

Mg–Al Mixed Oxides as Highly Active Acid–Base Catalysts for Cycloaddition of Carbon Dioxide to Epoxides

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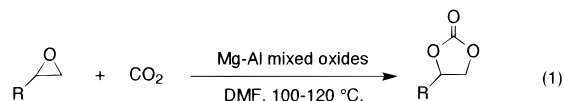
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The efficient transformation of harmful wastes such as CO₂ into useful chemicals is an important contribution to the preservation of the earth. Chemical fixation of CO₂ onto organic compounds is interesting because of a synthetic merit; one carbon atom and two oxygen atoms can be incorporated in one step with a high atom efficiency. In this sense, the addition reaction of CO₂ to epoxides is a powerful candidate for CO₂ fixation to produce five-membered cyclic carbonate which can be used as valuable raw materials for engineering plastics and highly polar solvents.¹ Various catalysts such as metal halides, onium halides, and MgO have been continuously explored in the addition of CO₂ to epoxides.¹ A key step in the above reaction, as well as other chemical fixation reactions of CO₂, is activation of the unreactive CO₂ molecule with metal catalysts and light.

Hydrotalcites consist of Brucite-like layers having a positive charge with anionic species in the interlayer, forming neutral clay materials.² We have already reported that hydrotalcites are excellent catalysts for the Baeyer–Villiger oxidation,³ epoxidation,⁴ and oxidative dehydrogenation⁵ with the use of H₂O₂ and molecular oxygen as oxidants. Further, hydrotalcites have been often used as precursors for active Mg–Al mixed oxide catalysts having strong basic sites on their surface.⁶ Here, we found that the Mg–Al mixed oxides obtained by calcination of the hydrotalcites were effective catalysts for the fixation of CO₂ to various epoxides to form the corresponding five-membered cyclic carbonates. Compared with other reported catalysts for this addition reaction, the Mg–Al mixed oxides have the following advantages: (1) highly catalytic activity even under an atmospheric CO₂ pressure, (2) reusable catalysts, and (3) the stereospecific

addition via a retention of the configuration of epoxides. In this paper, we report the unique catalysis of the Mg–Al mixed oxides for the selective formation of cyclic carbonates on the basis of characterization of the oxide catalysts using physicochemical methods.



To optimize Mg/Al ratios in Mg–Al mixed oxides for the addition reaction of CO₂ with styrene oxide, hydrotalcites with Mg/Al ratios from 3 to 8 were prepared and calcined at various temperatures between 400 and 1000 °C.² Their catalytic activities were evaluated from the yields of styrene carbonate normalized to surface areas.⁷ We found that the Mg–Al oxide with the Mg/Al ratio of 5 calcined at 400 °C was the most active catalyst for the addition reaction and DMF was the best solvent.⁸ By using the Mg–Al oxide with the Mg/Al ratio of 5 calcined at 400 °C, various kinds of epoxides could be quantitatively converted to the corresponding cyclic carbonates, as shown in Table 1. The reaction hardly occurred in the absence of Mg–Al mixed oxides. Interestingly, the substitution of the para hydrogen of styrene oxide for CH₃ and Cl groups did not strongly affect the reaction rates.⁹ This addition reaction proceeded with a retention of stereochemistry of epoxides; the reactions of CO₂ with (*R*)- and (*S*)-benzyl glycidyl ethers gave (*R*)- and (*S*)-4-(benzyloxymethyl)-1,3-dioxolane-2-one in 78 and 76% chemical yields with >99% *ee*, respectively.¹⁰ Moreover, the mixed oxide catalysts could be reused without losing its high catalytic activity and selectivity; the yield of styrene carbonate could be kept over 90% in the third reuse experiment.

In the reaction of CO₂ and styrene oxide, the yields of styrene carbonate were proportional to the basicity of calcined hydrotalcites.³ Although the uncalcined hydrotalcites had high basicity, the catalytic activities were lower than those of the above calcined ones. These results indicate that the Lewis basic sites of the mixed oxide catalysts would play an important role in this addition reaction. Further, the calcined hydrotalcite catalysts had higher catalytic activities than the MgO. From the temperature-programmed desorption (TPD) of ammonia, it became clear that the acid sites also existed on the surface of the active Mg–Al mixed oxides and that no acid site was observed on the MgO and the mixed oxide with the Mg/Al ratio of 3.^{6b,11} Therefore, the noble catalysis of the active Mg–Al mixed oxides could be caused by the cooperation of the acid sites and the strong basic sites.

The XRD peak positions of the calcined hydrotalcites did not vary with the Mg/Al ratios, which were similar to that of MgO.

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
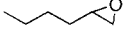
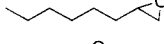
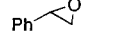
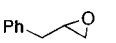



(7) A typical example for the addition of CO₂ to epoxides is as follows. Into a stainless steel autoclave (100 mL) were placed styrene oxide (0.96 g, 8 mmol), calcined hydrotalcite (1.0 g), DMF (6 mL), and CO₂ (5 atm). The resulting mixture was stirred at 100 °C for 15 h. The hydrotalcite was separated by filtration. The filtrate was subjected to column chromatography on silica gel and yielded styrene carbonate (1.20 g, 91%). The spent Mg–Al mixed oxide was calcined at 400 °C, and then the calcined mixed oxide could be reused without losing its high catalytic activity and selectivity.

(8) CO₂ pressure during 1–20 atm did not strongly influence the yields of styrene carbonate under our reaction conditions. The increase of the reaction temperature over 120 °C resulted in low selectivity to carbonate because of the formation of styrene glycol.

(9) The relative reactivity of para-substituted styrene oxides was examined to give *p*-methylstyrene oxide (1.3), styrene oxide (1.0), and *p*-chlorostyrene oxide (1.0). The values in the parentheses are relative initial rates for the addition reaction, which are normalized to that of styrene oxide.

(10) The enantiomeric excesses of (*R*)- and (*S*)-4-(benzyloxymethyl)-1,3-dioxolane-2-one were determined by HPLC (Daicel Chiralcel OD, *n*-hexane/2-propanol (9:1 v/v), 1.0 mL/min, 254 nm). Configurations of the above carbonates were determined by optical purities of 3-benzyloxy-1,2-propanediols derived from the hydrolysis using NaOH, respectively; (*R*)-3-benzyloxy-1,2-propanediol, $[\alpha]_D^{20} +5.8^\circ$ (neat).

Table 1. Cycloaddition of CO₂ to Various Epoxides Catalyzed by the Mg–Al mixed Oxide^a

entry	substrate	convn(%) ^b	yield of carbonate(%) ^b
1 ^c		96	88
2 ^c		100	89
3 ^c		100	>99
4 ^d		92	90(91)
5 ^e	Ph 	39	38
6	Ph 	100	94
7	MeO 	100	>99
8 ^d	PhO 	94	90(86)

^a Reaction conditions: Mg–Al mixed oxide (Mg/Al = 5, calcined at 400 °C) 0.5 g, epoxide 4 mmol, DMF 3 ml, CO₂ pressure 5 atm, 100 °C, and 24 h. ^b Yields of carbonates were determined by GLC analysis using internal standards, based on epoxides. Values in parentheses are isolated yields. In the case of the product isolation experiments, the reaction scale was twice as much as that of reaction conditions (a). ^c 120 °C. ^d 15 h. ^e A physical mixture of MgO and Al₂O₃ (Mg/Al = 5) was used in place of the above Mg–Al mixed oxide.

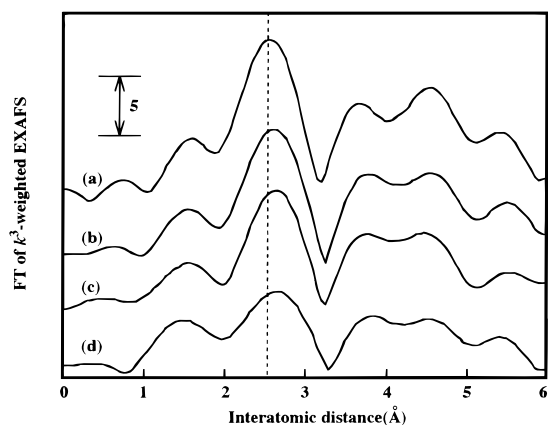


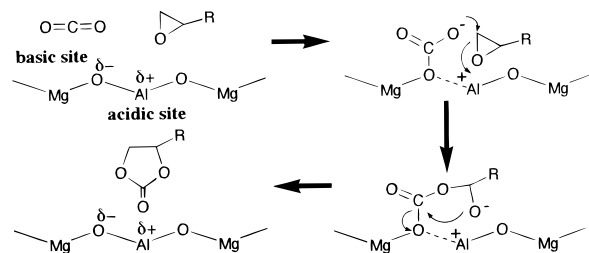
Figure 1. Fourier transforms of k^3 -weighted Mg K-edge EXAFS of (a) MgO calcined at 400 °C and those of Mg–Al mixed oxides obtained by calcination of hydrotalcites with Mg/Al of (b) 8, (c) 5, and (d) 3 at 400 °C.

However, the full width at half-maximum of (200) diffraction peaks of calcined hydrotalcites gradually increased with increasing the Al content. The Mg K-edge XANES spectrum of the calcined hydrotalcite with the Mg/Al of 5 at 400 °C was closely resemble to that of the MgO, while the Al K-edge XANES showed an existence of a six-coordinated Al³⁺ ion within a local structure.¹² Figure 1 depicts Fourier transforms of k^3 -weighted Mg K-edge EXAFS of the Mg–Al mixed oxides with different Mg/Al ratios calcined at 400 °C. The peaks around 2.6 Å attributable to the Mg–Mg shell of MgO with 2.97 Å distance¹³ varied in their intensities and positions with an increase of the Al content, whereas those of the peaks around 1.5 Å due to the Mg–O shell did not change. The curve-fitting analysis of the peak around 2.6 Å observed for the oxide with the Mg/Al ratio of 3 showed the existence of the second neighboring cations located at a longer

(11) The NH₃-TPD profiles were obtained by Q-mass spectrometer after adsorption of NH₃ onto the samples at 100 °C. The peak positions of the desorbed NH₃ of ca. 240 °C for the mixed oxides with the Mg/Al ratio of 5 and 8 calcined at 400 °C were higher than that of a low-temperature desorption peak observed for hydrogen-bonded NH₃ species on the zeolite. See; Katada, K.; Igi, H.; Kim, J.-H.; Niwa, M. *J. Phys. Chem. B* **1997**, *101*, 5969.

(12) X-ray absorption spectra were recorded at the beam line 7 A station attached with a beryl two-crystal monochromator ($d = 7.9825$ Å) at UVSOR of the Institute for Molecular Science, Okazaki, Japan. Data were collected in a total electron yield mode, which mainly monitors X-ray energy dependence of Mg KLL auger electron yield.

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Scheme 1

distance of 3.12 Å with a coordination number of about 2. These results mean the severe disordering of the MgO-like surface structure by the introduction of an excess Al³⁺ ion. *Vide supra*, the calcined hydrotalcite with the Mg/Al ratio of 3 did not have acid and strong basic sites, which would be caused by the severe disordering of the MgO-like structure. Judging from the small degrees of the EXAFS damping and XRD broadening observed for the mixed oxide with Mg/Al ratio of 5, a mild disordering of the MgO structure occurred on this oxide; Mg²⁺ ions are isomorphically substituted by Al³⁺ ions to form Mg–O–Al bonds to disorder the small portion of the Mg–Mg shell, which would bring about the formation of acid and strong basic sites on the surface of the mixed oxides.¹⁴

We propose a possible reaction mechanism of the addition reaction as shown in Scheme 1. The addition reaction is initiated by adsorption of CO₂ on the Lewis basic sites to form a carbonate species, and independently, an epoxide is coordinated on the neighboring an acid site on the surface. The coordinated epoxide is ring-opened by a nucleophilic attack of the carbonate species, which leads to an oxy anion species yielding the corresponding cyclic carbonate as a product. The activity of the Mg–Al mixed oxide was greatly larger than that of a physical mixture of MgO and Al₂O₃ (entry 5, Table 1). Therefore, it is likely that a prominent feature of the active Mg–Al mixed oxide catalysts can be found to originate from the cooperative action of both the basic and acidic sites located in a neighbor on the surface. Kinetics data of this addition reaction could be well accommodated with a rate equation based on the Langmuir–Hinshelwood model where the CO₂ and epoxide are independently adsorbed on the different sites, i.e., basic sites and acidic sites, respectively.¹⁵

In conclusion, the Mg–Al mixed oxides obtained by the calcination of hydrotalcites acted as efficient catalysts for the addition of CO₂ with various epoxides under mild reaction conditions; in particular, the mixed oxide with the Mg/Al ratio of 5 calcined at 400 °C showed the highest catalytic activity. This unique catalysis is due to the cooperative action of acid–base sites derived from the formation of Mg–O–Al bonds, i.e., the substitution of Al for Mg in MgO matrix, on the surface of mixed oxides. The Mg–Al mixed oxide catalysts were reusable and could be proved effective for many organic reactions as environmentally friendly acid–base catalysts.

Acknowledgment. We thank DAISO Co., Ltd. for providing chiral epoxides of (*R*)- and (*S*)-benzyl glycidyl ether. X-ray absorption experiments were approved by the Joint Studies Program (1997) of UVSOR of the Institute for Molecular Science. We thank Professor Tsunehiro Tanaka, Kyoto University, for providing his program for analysis of EXAFS.

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(14) The severely disordered surface of the Mg–Al oxide with Mg/Al ratio of 3 cannot act as acid and strong base. This is related to the existence of extraframework Al³⁺ with a five or four-coordinated Al³⁺ as evidenced by Al K-edge XANES.

(15) The rate (R) of the reaction of styrene oxide with CO₂ could be expressed as $R = k_{\text{obs}} K[S]\{[A]/(1 + K[S])\}$, where k_{obs} is an apparent rate constant of the surface reaction of epoxide and CO₂, K is an adsorption equilibrium constant for epoxide adsorption on the acidic site of the Mg–Al mixed oxide, $[A]$ is the amount of the catalyst, and $[S]$ is the concentration of styrene oxide. The apparent activation energy of the addition reaction of CO₂ with styrene oxide was estimated to be 78.0 kJ mol⁻¹.