B/A/W ratio of 1 : 5 : 5.

XRD patterns of reference samples

Fig. 6 shows the X-ray diffraction patterns of the reference samples (MgO, γ-Al_2O_3, and a physical mixture of MgO and γ-Al_2O_3 before and after reaction. The γ-Al_2O_3 before and after

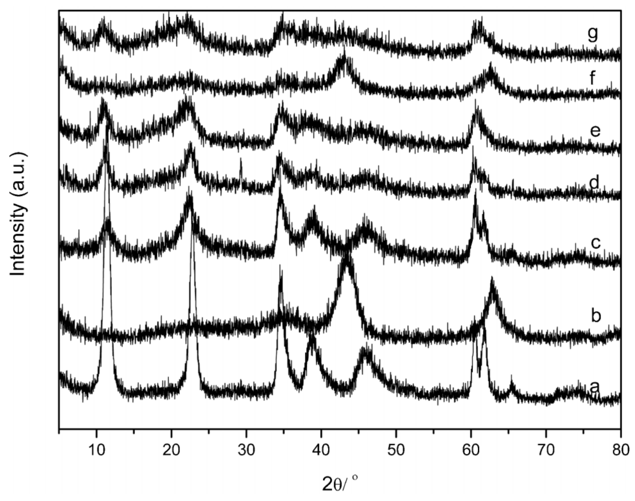


Fig. 4 X-ray diffraction patterns of (a) as-synthesizedHT-3; (b) Mg(Al)O-3; and (c–g) the *in-situ* rehydrated samples under different ratios of benzaldehyde/acetone/water: (c) 1 : 5 : 5, (d) 1 : 1 : 1, (e) 1 : 1 : 5, (f) 1 : 5 : 1, (g) 1 : 15 : 5.

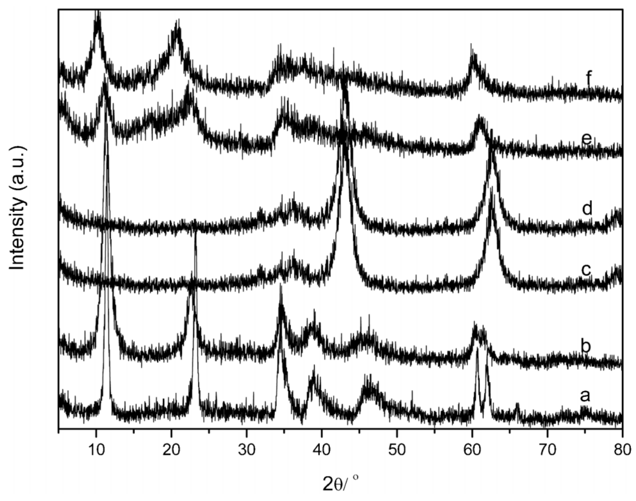


Fig. 5 X-ray diffraction patterns of (a) as-synthesized HT-2; (b) as-synthesized HT-4; (c) Mg(Al)O-2; (d) Mg(Al)O-4; (e) *in-situ* rehydrated HT-2; (f) *in-situ* rehydrated HT-4.

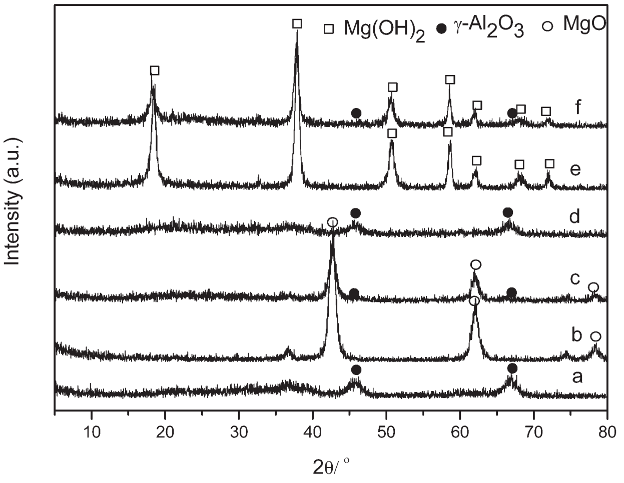


Fig. 6 X-ray diffraction patterns of the reference samples before and after reaction. (a) γ-Al_2O_3 before reaction; (b) MgO before reaction; (c) a physical mixture of MgO and γ-Al_2O_3 (before reaction); (d) γ-Al_2O_3 after reaction; (e) MgO after reaction; (f) a physical mixture of MgO and γ-Al_2O_3 (after reaction). Reaction conditions: benzaldehyde (0.02 mol), molar ratio of benzaldehyde/acetone/water (1 : 5 : 5), reaction temperature (65 °C), Mg(Al)O-3 catalyst amount (0.4245 g), reaction time (3 h).

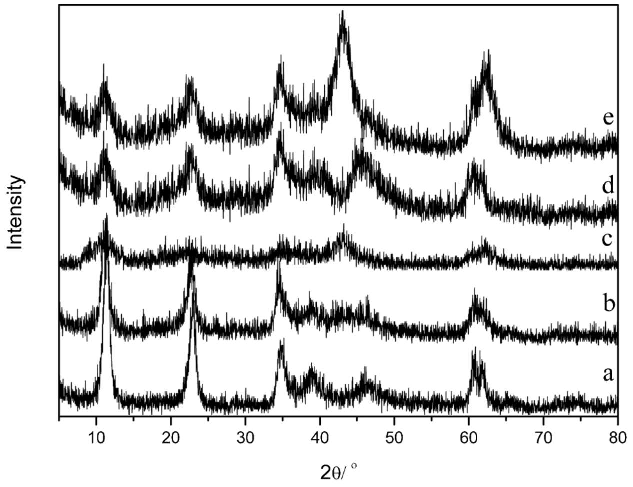


Fig. 7 X-ray diffraction patterns of rehydrated samples by conventional methods (a) HT-R, (b) HT-R after reaction, (c) HT-RAA, (d) HT-RE, (e) HT-RA.

reaction displayed the typical X-ray diffractograms of γ-Al_2O_3, which indicated that γ-Al_2O_3 did not *in-situ* rehydrate to form the rehydration product. MgO before reaction showed diffraction peaks ascribed to MgO, whereas MgO after reaction showed X-ray diffractograms typical of $Mg(OH)_2$. This indicates that MgO was *in-situ* rehydrated to form $Mg(OH)_2$ in the aqueous-phase reaction system of the aldol condensation. For the physical mixture of MgO and γ-Al_2O_3, a similar phenomenon was observed. Before reaction, the physical mixture of MgO and γ-Al_2O_3 showed the diffraction peaks ascribed to MgO and γ-Al_2O_3, after reaction, it showed, in addition to γ-Al_2O_3, a series of new diffraction peaks ascribed to $Mg(OH)_2$. Fig. 7 shows the X-ray diffraction patterns of the rehydrated hydrotalcite prepared by the conventional method. All the rehydrated samples showed the typical X-ray diffractograms of hydrotalcite with a difference in the intensity of diffraction. HT-R showed the highest intensity of diffraction, while HT-RAA showed the lowest intensity. HT-R after reaction was also determined. It showed a similar diffraction pattern with the fresh one.

Effect of Mg/Al ratio on the catalytic activity of *in-situ* rehydrated hydrotalcite

The activity of *in-situ* rehydrated HT-2, HT-3 and HT-4 was tested under the same reaction conditions. The molar ratio of B/A/W was set as 1 : 5 : 5, where all three samples could be successfully *in-situ* rehydrated (Fig. 4 and Fig. 5). As shown in Table S2 (ESI†), the three rehydrated samples displayed different activities. *In-situ* rehydrated HT-3 displayed the highest activity, with 97% benzaldehyde conversion. Next was *in-situ* rehydrated HT-2, which showed the middle activity (benzaldehyde conversion, 56%). *In-situ* rehydrated HT-4 presented the lowest activity, in which the benzaldehyde conversion was 15%. This showed that the Mg/Al ratio affected the catalytic activity of the *in-situ* rehydrated hydrotalcites. The difference in the activity of *in-situ* rehydrated HT-2, HT-3 and HT-4 may be ascribed to the effect of the Mg/Al ratio on the process of their rehydration.[23]

However other workers have reported much smaller variations when using conventionally rehydrated hydrotalcites.[6] The reason for this discrepancy is discussed as follows. For the conventionally rehydrated methods, the catalyst was completely rehydrated before it was used for the aldol condensation.[6] Therefore, the rehydration rate of hydrotalcite did not affect its activity. However, for the *in-situ* rehydration method, the process of rehydration and the reaction of the aldol condensation happened almost simultaneously. Therefore, the *in-situ* rehydration rate of hydrotalcite affected its activity. It was reported that the rehydration rate of hydrotalcite was affected by the Mg/Al ratio.[23] Therefore, the Mg/Al ratio in *in-situ*

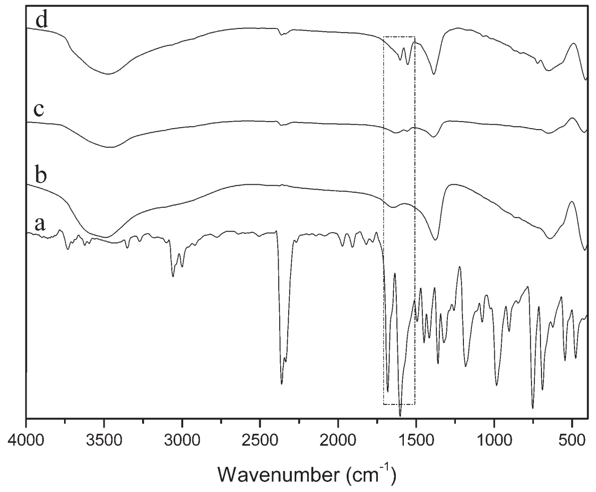


Fig. 8 The IR spectra of (a) benzalacetone ;(b) HT-R (before reaction); (c) *in-situ* rehydrated samples under a 1 : 5 : 5 B/A/W ratio; (d) *in-situ* rehydrated samples under a 1 : 1 : 1 B/A/W ratio.

rehydrated hydrotalcites had a marked effect on their catalytic activity.

FTIR analysis

The infrared spectrum of catalyst after reaction was determined. Fig. 8 shows the IR of benzalacetone, HT-R (before reaction) and *in-situ* rehydrated samples (after reaction). The IR spectra of the sample benzalacetone and HT-R indicated that they were typical benzalacetone and pure hydrotalcites, respectively. The infrared spectra of *in-situ* rehydrated samples (after reaction), in addition to two bands at 1604 cm^{-1} and 1558 cm^{-1}, were similar with that of HT-R (before reaction). The bands at 1604 cm^{-1} and 1558 cm^{-1} were due to the vibration of C=C of benzene ring, indicating the existence of benzalacetone on the surface of used catalyst. Furthermore, the result also showed that intensity of those two bands for B/A/W ratio of 1 : 1 : 1 was greater than that of 1 : 5 : 5. This indicated that the amount of benzalacetone adsorbed in B/A/W ratio of 1 : 1 : 1 was higher that in ratio of 1 : 5 : 5.

The XRD graphics could confirm that the materials after the reaction were only deposited on the surface, not in the interlayer space. If the materials after the reaction were in the interlayer space, the interlayer space of HT would increase. If the interlayer space of HT was increased, the original (003) and (006) reflections would move to a lower angle of diffraction.[24] However, as shown in Fig. 4, the XRD pattern of *in-situ* HT was similar to that of as-synthesized HT. This result showed that the interlayer space of *in-situ* HT was unchanged, and materials after reaction were deposited on the surface, not in the interlayer space.

Catalytic activity of *in-situ* rehydrated HT-3

The aldol condensation of benzaldehyde with acetone has been carried out to study the catalytic activity of *in-situ* rehydrated HT-3. The main product obtained is benzalacetone, formed by dehydration of 4-hydroxy-4-phenyl butan-2-one. The catalytic activity of *in-situ* rehydrated HT-3 was compared with that of as-synthesized HT-3, rehydrated HT-3 by the conventional method, and oxide (Table 2 and 3). In the absence of catalyst, no conversion of benzaldehyde was observed irrespective of the presence of H_2O (Table 3, entries 1 and 2). The as-synthesized HT-3 sample, with or without water, did not show apparent catalytic activity, with a benzaldehyde conversion <2% (Table 3, entries 3 and 4). Besides, MgO and γ-Al_2O_3, as well as a physical mixture of MgO and γ-Al_2O_3, were inactive (Table 3, entries 5–10). Mg(Al)O also displayed low activity (benzaldehyde conversion, 7%), in which no benzalacetone was detected (Table 3, entry 11). Rehydrated HT-3 prepared by the conventional method showed middle activity, with a benzaldehyde conversion of 25%–32% and a benzalacetone yield of 11%–16% (Table 2, entries 1–4). However, high benzaldehyde conversion (97%) and benzalacetone yield (77%) were obtained when *in-situ* rehydrated HT-3 was used as the catalyst (Table 2, entry 5). This indicates that *in-situ* rehydrated hydrotalcite could work as an active catalyst for the aldol condensation.

MgO could *in-situ* rehydrate to form $Mg(OH)_2$ (Fig. 6). The catalytic activity of the *in-situ* rehydrated $Mg(OH)_2$ was very low (Table 3, entry 5), suggesting that the hydroxyl groups coordinated to Mg in the brucite layers of *in-situ* rehydrate $Mg(OH)_2$ have negligible catalytic activity. The as-synthesized (mostly carbonate and hydroxyl anions, Brønsted basic sites), activated [Mg(Al)O, Lewis basic sites] and conventional reconstructed (mostly hydroxyl anions, Brønsted basic sites) hydrotalcite samples did not work well. At the start of the reaction, the material Mg(Al)O (activated hydrotalcite) has mostly Lewis basic sites. On introducing water to the reaction mixture, the Lewis basic sites convert to Brønsted basic sites. So, the activity of the material may be due to either the *in-situ* reconstruction (charge-balancing hydroxyl anions, the Brønsted basic sites) or due to the combined effect of Lewis and Brønsted basic sites.[6] The active sites of *in-situ* rehydrated hydrotalcite will be investigated in future work.

It was reported that the OH^- species (active sites), weakly adsorbed on the surface of rehydrated hydrotalcite, were easily removed as H_2O by the evacuation.[25] The *in-situ* rehydration method avoided the process of evacuation, whereas the conventional rehydration method did go through the process. Therefore, the amount of active sites on *in-situ* rehydrated HT-3 may be higher than that of rehydrated HT-3 prepared by the conventional method. The higher number of active sites on *in-situ* rehydrated HT-3 accounted for its high activity.

For the conventional method, the structure and activity of reconstructed hydrotalcite was strongly affected by the CO_2 in

Table 3 Catalytic activity of reference samples[a]

Entry	Catalyst[b]	Conversion of benzaldehyde (%)	Yield to benzalacetone (%)	Selectivity to benzalacetone (%)
1	Blank	0	0	0
2	H_2O	0	0	0
3	As-synthesized HT-3	2	0	0
4	H_2O + as-synthesized HT-3	1	0	0
5	MgO	13	1	8
6	MgO + H_2O	8	0	0
7	γ-Al_2O_3	7	0	0
8	γ-Al_2O_3 + H_2O	2	0	0
9	MgO + γ-Al_2O_3	12	1	8
10	MgO + γ-Al_2O_3 + H_2O	10	0	0
11	Mg(Al)O-3	7	0	0
12	H_2O + HT-R	25	10	40

[a] Reaction conditions as described in the Experimental section. [b] With or without water.

Table 4 Recycling experiments for the *in-situ* rehydrated HT-3 catalyst[a]

Entry	Catalytic cycles	Conversion of benzaldehyde (%)	Yield to benzalacetone (%)	Selectivity to benzalacetone (%)
1	1st use	97	77	81
2	2nd use[a]	43	2	4
3	3rd use[a]	4	1	18
4	2nd use[b]	20	0	0

[a] The spent *in-situ* rehydated HT-3 catalyst was separated from the reaction solution by centrifugation. It was taken as the catalyst for the repeated reactions without further treatment. The repeated reactions were run under the same reaction conditions to the last reaction. [b] The spent *in-situ* rehydated HT-3 catalyst was washed with acetone, then activated at 500 °C for 5 h.

the air. Therefore, extreme care was taken to avoid contact of the rehydrated hydrotalcite with air using an inert gas atmosphere in all operations during preparation, processing, and storage.[11–15] However, an inert gas atmosphere was not used during the entire *in-situ* rehydration process. There may be very strong chances to intercalate carbonate ions instead of hydroxyl ions in the interlayer space of *in-situ* reconstructed hydrotalcite. The high activity of the *in-situ* reconstructed hydrotalcite indicated that the *in-situ* reconstructed sample was not affected by the air.

Compared with the conventional rehydration method, the *in-situ* rehydration method was simple and time-saving. In the case of the *in-situ* rehydration method, the formation of rehydrated hydrotalcite and the catalytic reaction were simultaneously developed. Furthermore, an inert gas atmosphere was not used at all during the entire process. In the case of the conventional rehydration method, the rehydrated hydrotacite was prepared before the reaction. The preparation of rehydrated hydrotacite went through the process of contacting mixed oxide with water, filtration, washing, and drying. Furthermore, extreme care was taken to avoid contact of the rehydrated hydrotalcite with air using an inert gas atmosphere in all operations during preparation, processing, and storage.[11–15]

Reutilization of *in-situ* rehydrated hydrotalcite

Attempts to reuse the *in-situ* rehydrated hydrotalcite catalyst have as yet not been successful (Table 4), just as the reusability of rehydrated hydrotalcite prepared by the conventional method.[17] The benzaldehyde conversion over the catalyst after one run was 43% and the catalyst after two consecutive runs showed extremely low activity (benzaldehyde conversion, 4%). As shown in the previous section, the spent catalyst was deposited with reaction products (Fig. 8 and Fig. S1†). The deactivation of the *in-situ* rehydrated catalyst may be due to the adsorption of reaction products during the reaction. These deposits likely modify the nature of the few active OH^- centers left and/or its accessibility by reactants in subsequent reactions.[17] In order to decrease the effect of deposits, the spent solid was rinsed with acetone at room temperature, then activated at 500 °C for 5 h to convert washed material into Mg(Al)O and burn the deposits. The regenerated catalyst displayed an off-white color, not the white color of the fresh catalyst. Its off-white color may result from the deposited carbon, which was generated by the burning of the reaction products. The regenerated catalyst showed low activity, suggesting that the treatment with acetone and calcination did not increase the catalytic activity (Table 4, entry 4). The reusability of *in-situ* rehydrated hydrotalcite is supposed to be an area that can be the subject of further investigation.

Conclusions

In this work, water and Mg(Al)O were directly added to the mixed solution of benzaldehyde and acetone without the protection of an inert gas. Water worked as both the rehydrating agent to *in-situ* reconstruct hydrotalcite, and as the solvent of the aldol condensation between benzaldehyde and acetone. The amount of water affected both the formation of the rehydrated hydrotalcite and the activity of the *in-situ* reconstructed hydrotalcite. It was found that the Mg/Al ratio affected the catalytic activity of the *in-situ* rehydrated hydrotalcite. Under optimum conditions, 0.02 mol of benzaldehyde, 0.1 mol of acetone and 0.1 mol of de-ionized and de-carbonated water (mole ratio of B/A/W was 1 : 5 : 5) using 0.4245 g of Mg(Al)O catalyst at 65 °C for the specified time (3 h), Mg(Al)O was successfully *in-situ* rehydrated to form meixnerite. Furthermore, the *in-situ* rehydrated hydrotalcite showed higher activity (benzaldehyde conversion 97%, and benzalacetone yield 77%) than that of rehydrated hydrotalcite prepared by the conventional method (benzaldehyde conversion 40%, and benzalacetone yield 21%). The *in-situ* rehydrated hydrotalcite also had a higher tolerance to water than the rehydrated hydrotalcite prepared by the conventional method. This *in-situ* rehydration method was simple and time-saving, which avoided the shortcomings of the conventional rehydration method.

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