Supporting Information

Reconstructed Hydrotalcite as a Highly Active Heterogeneous Base Catalyst for Carbon–Carbon Bond Formations in the Presence of Water

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1. General Procedure and Preparation of Hydrotalcite

General. $\text{AlCl}_3 \cdot 9\text{H}_2\text{O}$, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{Mg}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, Na_2CO_3 , NaOH , KOH , and CaCl_2 were purchased as a special grade. *n*-Dodecyltrimethylammonium bromide was used as received. All organic reagents were purified by the standard procedures, and stored under an Ar atmosphere. All the products were characterized by comparison with the literature data of ^1H and ^{13}C NMR, IR, and MS. Decarbonated water was obtained by repeated freeze-thaw degassing cycles of deionized water, and stored under an Ar atmosphere. GC analysis was performed with a Shimadzu GC-8A gas chromatograph with a FID and a 25 m capillary column of CPB-20. GC-MS analysis was done using Shimadzu GCMS-QP5050 equipped with capillary column (HR-1, 30 m, 0.25 mmID). The glove box (DBO-1KP-MC type; Miwa Co. Ltd.), in which the humidity and oxygen concentration are regulated in ppm orders, was used for transfer the hydrotalcite sample to the plate for XRD measurement at atmospheric pressure of nitrogen. X-Ray diffraction (XRD) was measured on the X'pert diffractionmeter (Phillips Co., Ltd.).

General Procedure for Preparation of Hydrotalcite. Various hydrotalcites were prepared according to the literature procedure.¹ A typical example is for $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$. $\text{AlCl}_3 \cdot 9\text{H}_2\text{O}$ (50 mmol) and $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ (150 mmol) were dissolved in deionized water (100 mL), and a second aqueous solution (60 mL) containing Na_2CO_3 (60 mmol) and NaOH (210 mmol) was prepared. After the first solution was slowly added to the second one, the resulting mixture was heated at 65 °C for 18 h with vigorous stirring. The white slurry was then cooled to room temperature, filtered, washed with large amount of deionized water, and dried overnight at 110 °C. The HTs were stored in air.

2. Product identification

The products showed spectra in an excellent agreement with the reported data. Spectral data for the new compounds are shown below.

Table 2

1,1-Dimethoxybutan-3-ol (entry 1);² CAS registry number [39562-58-8]

1,1-Dimethoxy-2-methylpentan-3-ol (1:2 mixture of diastereoisomers) (entry 2);³ CAS registry number [844850-02-8]

1,1-Dimethoxy-2-ethylhexan-3-ol (A/B = 1:2 mixture of diastereo isomers) (entry 3); IR, 3504, 2960, 2935, 2873, 2832, 1462, 1378, 1106, 1073, 1067, 970; ¹H NMR (400 MHz, CDCl₃) as **Figure S1**: δ 4.42 (d, 1H, *J*=4.8 Hz, CH(OCH₃)₂ for **B**), 4.35 (d, 1H, *J* = 5.4 Hz, CH(OCH₃)₂ for **A**), 3.86 (m, 1H, CHOH for **A**), 3.70 (m, 1H, CHOH for **B**), 3.43 (s, 3H, OCH₃ for **A**), 3.40 (s, 3H, OCH₃ for **B**), 3.37 (s, 3H, OCH₃ for **A**), 3.30 (d, 1H, *J*=4.8 Hz, OH for **B**), 2.92 (d, 1H, *J* = 5.1 Hz, OH for **A**), 1.30-1.68 (m, 7H), 0.98 (tr, 3H, *J* = 7.5 Hz, CH₃ for **A**), 0.94 (tr, 3H, *J* = 7.0 Hz, CH₃ for **B**), 0.93 (tr, 3H, *J* = 7.4 Hz, CH₃ for **A** and **B**); ¹³C{¹H} NMR (100.4 MHz, CDCl₃) as **Figure S2**: δ 107.9 (**A**), 107.8 (**B**), 70.7 (**B**), 70.3 (**A**), 55.9 (**A**), 55.8 (**B**), 54.2 (**B**), 53.8 (**A**), 47.0 (**A**), 46.5 (**B**), 37.4 (**A**), 35.8 (**B**), 19.7, 19.1, 18.9, 17.8, 14.1 (**B**), 14.0 (**A**), 12.9 (**A**), 11.7 (**B**); MS(EI) *m/z* (%) 173 (M⁺-H₂O), 159, 147, 129, 115, 97, 86, 75(100), 71, 55.

Figure S1

Figure S2

4-Hydroxy-6-methylheptan-2-one (entry 5);⁴ CAS registry number [57548-36-4]

4-Hydroxy-5-methylhexan-2-one (entry 6);⁵ CAS registry number: [38836-21-4]

2-(1-Hydroxy-2-methylpropyl)cyclopentanone (entry 7);⁶ CAS registry number: [26620-52-0]

4-Hydroxyheptan-2-one (entry 8);⁷ CAS registry number: [25290-14-6]

3-Hydroxy-2-methylpentanal (note 31);⁸ CAS registry number: [615-30-5]

Table 3

(Z)-2,3-Diphenylacrylonitrile (entry 1);⁹ CAS registry number: [2510-95-4]

(Z)-3-(2-Furyl)-2-phenylacrylonitrile (entry 3);¹⁰ CAS registry number [1207-91-6]

(Z)-2-Phenyl-2-dodecenenitrile (entry 4); IR, 2935, 2853, 2217, 1948, 1877, 1800, 1683, 1620, 1496, 1450, 1377, 1343, 1075, 1023, 910, 876, 761, 692; ¹H NMR (400 MHz, CDCl₃) as **Figure S3**: δ 0.90 (tr, 3H, J = 6.8 Hz, CH₃), 1.23-1.43 (m, 8H, CH₂), 1.55 (quint,

c1ccccc1C(=C)CCCCCCCC#N

Figure S4

(Z)-2-Phenyl-3-isopropylacrylonitrile (entry 5); CAS registry number [6519-10-4].

(Z)-3-Cyclohexyl-2-phenylacrylonitrile (entry 6); CAS registry number [207672-08-0].

(1Z, 3E)-1-Cyano-1,4-diphenylbutadiene (entry 7); CAS registry number: [6443-79-4].

(E)-2-Cyano-3-phenylacrylamide (entry 8);¹¹ CAS registry number: [709-79-5]

(Z)-3-Phenyl-2-pyridin-2-yl-acrylonitrile (entry 9);¹² CAS registry number: [22345-98-8]

Benzylidenemalononitrile (entry 10);¹³ CAS registry number: [2700-22-3]

(E)-2-Cyano-3-phenylacrylic acid ethyl ester (entry 11);¹⁴ CAS registry number: [2025-40-3]

Table 4

α -(3-Oxocyclohexyl)phenylacetonitrile (entry 1, dr = **A/B** = 43/57);¹⁵ CAS registry number: [63064-15-3]

4-((Cyanophenyl)methyl)-2-nonanone (entry 2, dr = **A/B** = 50/50); IR, 2931, 2858, 2242, 1735, 1715, 1633, 1493, 1455, 1371, 1244, 1164, 1046, 757, 701; ¹H NMR (400 MHz, CDCl₃ as **Figure S5**): δ 0.81 (t, 3H, *J* = 7.0 Hz, CH₃ for **A**), 0.89 (t, 3H, *J* = 6.8 Hz, CH₃ for **B**), 1.09-1.45 (m, 8H, CH₂), 2.03 (s, 3H, COCH₃ for **A**), 2.17 (s, 3H, COCH₃ for **B**), 2.37-2.65 (m, 3H, CHCH₂CO), 4.11 (d, 1H, *J* = 4.9 Hz, PhCH for **A**), 4.17 (d, 1H, *J* = 4.9 Hz, PhCH for **B**), 7.30-7.39 (m, 5H, aromatic); ¹³C {¹H} NMR (100.4 MHz, CDCl₃, the mixture of two isomers as **Figure S6**): 13.92, 14.00, 22.38, 22.50, 26.53, 26.66, 29.28, 30.53, 30.60, 31.53, 31.64, 32.58, 38.57, 38.69, 40.55, 41.26, 44.15, 45.02, 119.14, 119.38, 127.71, 127.73, 127.87, 128.06, 128.75, 128.90, 133.88, 134.41, 206.29, 207.14; MS (EI) *m/z* (%) 257 (M⁺), 199, 145, 129, 117, 91, 71, 55, 43 (100); HRMS calcd for C₁₇H₂₃NO: 257.1780; found: 257.1758.

Figure S5

Figure S6

5-Oxo-2,3-diphenylhexanenitrile (entry 3, dr = A/B = 40/60);¹⁶ CAS registry number: [26848-03-3]

2,3-Diphenylglutaronitrile (entry 4, dr = A/B = 41/59);¹⁷ CAS registry number: [51764-05-7]

Scheme 2

α -(3-Oxocyclohexyl)-1-naphthylacetonitrile (dr = A/B = 57/43);¹⁵ CAS registry number: [371917-37-2]

3. Characterization of Reconstructed Hydrotalcite.

In-situ XRD measurement of the “wet” sample under an Ar atmosphere showed the layered structure typical of a HT, confirming reconstruction of the HT crystallines. The interlayer distance of the reconstructed HT was 3.0 Å, as estimated from the most intense diffraction peak (003), as shown in **Figure S7**. This value is the same as that of the parent HT (2.99 Å). However, the width at half-height of the diffraction peaks was larger than that of the parent hydrotalcite, indicating smaller crystalline size of the reconstructed HT.¹⁸ This observation is well accordance with the small crystals of the reconstructed HT in water.¹⁹ As illustrated in **Chart I**, the surface HCO_3^- species and CO_3^{2-} anions in the interlayer of the parent HT were substituted for OH^- anions in the reconstructed form, which is supported by the result of EDX analysis of oxygen and carbon.²⁰

Figure S7. XRD data

4. Location of Base Sites on the Surface of Reconstructed Hydrotalcite

According to the metal atom ordering on the HT surface,²¹ two types of hydroxyl site exist on the surface; one is connected to three Mg^{2+} ions (3Mg sites) and the other is bound to two Mg^{2+} and one Al^{3+} cations (2MgAl sites), as depicted in **Figure S8a**. Assuming a maximum distance between Al^{3+} ions at the surface, the calculated number of 2MgAl sites

per total sites is greatest at a Mg/Al of 3, whereas the number of 3Mg sites increased proportionally with an increase in the Mg/Al ratio (**Figure S8b**). For example, an increase in Mg/Al ratio from 3 to 5 resulted in a decrease in the number of 2MgAl sites and the amount of base sites, as described above. Correspondingly, the number of the 2MgAl sites well correlates with the yield of the aldol product in the reaction of propionaldehyde, as shown in **Figure S8b**. The $\text{Mg}(\text{OH})_2$ itself as well as a physical mixture of $\text{Mg}(\text{OH})_2$ and $\text{Al}(\text{OH})_3$ did not catalyze the aldol reaction (**Table 1**, entries 13 and 14). Therefore, we propose that generated OH^- species as base sites are closely connected to the surface 2MgAl sites of the reconstructed HT. The narrow distribution of base strength of the self-organized HT might be associated with a high ordering of the surface 2MgAl sites.

Figure S8. (a) A schematic view of hydrotalcite surface (Mg/Al ratio of 3) showing an arrangement of 36 metal cations and 25 OH groups, and (b) variations of 2MgAlOH and 3MgOH sites, and the catalytic activity for the self aldol reaction of propionaldehyde as a function of Mg/Al molar ratio of the hydrotalcite. The numbers of 2MgAlOH and 3MgOH sites in 25 OH sites were calculated by assuming a maximum distance between Al cations.

5. Hammett Plot

Figure S9. Hammett plot

6. References

- (1) (a) Miyata, S. *Clays Clay Miner.* **1980**, 28, 50. (b) Cavani, F.; Trifiró, F.; Vaccari, A. *Catal. Today* **1991**, 11, 173.
- (2) Durrwachter, J. R.; Wong, C.-H. *J. Org. Chem.* **1988**, 53, 4175.
- (3) Mangion, I. K.; Northrup, A. B.; MacMillan, D. W. C. *Angew. Chem. Int. Ed.* **2004**, 48, 6722.
- (4) Kourouli, T.; Kefalas, P.; Ragoussis, N.; Ragoussis, V. *J. Org. Chem.* **2002**, 67, 4615.
- (5) Batra, M. S.; Aguilar, F. J.; Brunet, E. *Tetrahedron* **1994**, 50, 8169.
- (6) Nakamura, E.; Shimizu, M.; Kuwajima, I.; Sakata, J.; Yokoyama, K. Noyori, R. *J. Org. Chem.* **1983**, 48, 932.
- (7) Tang, Z.; Jiang, F.; Yu, L.-T.; Cui, X.; Gong, L.-Z.; Mi, A.-Q.; Jiang, Y.-Z.; Wu, Y.-D. *J. Am. Chem. Soc.* **2003**, 125, 5262.
- (8) Mahrwald, R.; Costisella, B.; Gündogan, B. *Tetrahedron Lett.* **1997**, 38, 4543:
Mahrwald, R.; Costisella, B.; Gündogan, B. *Synthesis* **1998**, 262.
- (9) Kowalkowska, A.; Sucholbiak, D.; Jonczyk, A. *Eur. J. Org. Chem.* **2005**, 925.

- (10) Bottino, F. A.; Scarlata, G.; Sciotto, D.; Torre, M. *Tetrahedron* **1982**, 38, 3713.
- (11) Balalaie, S.; Nemati, N. *Synth. Commun.* **2000**, 30, 869.
- (12) Sakamoto, T.; Katoh, E.; Kondo, Y.; Yamanaka, H. *Chem. Pharm. Bull.* **1990**, 38, 1513.
- (13) Narsaiah, S. V.; Nagaiah, K. *Synth. Commun.* **2003**, 33, 3825.
- (14) Yadav, J. S.; Reddy, B. S.; Basak, A. K.; Visali, B.; Narsaiah, A. V.; Nagaiah, K. *Eur. J. Org. Chem.* **2004**, 3, 546.
- (15) Shimizu, S.; Shirakawa, S.; Suzuki, T.; Sasaki, Y. *Tetrahedron* **2001**, 57, 6169.
- (16) Reich, Hans J.; Biddle, Margaret M.; Edmonston, Robert J. *J. Org. Chem.* **2005**, 70, 3375.
- (17) Boyer, J.; Corriu, R. J. P.; Perz, R.; Reye, C. *Tetrahedron* **1983**, 39, 117.
- (18) Valente, J. S.; Figueras, F.; Gravelle, M.; Kumbhar, P.; Lopez, J.; Besse, J.-P. *J. Catal.* **2000**, 189, 370.
- (19) (a) Abelló, S.; Medina, F.; Tichit, D.; Pérez-Ramírez, J.; Groen, J. C.; Sueiras, J. E.; Salagre, P.; Cesteros, Y. *Chem. Eur. J.* **2005**, 11, 728. (b) Abelló, S.; Medina, F.; Tichit, D.; Pérez-Ramírez, J.; Cesteros, Y.; Salagre, P.; Sueiras, J. E. *Chem. Commun.* **2005**, 1453.
- (20) The content of carbon decreased from 37 to 17% by the rehydration. Since the reconstructed HT was subjected to the EDX measurement after an exposure to air, the sample considerably adsorbed CO₂ from air. The oxygen content in the HT increased from 50 to 60% by reconstruction.
- (21) Cai, H.; Hillier, A. C.; Franklin, K. R.; Nunn, C. C.; Ward, M. D. *Science* **1994**, 266, 1551.