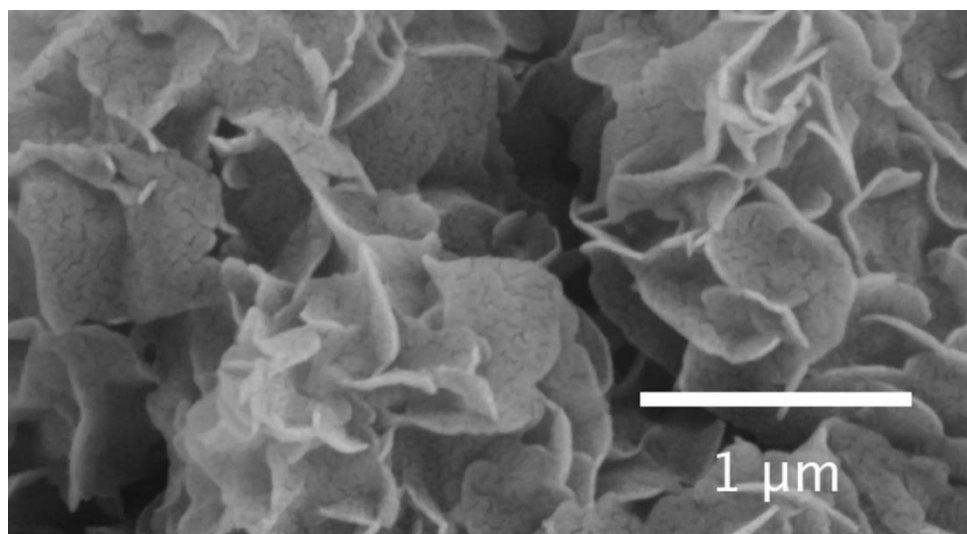


## Supplementary Materials:

# On the Effect of the $M^{3+}$ Origin on the Properties and Aldol Condensation Performance of $MgM^{3+}$ Hydrotalcites and Mixed Oxides

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### 1. SEM study



**Figure S1.** Enlarged SEM image of platelet structure for MgGa-R sample.

### 2. FTIR data for MgM materials (as-prepared, calcined and rehydrated).

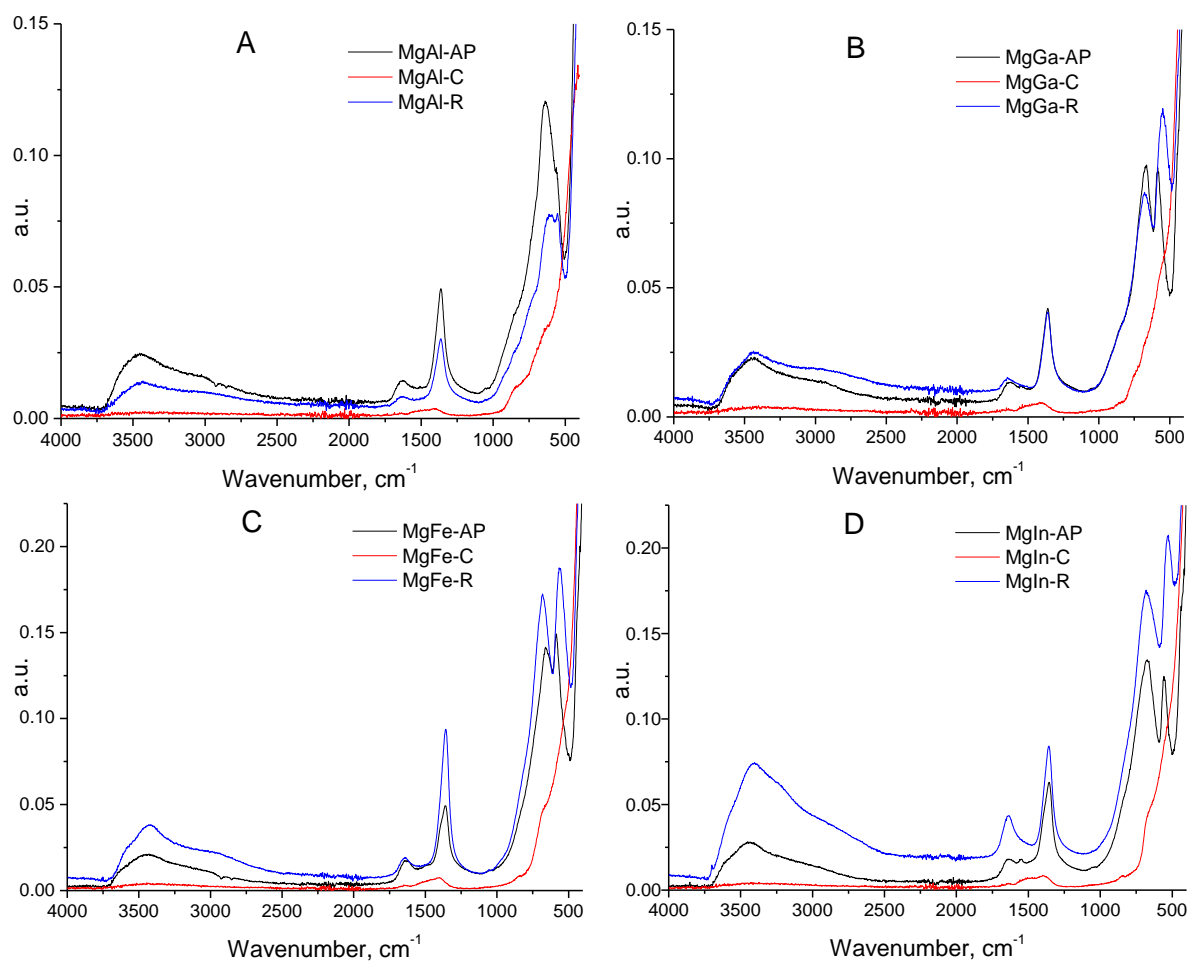
Figure 2S depicts FTIR spectra of the as-prepared hydrotalcites ( $MgM$ -AP), the derived mixed oxides ( $MgM$ -C) and the rehydrated materials ( $MgM$ -R).

The FTIR spectrum of  $MgAl$ -AP (Figure 2S(A)) resembled those published previously for similar materials [1–4]. A broad band with the maximum at  $\approx 3450\text{ cm}^{-1}$  was typical for the stretching vibrations of the structural hydroxyl groups in the brucite-like layer. The band at around  $1630\text{ cm}^{-1}$  was characteristic of the interlayer water molecules, whereas the absorption bands at  $1370$ ,  $850$ , and  $650\text{ cm}^{-1}$  could be attributed to the carbonate anions vibrations  $\gamma_3$ ,  $\gamma_2$  and  $\gamma_4$ , respectively. Additionally, a band at about  $560\text{ cm}^{-1}$  was observed that corresponded to the translation modes of hydroxyl groups influenced by  $Al^{3+}$  cations [3]. FTIR spectra for  $MgGa$ -AP,  $MgFe$ -AP and  $MgIn$ -AP (Figures 2S(B–D)) were very similar to the  $MgAl$ -AP spectrum. These spectra also evidenced presence of the broad band at  $3300$ – $3500\text{ cm}^{-1}$ , as well as bands at  $1630$ – $1650\text{ cm}^{-1}$ ,  $670$ – $680\text{ cm}^{-1}$  and  $540$ – $560\text{ cm}^{-1}$ . Previously, similar FTIR spectra were reported for  $MgGa$  and  $MgIn$  hydrotalcites [5,6]. A similarity in the FTIR spectra of the samples prepared in the present study suggested a similarity in their structural properties, the amount and the nature of both interlayer and adsorbed species.

The FTIR spectra of the mixed oxides (Figure 2S) evidenced that, independently on the nature of the  $M^{3+}$  cation, the band at  $1640\text{ cm}^{-1}$  (water bending vibrations) disappeared, while the bands at around  $3460$ – $3500\text{ cm}^{-1}$  and  $1370\text{ cm}^{-1}$  (interlayer carbonates) substantially decreased in intensity. The change in the type of the spectrum for the calcined samples (Figure 2S) confirmed the expected removal of the interlayer water, the dehydroxylation of the brucite-like layers as well as the decomposition of the carbonate groups. The

small bands near  $1390\text{ cm}^{-1}$  and  $1638\text{ cm}^{-1}$  in the FTIR spectra of the calcined samples allowed assuming that only residual carbonate and hydroxyls anions, respectively, could still be present in the mixed oxides, possibly due to the contact of the calcined samples with air during the measurements.

The FTIR spectra of the rehydrated samples (Figure 2S) differed significantly from those for the calcined samples and were very similar to the spectra for the as-prepared HTCs. The re-appearance of the specific bands at  $3460\text{--}3500\text{ cm}^{-1}$ ,  $1640\text{ cm}^{-1}$  and  $1370\text{ cm}^{-1}$  in the FTIR spectra proved, regardless of the nature of  $M^{3+}$  cation, the recovery of the HTC structure as a result of the rehydration, with the re-appearance of the structural hydroxyl groups in brucite-like layers, adsorbed water, as well as interlayer anions. The latter groups were hydroxyls just after the rehydration step that were, however, readily transformed to carbonates due to the interaction of the interlayer hydroxyls with  $\text{CO}_2$  from air [5].



**Figure S2.** The FTIR spectra of the as-prepared, calcined, and rehydrated MgM samples. A–MgAl, B–MgGa, C–MgFe, D–MgIn.

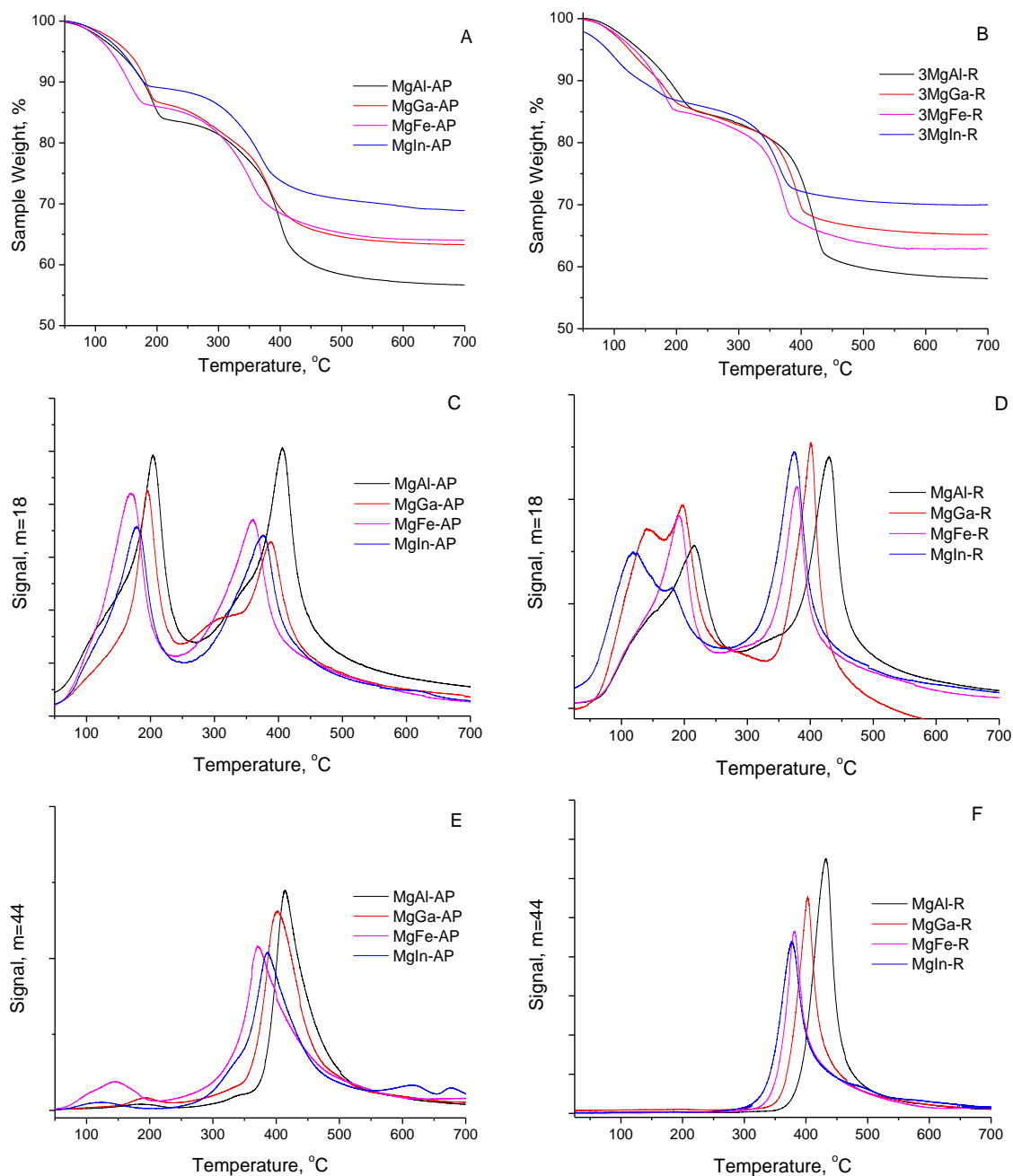
### 3. TGA-MS data

Figure 3S presents the thermal analysis results of the prepared samples. The TGA profiles of the as-prepared samples (Figure 3S(A)) were mostly similar to those reported previously for different samples with HTC structure [7–9]; they possessed several characteristic features corresponding to: i) the removal of the physisorbed and interlayer water, as well as the removal of  $\text{CO}_2$  adsorbed on the surface of the samples ( $T = 25\text{--}250\text{ }^{\circ}\text{C}$ ); ii) the dehydroxylation of brucite-like layers and the decomposition of the interlayer carbonates ( $T = 250\text{--}450\text{ }^{\circ}\text{C}$ ); iii) the decomposition of the residual surface species ( $T > 450\text{ }^{\circ}\text{C}$ ). Figure 3S(A) also showed that the overall weight loss depended on the nature of the  $M^{3+}$  cation. The total weight loss of MgAl-AP was 43.4 wt.% which was consistent with

TGA results for MgAl HTCs published elsewhere [1,3,10,11]. The total weight loss of MgGa-AP was lower, 36.8%, nonetheless this value was also in line with that reported earlier for similar MgGa materials [5]. Total weight loss for MgFe-AP and MgIn-AP was even lower, 36.0% and 31.0% respectively. The decrease in the total weight loss can be attributed to the mass of  $M^{3+}$  cation: the heavier the element, the lower the weight loss according to TGA measurements. The good agreement between the theoretical weight loss calculated based on the chemical composition and the experimentally determined by TGA confirms that the as-prepared materials are indeed hydrotalcites having the composition reported in Table 1. The evolution of  $H_2O$  and  $CO_2$  species from the as-prepared materials was evaluated by TGA-MS. The MS spectra of the evolved water for all as-prepared samples (Figure 3S(C)) demonstrated the existence of two well-expressed signals. A low-temperature signal observed at temperature below 250 °C had a maximum at  $T = 170\text{--}205$  °C and a shoulder at  $T = 100\text{--}120$  °C. The latter could be attributed to the removal of physisorbed water, while the former could be attributed to the removal of the interlayer water. Above 250 °C, the TGA-MS- $H_2O$  spectra of the MgM-AP HTCs demonstrated a second well-expressed signal with a maximum in the range of 360–410 °C which could be attributed to the occurrence of a dehydroxylation process. According to TGA-MS- $CO_2$ , the total profile of  $CO_2$  evolved from the as-prepared samples could also be divided into two signals (Figure 3S(E)). The low-intensity signal below 250 °C could be explained by the removal of  $CO_2$  molecules adsorbed on the basic sites varied in their strength [13], while the high-temperature signal in the range of  $T = 370\text{--}415$  °C could be unambiguously attributed to the removal of  $CO_2$  by the decomposition of the interlayer carbonates. By comparing the temperature profiles shown in Figures 2S(C) and 2S(E) it could be concluded that the dehydroxylation of brucite-like layers and the decomposition of the interlayer carbonates occurred at the same temperature range. It can, thus, be suggested that the processes are linked. The differences in the position of the maximum of the high-temperature peak in the TGA-MS- $H_2O$  and TGA-MS- $CO_2$  profiles could be associated with the different thermal stability of an HTC structure in dependence on the nature of  $M^{3+}$  cation. Such a decrease in the thermal stability could be interpreted in terms of a decrease in the strength of hydrogen bonding, and a reduced electrostatic interaction between the layers and the carbonate anions due to the incorporation of  $M^{3+}$  ions into the lattices [13]. Additionally, a slight increase in both TGA-MS- $H_2O$  and TGA-MS- $CO_2$  profiles at temperature above 450 °C might suggest the residual dehydroxylation and decarboxylation due to the decomposition of the most thermally stable species present in the composition of the generated MgM-C mixed oxides.

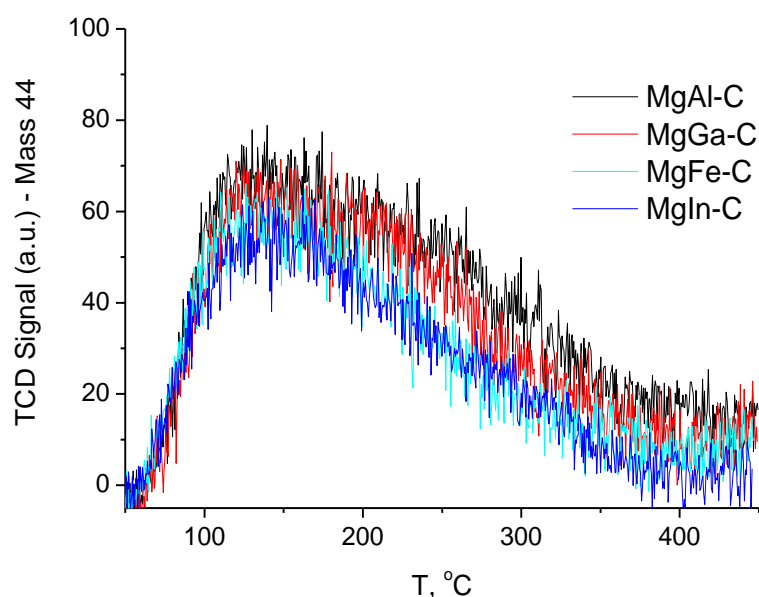
Figure 3S(B) depicts that the total weight loss of the reconstructed MgM-R samples ranged from 41.9% to 30.0%, and it apparently decreased with increasing atomic mass of the  $M^{3+}$  cation from aluminium to indium, thereby repeating the trend observed for the as-prepared HTCs. At the same time, the ratio of weight loss in the rehydrated material to the one in the as-prepared material was close to unity. The obtained TGA results provided a further evidence for the nearly complete reconstruction of the HTC structure by mixed oxide rehydration, independent on the nature of the  $M^{3+}$  cations used in this study. As in case of the as-prepared materials, TGA-MS- $H_2O$  profiles of reconstructed samples evidenced that water was removed in two stages: in the low-temperature region of  $T = 25\text{--}250$  °C, physisorbed and interlayer water was removed, while in the range of  $T = 250\text{--}450$  °C, dehydroxylation of brucite-like layers occurred. The TGA-MS- $CO_2$  profile (Figure 3S(F)) indicated that  $CO_2$  was removed from the rehydrated samples at about 400 °C. The intensity and the position of this signal was very similar to that corresponding to the decomposition of the interlayer carbonates in the as-prepared samples. The observed similarity suggested that the rehydrated samples also contained significant amounts of carbonates. Previously we have suggested that the interaction of MgAl or MgGa mixed oxides with pure water resulted in the reconstruction of the HTC structure where the positive charge of brucite-like layers was compensated by interlayer hydroxyls [1,5]. Nevertheless, these interlayer hydroxyls could easily interact with  $CO_2$  from the air, so the hydroxyls in the freshly rehydrated samples were converted back to carbonates, similar to

those in the as-prepared HTC. Figure 3S evidences that the rehydrated samples varied by  $M^{3+}$  cation prepared in the present study had a rather similar TGA and TGA-MS profiles. Therefore, it could be assumed that the interaction of MgM-C (where M = Al, Ga, Fe, In) with pure water resulted in the recovery of the HTC structure with interlayer hydroxyls as charge-compensating anions. These interlayer hydroxyls were assumed to act as Brønsted basic sites highly sensitive to interaction with  $CO_2$  from air [1] and active in a number of base-catalyzed reactions.



**Figure S3.** TGA (A,B) as well as TGA-MS-H<sub>2</sub>O (C,D) and TGA-MS-CO<sub>2</sub> (E,F) curves for the as-prepared (left column) and reconstructed (right column) hydrotalcites.

#### 4. CO<sub>2</sub>-TPD measurements



**Figure S4.** CO<sub>2</sub>-TPD profiles obtained for MgM-C mixed oxides.

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