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Ketones from carboxylic acids over supported magnesium oxide and related catalysts

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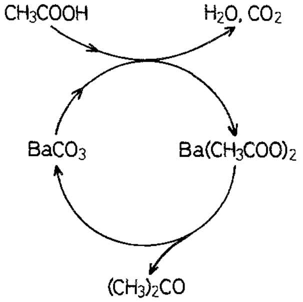
Silica-supported alkaline earth oxides revealed excellent activity to convert acetic acid selectively into acetone in a vapor-phase fixed-bed flow system. Acetone was obtained through the cyclic formation of alkaline earth acetate followed by decomposition. Magnesium oxide should be supported on the silica surface without formation of magnesium silicate, which was inactive for the present reaction. Attempted syntheses of benzophenone and acetophenone are also described.

Keywords: Alkaline earth carboxylates; ketones; supported magnesia

1. Introduction

Thermal decomposition of alkaline earth acetate gives acetone and the carbonate [1]. Carbonates could be converted into the acetate by displacement desorption of CO_2 in the presence of acetic acid. Thus acetone was obtained continuously from acetic acid in the fixed-bed flow system over calcium carbonate [2], barium carbonate [3], and related catalysts through the cyclic formation of the acetate followed by the decomposition (scheme 1).



Scheme 1.

Tableted single oxide, e.g. MgO, was pulverized through recycling of the acetate decomposition. Attempts were made in the present work to adapt alkaline earth and related oxides (Mg, Ca, Ba, and Zn) for the vapor-phase fixed-bed flow operation as catalysts supported on silica and/or activated carbon. The supported catalysts showed excellent activity to convert acetic acid selectively into acetone, while benzene was the predominant product from benzoic acid. MgO/C gave a rather good yield (18%) of benzophenone. Acetophenone was obtained in high yields through the acetate decomposition for mixtures of benzoic acid and acetic acid. Magnesium oxide should be supported on the silica surface without formation of magnesium silicate, which was inactive for the present reactions.

2. Experimental

The thermal decomposition behavior of alkaline earth acetate or benzoate was examined by means of Shimadzu DTG-40. The reaction was carried out by a fixed-bed continuous flow apparatus. The reaction solution (10 mol% CH_3COOH in H_2O or benzene, 2 mol% C_6H_5COOH in toluene, or 2 mol% CH_3COOH and C_6H_5COOH in toluene) was supplied by Micro-Feeder (type JP-S, Furue Science) into the reactor and diluted with N_2 to result in a partial pressure of CH_3COOH: 5 kPa, C_6H_5COOH: 1 kPa, or CH_3COOH: 1 kPa and C_6H_5COOH: 1 kPa, respectively. The volume of the catalyst was 2 cm^3. Monitoring of the reaction was done with GC (Hitachi 163-FID and/or Yanako G-2800-TCD).

Supported catalysts were prepared by impregnating SiO_2 (Silbead MS: Mizusawa Industrial Chemicals, Tokyo; calcined at 500°C for 5 h in air, 10–14 mesh, surface area 349 m^2/g) or activated carbon (Wako Pure Chemicals, Tokyo, surface area 1200 m^2/g) with alkaline or alkaline earth compounds of a given concentration. The corresponding samples will be denoted as MgO/SiO_2 or MgO/C. Binary SiO_2–MgO, which was reported to be weakly acidic [4], was prepared from $Na_2O \cdot 2SiO_2$ and $MgCl_2$ as shown in ref. [4]. A white paste of MgO (Wako) was dried at 100°C under vacuum and calcined at 500°C for 5 h. A particle size of 10–14 mesh was used.

The yield of ketone and CO_2 is defined as follows, respectively, based on the stoichiometry as $2RCOOH \rightarrow R_2CO + CO_2 + H_2O$ for acetone ($R = CH_3$) and benzophenone ($R = C_6H_5$) and $CH_3COOH + PhCOOH \rightarrow PhCOCH_3 + CO_2 + H_2O$ for acetophenone:

for acetone and benzophenone

$$\text{yield of ketone } (\%) = \frac{2 \times \text{moles of ketone produced}}{\text{moles of carboxylic acid introduced}} \times 100,$$

$$\text{yield of } CO_2 \ (\%) = \frac{2 \times \text{moles of } CO_2 \text{ produced}}{\text{moles of carboxylic acid introduced}} \times 100;$$

for acetophenone

$$\text{yield of acetophenone } (\%) = \frac{\text{moles of ketone produced}}{\text{moles of acetic acid introduced}} \times 100,$$

$$\text{yield of } CO_2\ (\%) = \frac{\text{moles of } CO_2 \text{ produced}}{\text{moles of acetic acid introduced}} \times 100.$$

3. Results and discussion

Conversion of acetic acid into acetone over magnesia evidently proceeds through the formation of magnesium acetate followed by decomposition.

When the substrate acetic acid was supplied with benzene as diluent, MgO (0.66_3 g, 16 mmol) showed a high conversion (92%) to afford acetone (yield 78%) continuously during 4 h on-stream at 400°C with a space velocity (SV) of 3600 h^{-1}. Within 2.5 h on-stream, the cumulative amount of acetone obtained in the illustrative run mentioned above exceeded the stoichiometric requirement based on MgO. Thus MgO was not acting as a stoichiometric reagent, but was a catalyst evidently regenerated in situ. In contrast, MgO was less active at the same condition employing water as dilutent, presumably due to hydrolysis of the intermediate acetate,

$$MgO + 2CH_3CHOOH \rightleftharpoons Mg(OCOCH_3)_2 + H_2O. \tag{1}$$

Thermogravimetric analysis for $Mg(OCOCH_3)_2 \cdot 4H_2O$ given in fig. 1 (solid line) shows that the tetrahydrate was dehydrated ($-4H_2O$) at 50–140°C, remained intact anhydrous up to 200°C, gradually decomposed to the carbonate at 200–300°C, and then quickly decarboxylated to the oxide level at 335°C without

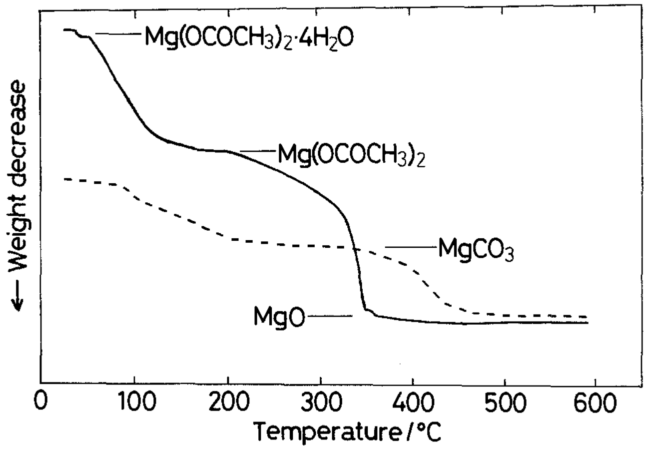


Fig. 1. Thermogravimetric analysis for $Mg(OCOCH_3)_2 \cdot 4H_2O$ (solid line) and $MgCO_3 \cdot 5H_2O$ (dashed line).

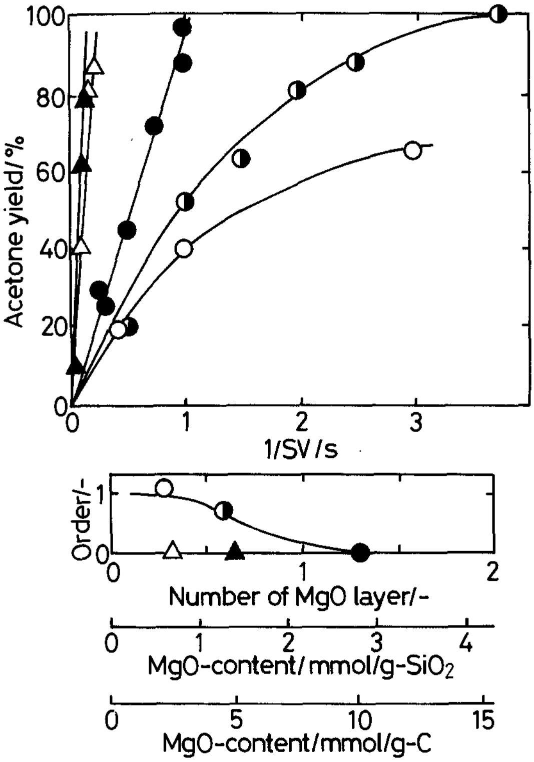


Fig. 2. Effect of MgO content for the reaction of acetic acid on MgO/SiO_2 (circle) and MgO/C (triangle) at 400°C.

showing the carbonate level. A comparative TGA for $MgCO_3 \cdot 5H_2O$ shows that $MgCO_3$ (fig. 1, dashed line) decomposes slowly in a wide temperature range at 300–450°C toward the oxide level.

The catalytic conversion of acetic acid into acetone was observed at above 325°C, just close to the decomposition temperature of magnesium acetate (323°C [5]), where the tableted MgO was found to be pulverized after 5 h on-stream. A variety of supported magnesia with different MgO contents on silica and/or activated carbon were prepared in the present work to avoid pulverization. The results for acetic acid conversion are summarized in fig. 2.

Zero-order kinetics was observed (fig. 2) at a higher content above monolayer ($N = 1$, nominally calculated as 7.68 A^2/MgO-unit) of MgO on SiO_2 (●) while the order of reaction increased with decreasing of MgO-content (◑ and ○) toward first-order kinetics at higher dispersion (○). Such a decrease in the catalytic activity at a higher dispersion of MgO on SiO_2 might be arising from the formation of magnesium silicate on the surface of the catalyst. A binary oxide SiO_2–MgO, where magnesium silicate is formed [4], was inactive, providing an evidence as an extreme case that Mg on SiO_2 should retain the nature of basic oxide to afford acetone from acetic acid.

Table 1
Catalytic activity for reaction of acetic acid on each catalyst (reaction temperature 400°C. SV = 3600 h^{-1})

Catalyst M/SiO_2	Metal content (mmol/g SiO_2)	Bulk density (g/cm^3)	Decomposition temp. (°C) [a]		Conversion (%) CH_3COOH	Yield (%)	
			acetate	carbonate		$(CH_3)_2CO$	CO_2
Mg	2.68	0.47	323	400	100	97	94
Ca	2.13	0.49	400 [b]	900	30	30	32
Ba	2.70	0.57	450 [b]	1360	36	37	48
Zn	2.00	0.55	200	300	100	100	100
Na	2.54	0.53	(324) [c]	(851) [c]	15	7	11

[a] Ref. [5] unless otherwise stated.
[b] This work.
[c] Melting point.

It is of interest that zero-order kinetics was observed for MgO/C (bulk density: 0.42–0.49 g/cm^3) even at a high dispersion of $N = 0.33–0.65$, where MgO would be dispersed without reaction with the carbon support and thus capable of retaining properties of the basic oxide.

Table 1 compares the catalytic activity of alkaline earth and related oxides for acetic acid conversion at 400°C with SV = 3600 h^{-1}. Mg and Zn, of which both acetate and carbonate decompose at below the present reaction temperature of 400°C, show high activity to produce acetone selectively. Ca and Ba, of which carbonates are stable even at temperatures much higher than the reaction condition, were less active, but gave acetone. It should be noted that the activity of the catalyst does not correlate with the decomposition temperature of the carbonate, but of the acetate decomposition. The surface carbonates suffered displacement desorption of CO_2 by the free acetic acid vapor to regenerate the acetate to yield acetone at around the temperature of the acetate decomposition

$$MgO + 2CH_3COOH \rightarrow Mg(OCOCH_3)_2 + H_2O, \tag{2}$$

$$Mg(OCOCH_3)_2 \rightarrow MgCO_3 + (CH_3)_2CO, \tag{3}$$

$$MgCO_3 + 2CH_3COOH \rightarrow Mg(OCOCH_3)_2 + CO_2 + H_2O, \tag{4}$$

which might be supported by the almost similar yield of acetone and CO_2 on Ca/SiO_2 and Ba/SiO_2 catalysts although the decomposition temperature for the carbonate is quite different to each other. Strongly basic Na showed low activity with less selectivity to acetone and turned brownish black due to carbon deposit.

A cyclic catalytic process for hydrazine synthesis from benzophenone, ammonia, and molecular oxygen via the azine with recycling of benzophenone has been proposed earlier by the authors [6–8]. Benzophenone is unique for the

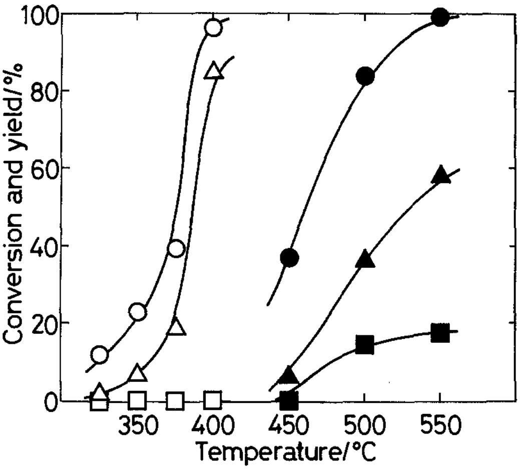


Fig. 3. Temperature effect for the reaction of benzoic acid on ZnO/SiO_2 (open symbols) and MgO/C (filled symbols) at SV = 3600 h^{-1}. (○) Conversion of benzoic acid, (△) yield of benzene, (□) yield of benzophenone.

process but unfortunately expensive. Thus an approach to the attempted synthesis of benzophenone through the benzoate decomposition has been made in the present work. However, benzoates of alkaline earth metals are generally stable at higher temperature and benzene was the predominant product with a minor yield of benzophenone, differing from the selective conversion of acetic acid to acetone,

$$C_6H_5COOH \rightarrow C_6H_6 + CO_2, \tag{5}$$

$$2C_6H_5COOH \rightarrow (C_6H_5)_2CO + CO_2 + H_2O. \tag{6}$$

Slow decomposition of magnesium benzoate to magnesium oxide was observed at a wide temperature range of 300–525°C by TGA. Benzene (20%) was obtained with a small amount of benzophenone (1%) at 500°C on MgO/SiO_2 with a 50% conversion of benzoic acid. Selectivity to benzophenone was improved up to 18% employing activated carbon as support for MgO as shown in fig. 3, but benzene was still the major product. Zinc benzoate decomposed at 300–400°C and ZnO/SiO_2 showed high activity at lower temperature as given in fig. 3, but exclusively gave benzene. Thus the present reaction seems to be affected by the decomposition of the benzoate. Li_2CO_3 was reported in refs. [1,9] as an effective catalyst for conversion of benzoic acid into benzophenone, but Li_2CO_3/SiO_2 in the present work gave a disappointing result of 82% conversion with 8% benzophenone at 500°C.

In the case of an equimolar feed of acetic acid and benzoic acid to MgO/SiO_2 and MgO/C, acetophenone was obtained in high yield as illustrated in fig. 4. Although a small amount of benzene was detected at a high temperature around 450°C, which corresponds to the temperature for the benzoate decomposition, it

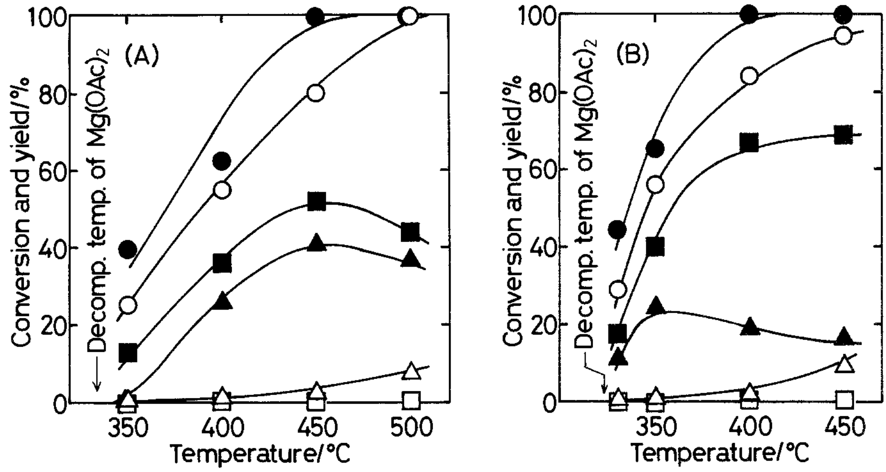


Fig. 4. Temperature effect for the reaction of equimolar mixture of acetic acid and benzoic acid on MgO/SiO_2 (A) and MgO/C (B) at SV = 3600 h^{-1}. (○) Conversion of benzoic acid, (△) yield of benzene, (□) yield of benzophenone. (●) Conversion of acetic acid, (▲) yield of acetone, (■) yield of acetophenone.

is evident that acetophenone was formed through the acetate decomposition as indicated in fig. 4 (323°C; arrow).

In conclusion, alkaline earth silicate should retain the nature of the basic oxide for the synthesis of ketone from carboxylic acid, and generally catalysts supported on activated carbon were more active than silica-supported catalysts. Ketone formation was dependent on the decomposition temperature of the acetate or benzoate, and was not affected by the carbonate decomposition.

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