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# Catalysis of transition metal-functionalized hydrotalcites for the Baeyer–Villiger oxidation of ketones in the presence of molecular oxygen and benzaldehyde

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## Abstract

Multi-metallic hydrotalcites consisting of magnesium, aluminum, and iron, or copper elements were prepared, which catalyzed the Baeyer–Villiger oxidation using a combination system of molecular oxygen and benzaldehyde. In particular, the Mg–Al–Fe–CO<sub>3</sub> hydrotalcite efficiently oxidized various cyclic ketones to give high yields of the corresponding lactones, while in the case of the Mg–Al–Cu–CO<sub>3</sub> hydrotalcite, bicyclic ketones were oxidized almost quantitatively.

*Keywords:* Aldehyde; Baeyer–Villiger oxidation; Hydrotalcite; Molecular oxygen; Oxidation

Hydrotalcites consist of the Brucite-like layer with positive charge and anionic compounds in the interlayer to form neutral materials [1]. Combination of several elements in the Brucite-like layer and selection of anionic compounds can tune up basicity of the hydrotalcites and their interlayer distance. If hydrotalcites containing transition metal elements in the Brucite-like layer and/or the interlayer are used as catalysts, the embedded transition metals will be invested with potential abilities not only to induce shape selective reactions, but also to produce cooperative action together with base function in organic reactions [2]. These studies about catalysis of hydrotalcites, however, have not extensively been carried out, compared with those of zeolites. It is known that the Baeyer–Villiger oxidations with a com-

ination of molecular oxygen and aldehydes and, with organic peracids are catalyzed by transition metal compounds of nickel, iron, and copper, by heteropoly acids, and by bases [3]. Recently, we have reported that hydrotalcites, e.g., Mg<sub>10</sub>Al<sub>2</sub>(OH)<sub>24</sub>CO<sub>3</sub> and Mg<sub>5</sub>Al(OH)<sub>12</sub>Cl had high catalytic activities for the Baeyer–Villiger oxidation using a combination system of molecular oxygen and aldehydes [4]. Here, we report the preparation of multi-metallic hydrotalcites consisting of magnesium, aluminum, and iron, or copper elements, and the catalysis for the Baeyer–Villiger oxidation of various ketones. The multi-metallic hydrotalcite systems can be regarded as one of heterogenized-metal catalysts (*hybrid catalysts*) [5].

Mg<sub>6</sub>Al<sub>2</sub>(OH)<sub>16</sub>CO<sub>3</sub> was prepared by the procedure of Reichle et al. [6]. Multi-metallic types of Mg–Al–Fe–CO<sub>3</sub> and Mg–Al–Cu–CO<sub>3</sub> hydro-

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talcites were prepared according to a modification of the literature procedure [1].  $\text{Fe}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$  (0.003 mol),  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.03 mol), and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.01 mol) were dissolved in distilled water (50 ml). To a  $\text{H}_2\text{O}$  solution (60 ml) of  $\text{Na}_2\text{CO}_3$  (0.03 mol) and  $\text{NaOH}$  (0.07 mol) was slowly added the above solution. The mixture was heated at  $65^\circ\text{C}$  for 18 h with stirring. The slurry was then cooled to room temperature and filtered. A beige powder that resulted was washed with a large amount of water and dried overnight at  $110^\circ\text{C}$ . Anal. Calcd for  $\text{Mg}_6\text{Al}_2\text{Fe}_{0.6}(\text{OH})_{17.2}(\text{CO}_3)_{1.3} \cdot 4\text{H}_2\text{O}$ : Mg, 21.60; Al, 7.79; Fe, 4.96. Found: Mg, 21.5; Al, 7.79; Fe, 5.06. Preparation of a Mg–Al–Cu– $\text{CO}_3$  type hydrotalcite, a blue powder, using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was carried out by a method similar to the above Mg–Al–Fe– $\text{CO}_3$  one. Anal. Calcd for  $\text{Mg}_6\text{Al}_2\text{Cu}_{0.6}(\text{OH})_{17.2}\text{CO}_3 \cdot 6\text{H}_2\text{O}$ : Mg, 20.88; Al, 7.73; Cu, 5.46. Found: Mg, 20.7; Al, 7.45; Cu, 5.38. XRD spectra of the Mg–Al–Fe– $\text{CO}_3$  and Mg–Al–Cu– $\text{CO}_3$  type hydrotalcites showed 7.75 and 7.86 Å of  $d$  spacings, respectively, which are almost the same values as 7.66 Å of  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$  [7]. These results confirm that the Mg–Al–Fe– $\text{CO}_3$  and Mg–Al–Cu– $\text{CO}_3$  type hydrotalcites had layer structures with formulas of  $\text{Mg}_6\text{Al}_2\text{Fe}_{0.6}(\text{OH})_{17.2}(\text{CO}_3)_{1.3}$  and  $\text{Mg}_6\text{Al}_2\text{Cu}_{0.6}(\text{OH})_{17.2}\text{CO}_3$ , respectively. Base strength distributions of the Mg–Al– $\text{CO}_3$  and the Mg–Al–Cu– $\text{CO}_3$  type hydrotalcites were measured by titration with different indicators [8]: for the Mg–Al– $\text{CO}_3$ , 0.105 mmol of benzoic acid/g (7.1–15.0  $\text{p}K_{\text{BH}}$ ) and 0.416 mmol/g (15.0–17.2  $\text{p}K_{\text{BH}}$ ); for the Mg–Al–Cu– $\text{CO}_3$  type hydrotalcites, 0.068 mmol of benzoic acid/g (7.1–15.0  $\text{p}K_{\text{BH}}$ ) and 0.391 mmol/g (15.0–17.2  $\text{p}K_{\text{BH}}$ ). An indicator of 4-chloro-2-nitroaniline did not detect base strengths over 17.2  $\text{p}K_{\text{BH}}$  in the above two hydrotalcites <sup>1</sup>.

A typical procedure of the Baeyer–Villiger oxidation of ketones is as follows. Into a three necked

flask with a reflux condenser cooled at  $-15^\circ\text{C}$  were placed the hydrotalcite of Mg–Al–Fe– $\text{CO}_3$  (25 mg), benzaldehyde (12 mmol) and 1,2-dichloroethane (15 ml), and oxygen was bubbled into a stirred heterogeneous mixture at  $40^\circ\text{C}$  for 30 min. A 1,2-dichloroethane solution (5 ml) of cyclopentanone (4 mmol) was added and the resulting mixture was stirred with bubbling of oxygen at  $40^\circ\text{C}$  for 4.5 h. The hydrotalcite was separated by filtration <sup>2</sup>. GLC analysis of the filtrate showed a quantitative yield of  $\delta$ -valerolactone. The filtrate was successively treated with aqueous  $\text{Na}_2\text{SO}_3$  and  $\text{NaHCO}_3$  solution.  $\delta$ -Valerolactone (0.328 g, 82%) was isolated by column chromatography on silica gel (hexane/ethyl acetate, 3:1).

In the Baeyer–Villiger oxidation with Mg–Al– $\text{CO}_3$  hydrotalcites containing no transition metals, benzaldehyde and 1,2-dichloroethane were found to be the best aldehyde and solvent, respectively [5]. Oxidations of various ketones using a combination system of molecular oxygen and benzaldehyde in 1,2-dichloroethane solvent were carried out in the presence of the Mg–Al–Fe– $\text{CO}_3$  and Mg–Al–Cu– $\text{CO}_3$  type hydrotalcites, respectively. Typical results are shown in Table 1 together with that using the corresponding hydrotalcite of  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$  and that in the absence of hydrotalcites <sup>3</sup>. Both multi-metallic hydrotalcites had higher catalytic activities for the Baeyer–Villiger oxidation of many ketones except a few examples than the  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3$ . In particular, the Mg–Al–Fe– $\text{CO}_3$  hydrotalcite could efficiently oxidize various cyclic ketones to give high yields of the corresponding lactones (entries 1–6), while in the case of the Mg–Al–Cu– $\text{CO}_3$  hydrotalcite, bicyclic ketones were oxidized almost quantitatively (entries 6 and 7). It is noteworthy that the hydrotalcites act as heterogeneous















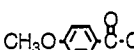
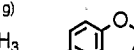

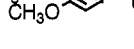




<sup>2</sup> In the case of the Mg–Al–Fe– $\text{CO}_3$  type hydrotalcite, analysis of the filtrate after the oxidation of cyclohexanone showed leaching of 5.5% Fe from the hydrotalcite and leaching of 15% Cu was observed by a similar analysis of the Mg–Al–Cu– $\text{CO}_3$  type hydrotalcite experiment.

<sup>3</sup> It has been reported that an oxidant system of molecular oxygen and benzaldehyde gave the Baeyer–Villiger products from various ketones in the absence of metal catalysts (see Refs. [3](c), [9]).

<sup>1</sup> Unfortunately, the above titration method could not be applied to the Mg–Al–Fe– $\text{CO}_3$  type hydrotalcite because the yellow color of the Fe type hydrotalcite was difficult to distinguish from the coloration with indicators.

Table 1

Table 1. Baeyer-Villiger Oxidation of Ketones Using Various Hydrotalcites in the Presence of Molecular Oxygen and Benzaldehyde<sup>a)</sup>

Entry	Substrate	Products <sup>b)</sup>	Reaction Time (h)	Conv., Yield (%) <sup>c)</sup>			
				Mg-Al-Fe-CO <sub>3</sub> (Mg:Al:Fe=3:1:0.3)	Mg-Al-Cu-CO <sub>3</sub> (Mg:Al:Cu=3:1:0.3)	Mg-Al-CO <sub>3</sub> (Mg:Al=3:1)	Blank (without hydrotalcite)
1			5	92, 83	60, 45	56, 46 <sup>d)</sup>	45, 40
2			5	100, quantitative	72, 72	66, 65	83, 80
3			5	100, quantitative	73, 62 (91) <sup>e)</sup>	79, 79	50, 49
4		 <sup>f)</sup>	5	93, 93	68, 64	70, 69	57, 55
5			24	89, 89	66, 66	78, 78	32, 30
6			5	100, quantitative	100, 94 (76) <sup>e)</sup>	82, 70	26, 24
7			5	54, 54	100, quantitative (81) <sup>e)</sup>	41, 41	43, 43
8			5	51, 51	72, 72 (33) <sup>e)</sup>	51, 51	
9			24	90, 88	86, 86	90, 90	16, 15
10			5	51, 45	72, 66	25, 16	
11			24	64, 57	93, 92	59, 48	43, 38

<sup>a)</sup> Reaction conditions: catalyst 0.025g, substrate 4 mmol, benzaldehyde 12 mmol, 1, 2-dichloroethane 20 ml, 40 °C. <sup>b)</sup> Structures of oxygenated products were determined by using NMR, IR, and GC-MS spectroscopy. <sup>c)</sup> Conversions and yields were calculated by GLC method.

<sup>d)</sup> Taken from Ref. 4. <sup>e)</sup> Values in parenthesis taken from Ref. 3c.

<sup>f)</sup> Ratios of two regioisomers were about 1:1 in three hydrotalcite catalysts.

<sup>g)</sup> Catalyst 0.05g, substrate 2 mmol, benzaldehyde 6 mmol.

catalysts and can be reused for the Baeyer-Villiger oxidation. After oxidation of cyclohexanone, a separated Mg-Al-Fe-CO<sub>3</sub> hydrotalcite was washed with 1,2-dichloroethane. Then, oxidation

of cyclohexanone with the spent hydrotalcite was carried out anew under the same conditions as those of fresh one and gave a quantitative yield of ε-caprolactone. In addition, again the spent hydro-

talcaite without transition metals had an extremely low catalytic activity, but treatment of the hydrotalcite with aqueous  $\text{Na}_2\text{CO}_3$  solution regenerated the activity satisfactorily.

Bolm et al. have studied the Baeyer–Villiger oxidation using a homogeneous  $\text{Cu}(\text{acetate})_2$  catalyst [3c]. Catalytic activities of the Mg–Al–Cu– $\text{CO}_3$  hydrotalcite are compared with those of  $\text{Cu}(\text{acetate})_2$  for various ketones in Table 1. Interestingly, reactivities of several ketones are quite different between oxidations using two Cu catalysts: in the heterogeneous Cu hydrotalcite, bicyclic ketones were oxidized more efficiently than monocyclic ones (entries 6 and 7), while the homogeneous  $\text{Cu}(\text{acetate})_2$  catalyst can oxidize a monocyclic ketone to give a high yield of the corresponding lactone (entry 3). The Mg–Al–Cu– $\text{CO}_3$  catalyst had higher activities for oxidation of bicyclic and acyclic ketones than the corresponding Mg–Al– $\text{CO}_3$  catalyst in spite of similar basicities of two catalysts (vide supra). Introduction of some transition metals into the Brucite-like layer leads to increase of catalytic activity of hydrotalcites in the oxidation, which might be due to cooperative action originated from basic sites of the hydrotalcites and transition metal sites. In our separate experiments, it was found that hydrotalcites catalyzed Baeyer–Villiger oxidation of ketones with *m*-CPBA oxidant. We think tentatively that the present Baeyer–Villiger oxidation might occur as follows. At first, autoxidation of benzaldehyde gives perbenzoic acid [9], then, hydrotalcites assist oxygen transfer step of perbenzoic acid to ketones; hydroxyl groups on metal ions of Mg, Al, Fe, and Cu act as a base.

Transition metals of Fe and Cu also accelerate an autoxidation of benzaldehyde. This interesting catalysis of multi-metallic hydrotalcites having various transition metals in the Baeyer–Villiger oxidation has been continuously studied in our laboratory.

## References

- [1] F. Cavani, F. Trifiro and A. Voccari, *Catal. Today*, 11 (1991) 173.
- [2] (a) T. Nakatsuka, H. Kawasaki, S. Yamashita and S. Kohkiya, *Bull. Chem. Soc. Jpn.*, 52 (1979) 2449. (b) S. Kohkiya, T. Sato, T. Nakayama and S. Yamashita, *Makromol. Chem., Rapid Commun.*, 2 (1981) 231. (c) W.T. Reichle, *J. Catal.*, 94 (1985) 547. (d) E. Suzuki and Y. Ono, *Bull. Chem. Soc. Jpn.*, 61 (1988) 1008. (e) R. Spinicci and A. Ullbarri, *Mater. Chem. Phys.*, 26 (1990) 1. (f) D.E. Laycock, R.J. Collocott, D.A. Skelton and M.F. Tahir, *J. Catal.*, 130 (1991) 354. (g) A. Corma, V. Fornes, R.M. Martin-Aranda and F. Rey, *J. Catal.*, 134 (1992) 58. (h) T. Tatsumi, K. Yamamoto, H. Tajima and H. Tominaga, *Chem. Lett.*, (1992) 815.
- [3] (a) Ni: T. Yamada, K. Takahashi, K. Kato, T. Takai, S. Inoki and T. Mukaiyama, *Chem. Lett.*, (1991) 641. (b) Fe: S.-I. Murahashi, Y. Oda and T. Naota, *Tetrahedron Lett.*, 33 (1992) 7557. (c) Cu: C. Bolm, G. Schlinggloff and K. Weickhardt, *Tetrahedron Lett.*, 34 (1993) 3405. (d) Heteropoly acid: M. Hamamoto, K. Nakayama, Y. Nishiyama and Y. Ishii, *J. Org. Chem.*, 58 (1993) 6421. (e) Base ( $\text{Na}_2\text{CO}_3$ ): J.K. Ehtesell, R.S. Matthews and A.M. Helbling, *J. Org. Chem.*, 43 (1978) 784. (f) Base ( $\text{Na}_2\text{CO}_3$ ): G.R. Krow, C.A. Johnson, J.P. Guare, D. Kubrak, K.J. Henz, D.A. Shaw, S.W. Szczepanski and J.T. Carey, *J. Org. Chem.*, 47 (1982) 5239.
- [4] K. Kaneda, S. Ueno and T. Imanaka, *J. Chem. Soc., Chem. Commun.*, (1994) 797.
- [5] R.H. Grubbs, *CHEMTECH*, 7 (1977) 512.
- [6] W.T. Reichle, S.Y. Kang and D.S. Everhardt, *J. Catal.*, 101 (1986) 352.
- [7] S. Miyata, *Clays Clay Miner.*, 31 (1983) 305.
- [8] J. Take, N. Kikuchi and Y. Yoneda, *J. Catal.*, 21 (1971) 164.
- [9] K. Kaneda, S. Ueno and T. Imanaka, E. Shimotsuma, Y. Nishiyama and Y. Ishii, *J. Org. Chem.*, 59 (1994) 2915.