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In Situ Generation of Strong Bases from Alkaline and Alkaline–Earth Carbonates

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Strong bases from alkaline and alkaline-earth metal carbonates were generated *in situ* by adding a small amount of acetic acid at reflux in toluene under water-free conditions. Their basic strength reached superbasicity thus changing the color of 4-chloroaniline ($H_{-} = 26.5$). The high conversion of ethyl acetate in its self-condensation over decomposed carbonates, which require strong basicity to abstract protons from ethyl acetate ($pK_a = 25$), also confirmed the formation of strong bases. Adding acetic acid during the reaction indicated that metal oxides—decomposed materials from carbonates—were responsible for their high catalytic activity. The lack of sufficient coordination of *in situ* generated metal oxides was considered to be a plausible cause for their strong basicity. © 2002 Elsevier Science

Key Words: **strong bases; alkaline and alkaline-earth carbonates; condensation reaction; ethyl acetate.**

INTRODUCTION

Bases were used as catalysts in various organic reactions such as Knoevenagel condensation, Claisen condensation, and Michael addition reactions (1–4). Anions formed from reactants through deprotonation by bases work as active intermediates. Therefore, the catalytic activities of bases are strongly dependent on their basicity which determines the possible formation of active anions. Stronger bases are required in the deprotonation of reactants.

Because of their high catalytic performance, superbases are promising materials in organic reactions that demand strong basic catalysts (5–8). The easy deprotonation of anions formed from reactants by superbases enhances the concentration of active anion intermediates, resulting in rapid catalytic reactions. Their commercial use as catalysts, however, has not been reported because of the difficulties ensued in their preparation and operation. Because they are rapidly deactivated by water and acidic vapor (9), metal oxide superbases such as MgO and CaO, prior to their application as catalysts, require careful pretreatments. Supported alkaline metals and compounds also exhibit superbasicity when they are highly dispersed on alumina supports (10, 11). The difficulty in achieving the high dispersion of active species inhibits the wide application of superbases to organic reactions, despite their high catalytic activity.

Claisen condensation is suitable for the synthesis of β-ketoesters from esters over base catalysts. Bases which can convert esters with acidic C–H bonds into active anions accelerate the condensation reaction. Strong bases such as NaOEt and Na metal are required for the self-condensation of ethyl acetate, because the pK_a value of about 25 for the deprotonation reaction of ethyl acetate is considerably high (12). These bases, so-called superbases with $H_{-} > 26$, are active for deprotonation and show good catalytic activity, but their manipulation in organic media is difficult and hazardous. Furthermore, the application of alkaline-earth metal oxides as basic catalysts, although they have superbasicity, is also inconvenient due to the careful calcination treatment at higher temperatures to prevent water adsorption.

Alkaline carbonates were used as catalysts in base-catalyzed reactions such as the Aldol reaction (13) and the Knoevenagel condensation between benzaldehyde and malonitrile (14). These reactions can proceed on moderately strong bases because the deprotonation of malonitrile is not too difficult ($pK_a = 11$). Alkaline and alkaline-earth carbonates become strong bases through decomposition at temperatures above 600°C, and the insufficient coordination sites of decomposed metal oxides cause their high basicity (15). The requirement of high-temperature calcination and a completely dried state, however, reduces the reproducibility of strong base formation, limiting a wide application of carbonates as strong base precursors. Therefore, the generation of strong bases at low temperatures and even under *in situ* conditions is considerably useful for base-catalyzed organic synthesis. *In situ* generation of strong bases formed from Various alkaline and alkaline-earth carbonates by adding acetic acid was studied. Since deprotonation of ethyl acetate ($pK_a = 25$) took place on only strong basic sites, self-condensation was employed to confirm the formation of strong bases with $H_{-} > 25$. The role of acetic acid in the decomposition of carbonates was also examined.

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EXPERIMENTAL AND METHODS

Self-condensation of ethyl acetate was carried out in a triple-neck flask equipped with a reflux condenser. Ethyl acetate (Carlo Erba Reagent, 99.9%), 10.0 g (0.12 mol), was dissolved in 20.0 mL toluene (Duksan Chemical, 99%). Dodecane (Aldrich, 99%), 0.17 g (1.00 mmol), was added as an internal standard, and a small amount of acetic acid (20.0 μl, 0.30 mmol, Dongyang Chemical) was added for the decomposition of carbonates. Reaction mixtures were heated to 100°C under nitrogen atmosphere, and subsequently 0.31 g (2.00 mmol) of potassium carbonate (Shehwa Industrial, 98%) was added. After reaction for 3 h, solid particles were recovered by filtration. The collected solid particles were washed with acetone and dried in a vacuum oven. *p*-Xylene (Aldrich, 98%) was used as solvent for the reaction at 120°C, and mesitylene (Aldrich, 99%) was used for the reaction at 150°C.

Ethyl acetate was washed with 5% sodium carbonate solution. A saturated sodium chloride aqueous solution was used as a secondary washing reagent. Ethyl acetate was then dried with anhydrous magnesium sulfate (Duksan Chemical, 98%) and distilled at 77–78°C. Toluene was dried by contact with calcium hydride and then distilled. Sodium carbonate (99%), magnesium carbonate (99%), calcium carbonate (99%), and barium carbonate (99%) were purchased from Duksan Chemical and *they were* used as received, while magnesium carbonate was pretreated at 300°C for 3 h due to its excessive water content.

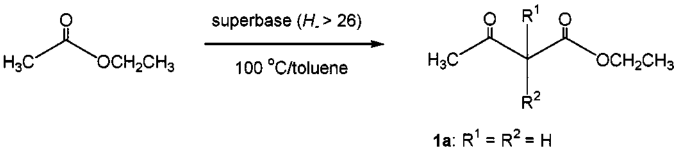
Reaction products were taken at certain intervals, and their chemical compositions were determined using a gas chromatograph (Donam DS6200) equipped with a capillary column (HP-1) and a flame ionization detector. In addition, a GC/MS (Hewlett–Packard 5890II gas chromatograph and a 5971A mass spectrometer) was also employed to assign products. Conversion was defined as the fraction of ethyl acetate consumed, and selectivity was denoted as the mole percentage of condensation products to that of consumed ethyl acetate.

The basic strength of *in situ* generated bases from carbonates was measured using 4-chloroaniline, $H_- = 26.5$, which was suitable for confirming the formation of superbases with $H_- > 26$. Carbonates were dehydrated at 390°C for 2 h in nitrogen flow and then cooled at 100°C. 4-Chloroaniline dissolved in toluene was added to carbonates, and the appearance of the basic-form color was observed under reflux conditions. A small amount of acetic acid (20 μl) was added for the decomposition of carbonates.

The decomposition of carbonates was confirmed by IR spectra recorded on a BIO-RAD FT-IR (FTS-175C) spectrophotometer.

RESULTS AND DISCUSSION

Bases are usually employed in organic reactions to deprotonate and form anion intermediates. Since the deprotonation of ethyl acetate ($pK_a = 25$) is extremely difficult, its self-condensation requires very strong bases. Further condensation products can be produced on moderate basic sites because of the higher acidic C–H bond; however, the initiation of self-condensation is possible only on strong basic sites so as to remove protons from ethyl acetate. Therefore, the formation of ethyl acetoacetate (**1a**) is observed only over strong bases.



1a: $R^1 = R^2 = H$
1b: $R^1 = H$, $R^2 = C(O)CH_3$
1c: $R^1 = R^2 = C(O)CH_3$

Figure 1 shows the increase in the conversion and the decrease in the selectivity for the primary condensation product in the self-condensation of ethyl acetate over a calcium carbonate catalyst treated with a small amount of acetic acid. These results indicate the consecutive progress of the self-condensation reaction forming secondary and tertiary condensation products. Although carbonates are not strong bases able to abstract protons from ethyl acetate, decomposed carbonates due to the addition of a small amount of acetic acid were active in the formation of condensation products. This means that strong basic sites with high basicity, $H_- = 25$, are produced *in situ* during the condensation reaction. Therefore, the decomposed materials from calcium carbonate by acetic acid are responsible for the strong-base-producing active anion intermediates.

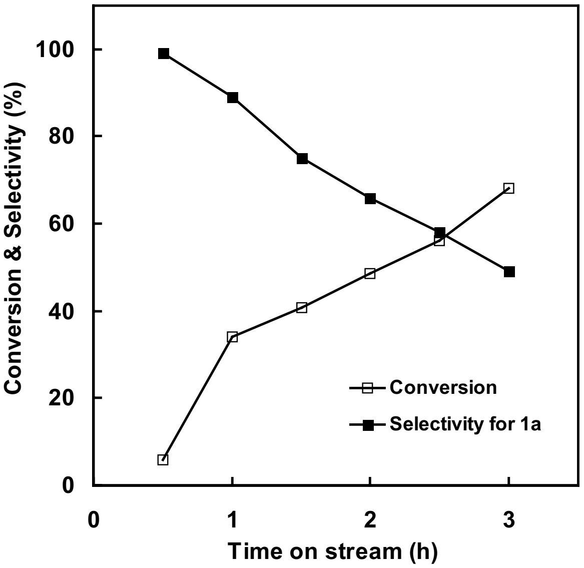


FIG. 1. The conversion and selectivity for the primary condensation product over decomposed calcium carbonate in the self-condensation of ethyl acetate at 100°C. [moles carbonate]/[moles ethyl acetate] = 0.02.

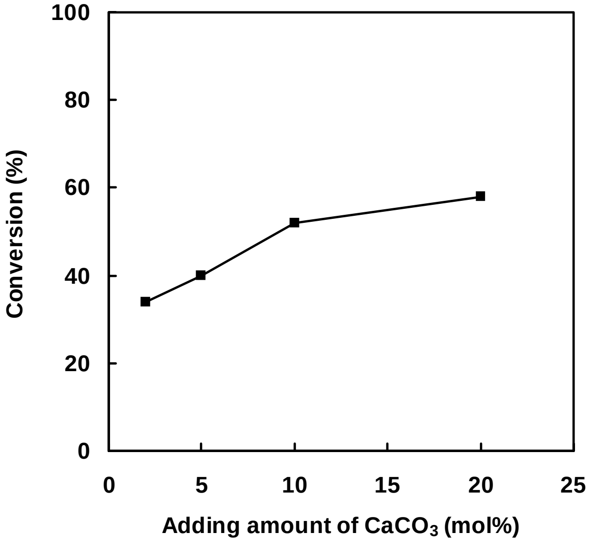


FIG. 2. Variation of the conversion with the added amount of calcium carbonate in the self-condensation of ethyl acetate at 100°C. The added amount is denoted as a percentage (mol%) of ethyl acetate. Data were obtained after 1 h reaction.

TABLE 1

Self-Condensation of Ethyl acetate over Various Alkaline and Alkaline-Earth Carbonates[a]

Carbonate	Conversion (%)	Selectivity (%)			
		1a	**1b**	**1c**	Others[b]
Na_2CO_3	32	58	—	20	22
K_2CO_3	37	48	5	22	25
$MgCO_3$	83	67	—	8	25
$CaCO_3$	68	43	—	37	20
$BaCO_3$	—	—	—	—	—

[a] [moles carbonate]/[moles ethyl acetate] = 0.02.

[b] Hydrolysis products of ethyl acetate due to the presence of H^+/H_2O.

The content of calcium carbonate in the reactant was very small compared to that of ethyl acetate as [moles $CaCO_3$]/[moles ethyl acetate] = 0.02. However, the conversion was high, up to 68%, with a time on stream of 3 h. This means that calcium carbonate is not a reactant but a catalyst precursor converted to a strong base which can continuously produce active anion intermediates.

The variations of the conversion of ethyl acetate with added amounts of calcium carbonate were studied to verify its catalytic role. As shown in Fig. 2, a large amount of calcium carbonate was not effective in enhancing the conversion. The 1-h time-on-stream conversion slowly increased when the added amount of calcium carbonate was about 10 mol%. A small amount of calcium carbonate compared to that of ethyl acetate is sufficient for the self-condensation of ethyl acetate, illustrating its catalytic function.

The strength of *in situ* generated bases from calcium carbonate was measured by using 4-chloroaniline. Since its H_- is known to be 26.5 (16), the change in color to the basic form indicates the presence of a superbase with $H_- > 26$. The acidic color of 4-chloroaniline remained the same when it was adsorbed on dehydrated calcium carbonates. However, with the addition of acetic acid, a clear pink color in the basic form appeared, indicating the generation of strong basic sites. This result strongly suggests that the generated strong bases are not attributed to carbonates themselves but to oxides decomposed from carbonates by acid.

In addition to calcium carbonate, alkaline and alkaline earth metal carbonates were catalytically active in the self-condensation of ethyl acetate when *they were* treated with a small amount of acetic acid, as shown in Table 1. The addition of acetic acid was also essential to the progress of self-condensation, even though the required amount was as small as 20 μl. Although there were some differences in their catalytic activities, all carbonates, except barium carbonate, show catalytic activity in self-condensation.

The removal of carbon dioxide from carbonates by acetic acid produces metal oxides without regular structures. A sponge-type metal oxide, showing a strong basic character, may have some unusual coordination sites. In contrast, barium carbonate was inactive, because it was not decomposed by weak acetic acid under this reaction condition.

The necessity of carbonate decomposition for its catalytic activity may be indicated by the temperature dependence of the conversion as shown in Fig. 3. The conversions over both potassium and calcium carbonates were zero even at 80°C, but the conversion increased sharply with a small increase in temperature. The conversions were 38 and 65% at 100°C over potassium and calcium carbonates, respectively.

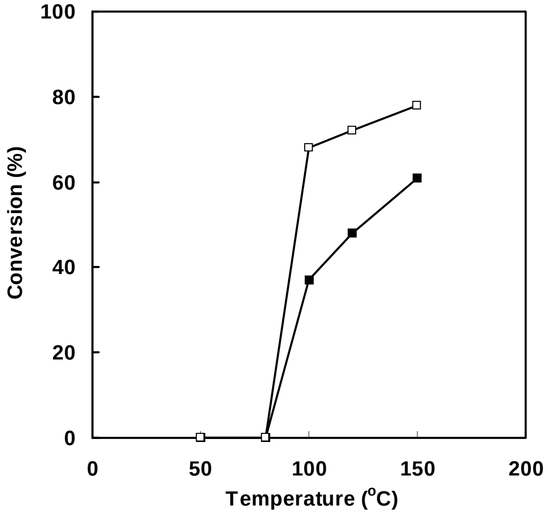


FIG. 3. Temperature dependence of the conversion in the self-condensation of ethyl acetate over decomposed calcium and potassium carbonates. [moles carbonate]/[moles ethyl acetate] = 0.02.

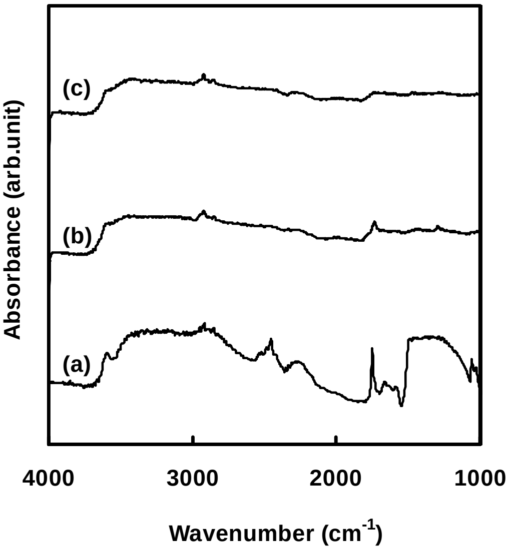


FIG. 4. FT–IR spectra of (a) fresh calcium carbonate, (b) the collected solid from the self-condensation reaction system starting with calcium carbonates, and (c) decomposed calcium carbonate exposed to acetic acid vapor and evacuated at 100°C.

However, the further increase in the conversion with the reaction temperature was relatively small. The increase in the conversion from 80 to 100°C is much higher than that expected from the elevation of the reaction temperature. The changes in chemical species around 100°C, is a plausible explanation for the steep increase in the catalytic activity of the decomposed carbonates.

Decomposition of carbonates induces the loss of carbonyl groups. Thus, FT–IR spectra of calcium carbonate and the collected solid after the self-condensation reaction must be different. As shown in Fig. 4, absorption bands attributed to carbonyl groups were not observed in the collected solid. Calcium carbonate exposed to acetic acid vapor and evacuated at 100°C showed an identical IR spectrum to that of the collected solid. This means that the carbon dioxide in calcium carbonate must be removed during the self-condensation reaction.

Since the high basicity of decomposed carbonates causes their catalytic activity in the condensation reaction, higher catalytic activities of sodium and potassium carbonates than those of magnesium and calcium carbonates are expected according to the basicity order of alkaline and alkaline-earth oxides. The low activity of alkaline carbonate might be, however, due to the nature of basic sites generated from carbonates. In the decomposition of carbonates by acid, escaping of carbon dioxide remains a metal oxide, without having any regular and stable structures. As a result, some oxygen atoms of metal oxides are not sufficiently coordinated with neighboring atoms which are similar to decomposed carbonates above 600°C (15). The lack of a sufficient coordination of oxygen atoms induces unusually high concentrations of electrons revealing strong basic properties. Alkaline metal oxide has intrinsically high basicity compared to that of alkaline-earth metal oxide. Nevertheless, a high solubility of alkaline metal oxides causes their rapid dissolution and loss of their high basicity when they come into contact with water, resulting in lower conversions. In contrast, a low solubility of alkaline-earth metal oxides maintains their unstable structures during self-condensation for a longer period of time, resulting in higher conversions.

CONCLUSIONS

Alkaline and alkaline-earth metal carbonates with the addition of a small amount of acetic acid showed considerably high catalytic activity in the self-condensation of ethyl acetate. The production of ethyl acetoacetate, the condensation product, confirmed *in situ* generation of strong bases effective for the deprotonation of ethyl acetate. The change in color of 4-chloroaniline indicated that generated bases had extremely stronger basic sites, so called superbases with $H_{-} > 26$. Alkaline and alkaline-earth metal oxides decomposed from carbonates by adding a small amount of acetic acid did not have sufficient coordination. Therefore, the lack of sufficient coordination is considered to be a plausible cause for the formation of strong basic sites such as superbasic metal oxides that were decomposed at high temperatures.

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