Journal of Catalysis **204,** 393–401 (2001)
doi:10.1006/jcat.2001.3414, available online at http://www.idealibrary.com on IDEAL®

Mixed Tishchenko Reaction over Solid Base Catalysts

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Received April 24, 2001; revised September 10, 2001; accepted September 10, 2001

Catalytic behaviors of solid base catalysts for mixed Tishchenko reactions were investigated to elucidate the activity- and selectivity-determining factors in active sites of the catalysts and molecular structures of the reactants. A mixture containing equal amounts of two kinds of aldehydes was allowed to react at 353 K. The aldehydes used were benzaldehyde, pivalaldehyde, and cyclopropanecarbaldehyde. For all the reactions, the catalytic activity of alkaline earth oxides increased in the order of BaO $\ll$ MgO $<$ CaO $<$ SrO. As far as the alkaline earth oxides are concerned, it is suggested that a catalyst possessing strong basic sites and high surface area exhibits a high activity. Other solid base catalysts, such as La_2O_3, ZrO_2, ZnO, γ-alumina, hydrotalcite, KF/alumina, and KOH/alumina, were all inactive for the mixed Tishchenko reaction of benzaldehyde and pivalaldehyde; not only crossed-condensation products but also self-condensation products hardly formed. Quantum chemical calculations of the positive charges on the carbonyl carbon atoms of aldehydes and the structure parameters of the active species for the ester formations account for the observed selectivities to four Tishchenko dimers. The selectivities to four Tishchenko dimers over MgO and CaO are determined primarily in the step of the nucleophilic addition of the active species ($PhCH_2O^-$, $^tBuCH_2O^-$, and $C_3H_5CH_2O^-$) to the carbonyl carbon atoms of aldehydes. The reaction of the aldehyde having a more positively charged and sterically less-hindered carbonyl carbon atom with the active species having a less-hindered oxygen atom proceeds faster.

Key Words: **solid base catalyst; mixed Tishchenko reaction; crossed-condensation; self-condensation; benzaldehyde; pivalaldehyde; cyclopropanecarbaldehyde.**

1. INTRODUCTION

The classical Tishchenko reaction is a dimerization of aldehydes to the corresponding esters catalyzed by aluminum alkoxides (1–5). For about a century, the Tishchenko reaction has been studied well and new types of catalysts have been developed to obtain the product esters in high yields. Quite recently, some homogeneous catalysts, such as lanthanide complexes and bidentate aluminum catalysts, were found to be very active for Tishchenko reactions of aldehydes of various types (6–8). However, after synthesis, removal of these catalysts from the reaction mixture causes loss of catalysts and reduction of the product yields. Moreover, in view of environmental protection, we are encouraged to use environmentally benign catalysts in the industrial processes. Development of heterogeneous catalysis seems to be important in these respects. In the past, Tanabe and Saito found that alkaline earth oxides which possess both acidic and basic sites can catalyze the Tishchenko reaction of benzaldehyde via the formation of the active species of surface metal benzylate (9). More recently, alumina-supported KF catalysts (KF/alumina) were also found to be active for the Tishchenko reaction of benzaldehyde and pivalaldehyde (10, 11).

While some heterogeneous catalyses for the Tishchenko reaction have been investigated, as mentioned above, there have been no reports of the solid-base-catalyzed mixed Tishchenko reaction in which two different aldehydes are allowed to react (4). As shown in Scheme 1, a mixed Tishchenko reaction gives two crossed-condensation products (product A and product B) and two self-condensation products (product C and product D).

In the present work, we investigate mixed Tishchenko reactions over solid base catalysts to elucidate the activity- and selectivity-determining factors in active sites of the catalysts and the molecular structures of the reactants. A wide variety of solid base catalysts were examined, and aldehydes with different structures were used. The discussion focuses on the catalytic selectivities and activities of MgO and CaO for mixed Tishchenko reactions.

2. EXPERIMENTAL

2.1. Catalysts and Reagents

Alkaline earth oxides, MgO, CaO, SrO, and BaO, were prepared from $Mg(OH)_2$, $Ca(OH)_2$, $SrCO_3$, and $BaCO_3$, respectively, by thermal decomposition at elevated temperatures *in vacuo*. Lanthanum oxide was prepared from $La(OH)_3$ using the same procedures as for alkaline earth oxides, where $La(OH)_3$ was obtained from an aqueous solution of $La(NO_3)_3$ by hydrolysis with an aqueous ammonia,

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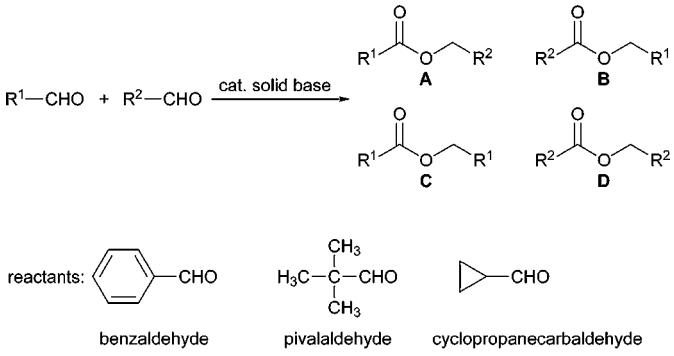
0021-9517/01 $35.00



SCHEME 1. Mixed Tishchenko reaction over solid base catalysts.

followed by washing with distilled water and drying at 373 K. Zirconium oxide and ZnO were prepared from $Zr(OH)_4$ and $Zn(OH)_2$, respectively, by thermal decomposition at elevated temperatures *in vacuo*. γ-Alumina used as catalyst and the support for KOH/alumina was supplied from the Catalysis Society of Japan (JRC-ALO4). Hydrotalcite (Mg/Al = 2) was synthesized as reported (12). Alumina-supported KF (KF/alumina) was purchased from Fluka, and its content of KF was determined to be 8.2 mmol g^{-1} by X-ray fluorescence XRF. An alumina-supported KOH catalyst (KOH/alumina) was prepared by impregnation of γ-alumina (JRC-ALO4) with an aqueous solution of KOH, followed by drying at 373 K in air. The content of KOH was 1.2 mmol g^{-1}. The surface areas of catalysts were determined by applying the BET equation to the nitrogen adsorption at 77 K. The pretreatment temperatures and surface areas of the catalysts examined are listed in Table 1.

Benzaldehyde, pivalaldehyde, and cyclopropanecarbaldehyde used as reactants were purchased from Aldrich. Benzaldehyde was purified by distillation under a reduced pressure. Pivalaldehyde and cyclopropanecarbaldehyde were purified by passage through 4-Å molecular sieves to remove water and carbon dioxide exclusively.

TABLE 1

Preparation of Solid Base Catalysts

Catalyst	Pretreatment temp (K)	Surface area[a] (m^2/g)
MgO	873	267
CaO	873	48
SrO	1273	12
BaO	1273	2
La_2O_3	873	33
ZrO_2	873	42
ZnO	873	2
γ-Alumina	773	171
Hydrotalcite (Mg/Al = 2)	673	118
Fluka–KF/alumina	673	40
1.2 mmol g^{-1} KOH/alumina	873	160

[a] Surface area was determined by BET method.

2.2. Reaction Procedures

The reaction was carried out in an H-shaped glass batch reactor. The two branches of the reactor were separated by a breakable seal. A sample of the catalyst precursor was placed in one branch, outgassed at an elevated temperature for 2 h, and sealed. A mixture of reactants was stored in the other branch until it was introduced through the breakable seal by distillation into the branch containing the catalyst thermostated at liquid nitrogen temperature. Reaction was initiated by melting the reactant mixture at a reaction temperature followed by stirring. The products were identified by ^{1}H NMR and gas chromatography (GC)–mass spectrometry analysis. GC analyses to determine yields and conversions of the product esters were carried out using a column of DB-1 (total length, 60 m; diameter, 0.25 mm).

2.3. Quantum Chemical Calculations

Quantum chemical calculations were carried out at the PM3–MO level of theory (13). A cluster model composed of $(MgO)_9$ was used in the calculations. The cluster model and all adsorption structures were fully optimized by means of the PM3 energy gradient method.

3. RESULTS AND DISCUSSION

3.1. Catalytic Activities of Solid Base Catalysts in the Mixed Tishchenko Reaction of Benzaldehyde and Pivalaldehyde

Table 2 shows the activities of solid base catalysts in the mixed Tishchenko reaction of benzaldehyde and pivalaldehyde. Reaction was carried out for 4 h at 353 K with 100 mg of each solid base catalyst.

As for the alkaline earth oxides, MgO, CaO, and SrO gave the product esters in high yields. With BaO, however, the reactions proceeded quite reluctantly, and the corresponding esters were obtained in considerably low yields. It should be noted that the catalytic activity of alkaline earth oxides for the present reaction is in the increasing order of BaO $\ll$ MgO $<$ CaO $<$ SrO.

Lanthanum oxide is considered to be rather strongly basic oxide and has been reported to catalyze several base-catalyzed reactions (14). However, its activity was very low for the mixed Tishchenko reaction of benzaldehyde and pivalaldehyde. Zirconium oxide and ZnO, which show both basic and acidic properties and, thus, are considered to act as an acid–base bifunctional catalyst (14), did not afford the Tishchenko dimers at all.

γ-Alumina, hydrotalcite, KF/alumina, and KOH/alumina were all inactive. KF/alumina has been reported to show high activities for the Tishchenko reaction of

TABLE 2

Activities of Solid Base Catalysts for the Mixed Tishchenko Reaction of Benzaldehyde and Pivalaldehyde[a]

Catalyst	Yield[b] (%)			
	Product A	Product B	Product C	Product D
MgO	28	12	15	18
CaO	28	26	21	23
SrO	24	34	19	23
BaO	<1	3	2	<1
La_2O_3	<1	<1	0	<1
ZrO_2	0	0	0	0
ZnO	0	0	0	0
γ-Alumina	<1	<1	0	<1
Hydrotalcite (Mg/Al = 2)	<1	<1	<1	0
Fluka–KF/alumina	<1	<1	<1	<1
1.2 mmol g^{-1} KOH/alumina	0	0	0	0

[a] Catalyst, 100 mg; benzaldehyde, 5 mmol; pivalaldehyde, 5 mmol; reaction temperature, 353 K; reaction time, 4 h. Products A, B, C, and D are defined as shown in Scheme 1 (R^1 = Ph, R^2 = ^{t}Bu).

[b] Yield was determined by GC analysis of the resulting solution and was calculated by the decrease in benzaldehyde and pivalaldehyde percentages converted to the corresponding esters.

benzaldeyde and pivalaldehyde when the aldehydes are allowed to react separately (10, 11). Thus, KF/alumina was expected to catalyze the mixed Tishchenko reaction of benzaldehyde and pivalaldehyde to a certain extent. However, KF/alumina gave only small amounts of the products when a mixture of two aldehydes was allowed to react. Even the self-condensation products, benzyl benzoate and neopentyl pivalate, hardly formed. The reason Tishchenko reactions hardly proceed over KF/alumina when the reactant aldehydes of benzaldehyde and pivalaldehyde are mixed seems to be difficult to understand, because the catalytically active species of KF/alumina is still a controversial problem and, therefore, the reaction mechanism is ambiguous (10, 11). The result that KOH/alumina did not afford the Tishchenko dimers agrees with the result that KOH/alumina was inactive for the Tishchenko reaction of benzaldehyde and pivalaldehyde even when they were allowed to react separately (10, 11).

3.2. Time Course of the Amounts of Reactants and Products in the Mixed Tishchenko Reaction of Benzaldehyde and Pivalaldehyde

Figure 1 shows the variations of molar percentages of the reactants and products as a function of reaction time in the mixed Tishchenko reaction of benzaldehyde and pivalaldehyde over SrO. Both benzaldehyde and pivalaldehyde continued to decrease, drawing reversed S-shaped curves as the reaction proceeded, and almost all the aldehydes were converted to crossed- and self-esterification products in 4 h. On the other hand, the product esters continued to increase, drawing S-shaped curves as the reaction proceeded. The crossed-esterification products (benzyl pivalate and neopentyl benzoate) formed in larger amounts than did the self-esterification products (benzyl benzoate and neopentyl pivalate).

It appears that the reaction has an induction period. Tanabe and Saito reported that they observed an induction period in the Tishchenko reaction of benzaldehyde over CaO (9). They attributed the induction period to the formation of the surface calcium benzylate, which acts as the active species for the ester formations. The reversed S-shaped curves and S-shaped curves observed in Fig. 1 may arise from the induction period for the formation of the active species in the mixed Tishchenko reaction.

3.3. Dependence of the Catalytic Activities of MgO and CaO in the Mixed Tishchenko Reaction of Benzaldehyde and Pivalaldehyde on Pretreatment Temperature of the Catalysts

In general, the catalytic activities of MgO and CaO in base-catalyzed reactions are affected strongly by the pretreatment temperature (14). Variations of molar percentages of the product esters for MgO- and CaO-catalyzed mixed Tishchenko reactions of benzaldehyde and pivalaldehyde as a function of pretreatment temperature are shown in Figs. 2 and 3, respectively. Magnesium oxide and

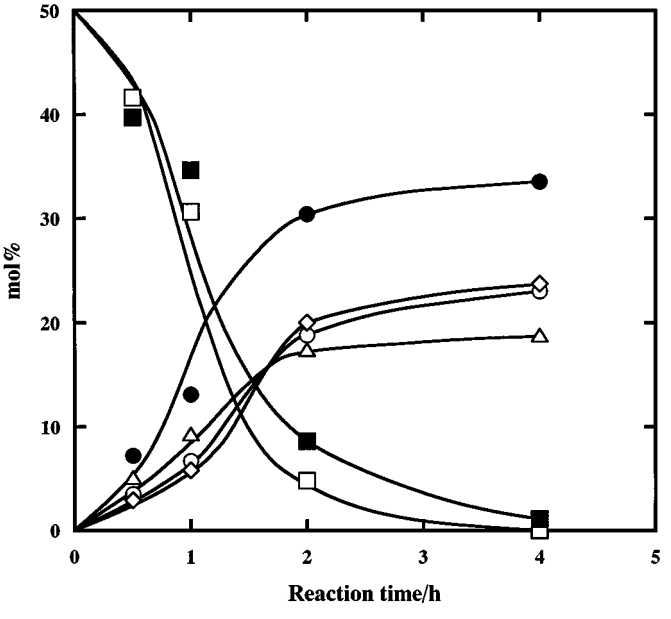


FIG. 1. Variations of molar percentages of reactants and products for SrO-catalyzed mixed Tishchenko reactions as a function of reaction time. Catalyst, 100 mg; benzaldehyde, 5 mmol; pivalaldehyde, 5 mmol; reaction temperature, 353 K. □, Pivalaldehyde; ■, benzaldehyde; ○, neopentyl pivalate; ●, benzyl pivalate; ◇, neopentyl benzoate; △, benzyl benzoate.

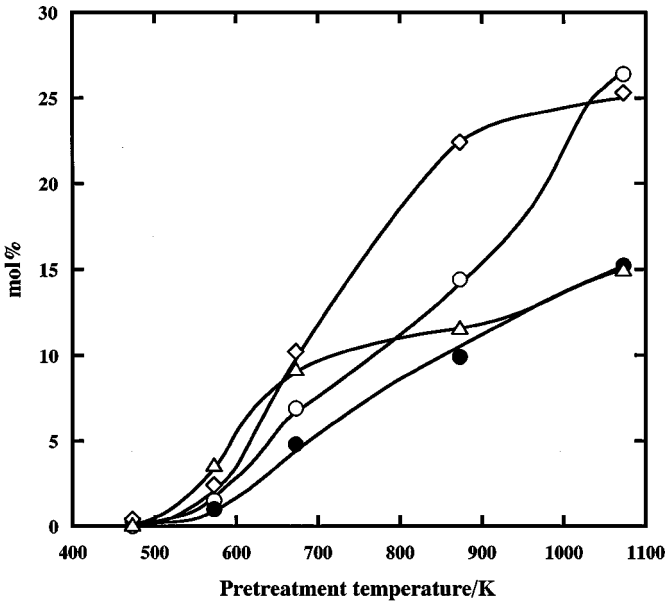


FIG. 2. Variations of molar percentages of reactants and products for MgO-catalyzed mixed Tishchenko reactions as a function of pretreatment temperature. Catalyst, 100 mg; benzaldehyde, 5 mmol; pivalaldehyde, 5 mmol; reaction temperature, 353 K; reaction time, 4 h. ○, Neopentyl pivalate; ●, benzyl pivalate; ◇, neopentyl benzoate; △, benzyl benzoate.

CaO exhibited almost no activities when they were pretreated below 573 K, indicating that the active basic sites for the present reaction are not OH groups, but O^{2-} ions on MgO and CaO.

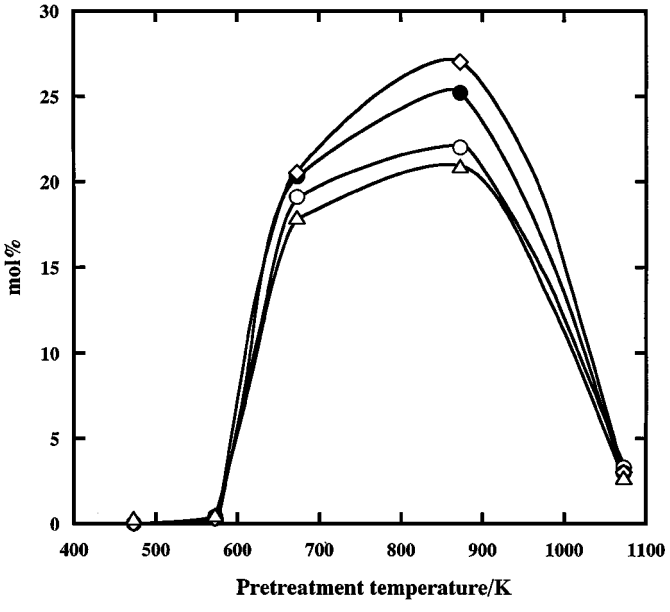


FIG. 3. Variations of molar percentages of reactants and products for CaO-catalyzed mixed Tishchenko reactions as a function of pretreatment temperature. Catalyst, 100 mg; benzaldehyde, 5 mmol; pivalaldehyde, 5 mmol; reaction temperature, 353 K; reaction time, 4 h. ○, Neopentyl pivalate; ●, benzyl pivalate; ◇, neopentyl benzoate; △, benzyl benzoate.

The activity of MgO increased with the pretreatment temperature in the range 473–1073 K, although pretreatment above 900 K brings about a decrease in surface basicity (14). On the other hand, the activity of CaO increased as the pretreatment temperature rose to a certain temperature around 900 K, and then it decreased rapidly. Since the surface areas of CaO were 48 and 32 m^2/g when CaO was pretreated at 873 and 1073 K, respectively, the rapid decrease in the activity cannot be explained by a decrease in surface area. The rapid decrease in the activity was also observed for other solid-base-catalyzed reactions (14), and due to the decrease in the surface basicity.

3.4. Comparison between Nonmixed and Mixed Tishchenko Reactions over SrO and KF/Alumina Using Benzaldehyde and Pivalaldehyde as Reactants

To investigate the difference between nonmixed and mixed Tishchenko reactions, benzaldehyde and pivalaldehyde were allowed to react separately and together over 100 mg of SrO and KF/alumina at 353 K. The reactions over SrO and KF/alumina were carried out for 30 min and 4 h, respectively. The results are summarized in Table 3.

For nonmixed Tishchenko reactions, benzaldehyde was much more reactive than pivalaldehyde over both catalysts. It is noted that the conversions were lower in the mixed Tishchenko reactions than in nonmixed Tishchenko reactions. Since 5 mmol of aldehyde was allowed to react in nonmixed Tishchenko reactions, while a mixture of a total of 10 mmol of aldehydes containing 5 mmol of each aldehyde was allowed to react in mixed Tishchenko reactions, it is understandable that the conversion is lower in the mixed Tishchenko reaction due to a lower concentration of the aldehyde. However, the observed low conversions in the mixed Tishchenko reactions cannot be explained only by the low concentration of the reactant. Some other factors should be involved. At present, the reason that the

TABLE 3

Comparison between Nonmixed and Mixed Tishchenko Reaction of Benzaldehyde and/or Pivalaldehyde over SrO and KF/Alumina[a]

Catalyst	Reactant	Conversion[b] (%)
SrO	PhCHO	96[c]
SrO	^{t}BuCHO	70[c]
SrO	PhCHO + ^{t}BuCHO	31[c]
Fluka–KF/alumina	PhCHO	22[d]
Fluka–KF/alumina	^{t}BuCHO	8[d]
Fluka–KF/alumina	PhCHO + ^{t}BuCHO	2[d]

[a] Catalyst, 100 mg; benzaldehyde, 5 mmol; pivalaldehyde, 5 mmol; reaction temperature, 353 K.

[b] Conversion was determined by GC analysis of the resulting solution and was calculated by the decrease in benzaldehyde and/or pivalaldehyde percentages converted to the corresponding esters.

[c] Reaction time, 30 min.

[d] Reaction time, 4 h.

TABLE 4

Activities of Alkaline Earth Oxides in the Mixed Tishchenko Reaction of Pivalaldehyde and Cyclopropanecarbaldehyde[a]

Catalyst	Yield[b] (%)			
	Product A	Product B	Product C	Product D
MgO	<1	25	7	6
CaO	5	26	20	7
SrO	10	30	30	17
BaO	0	0	0	0

[a] Catalyst, 100 mg; pivalaldehyde, 5 mmol; cyclopropanecarbaldehyde, 5 mmol; reaction temperature, 353 K; reaction time, 4 h. Products A, B, C, and D are defined as shown in Scheme 1 ($R^1 = {}^t$Bu, $R^2 = C_3H_5$).

[b] Yield was determined by GC analysis of the resulting solution and was calculated by the decrease in pivalaldehyde and cyclopropanecarbaldehyde percentages converted to the corresponding esters.

conversions were too low in the mixed Tishchenko reaction is not certain.

3.5. Catalytic Activities of Alkaline Earth Oxides in the Mixed Tishchenko Reaction of Pivalaldehyde and Cyclopropanecarbaldehyde

Table 4 shows the activities of alkaline earth oxides in the mixed Tishchenko reaction of pivalaldehyde and cyclopropanecarbaldehyde when the reaction was carried out for 4 h at 353 K in the presence of 100 mg of alkaline earth oxide.

Magnesium oxide, CaO, and SrO exhibited high activities, while BaO did not yield the product esters at all. The result that the catalytic activity increased in the order of BaO $\ll$ MgO < CaO < SrO for the present reaction agrees with the result observed in the mixed Tishchenko reaction of benzaldehyde and pivalaldehyde.

3.6. Catalytic Activities of Alkaline Earth Oxides in the Mixed Tishchenko Reaction of Cyclopropanecarbaldehyde and Benzaldehyde

The mixed Tishchenko reaction of cyclopropanecarbaldehyde and benzaldehyde was carried out at 353 K for 4 h using alkaline earth oxide as catalyst. The activities of the alkaline earth oxides for the mixed Tishchenko reaction of cyclopropanecarbaldehyde and benzaldehyde are shown in Table 5.

Magnesium oxide, CaO, and SrO showed activities in the present reaction, and the catalytic activity increased in the order of MgO < CaO < SrO. On BaO, however, the Tishchenko dimers were scarcely formed.

Together with the results shown in Tables 2 and 4, it can be concluded that the catalytic activity for mixed Tishchenko reactions increases in the order of BaO $\ll$ MgO < CaO < SrO when two aldehydes out of benzaldehyde, pivalaldehyde, and cyclopropanecarbaldehyde are allowed to react at 353 K. Zhang *et al.* estimated relative strengths and relative numbers of basic sites on the alkaline earth oxides by carrying out the TPD (temperature-programmed desorption) experiments under the same conditions (15). The TPD plots of carbon dioxide desorbed from alkaline earth oxides indicate that the strength of basic sites is in the increasing order of MgO < CaO < SrO < BaO. In the mixed Tischenko reactions, we observed that the catalytic activity increased in the order of BaO $\ll$ MgO < CaO < SrO. Thus, except BaO, it can be stated that strong basic sites and weak acidic sites (metal cation) are important for the formations of large quantities of the self- and crossed-condensation products, where weakness of acidic sites can be estimated using Pauling's electronegativity. The reason that BaO with the strongest basic sites exhibited the lowest activity for the mixed Tishchenko reactions should be related to a small surface area of 2 m^2/g.

3.7. Mechanistic Consideration of the Catalytic Selectivities and Activities of MgO and CaO in Mixed Tishchenko Reactions

Tanabe and Saito studied the Tishchenko reaction of benzaldehyde over alkaline earth oxides (9). They proposed the mechanism of the Tishchenko reaction of benzaldehyde over MgO and CaO, as shown in Scheme 2. The first step is the adsorption of aldehydes onto the basic (O^{2-}) and acidic (metal cation) sites, resulting in the formation of the intermediates (**I**) and (**II**), respectively. In the next step, hydride ion transfer from (**I**) to (**II**) occurs to form the intermediate (**III**) and the active species (**IV**) for the ester formation. The active species (**IV**) attacks the electrophilic carbonyl carbon atom of an aldehyde to form the intermediate (**V**). Then, the intermediate (**V**) draws another aldehyde onto metal cation, followed by hydride ion transfer to form a product ester and the active species (**IV**). Their kinetic investigation suggested that the rate-determining step in the catalytic

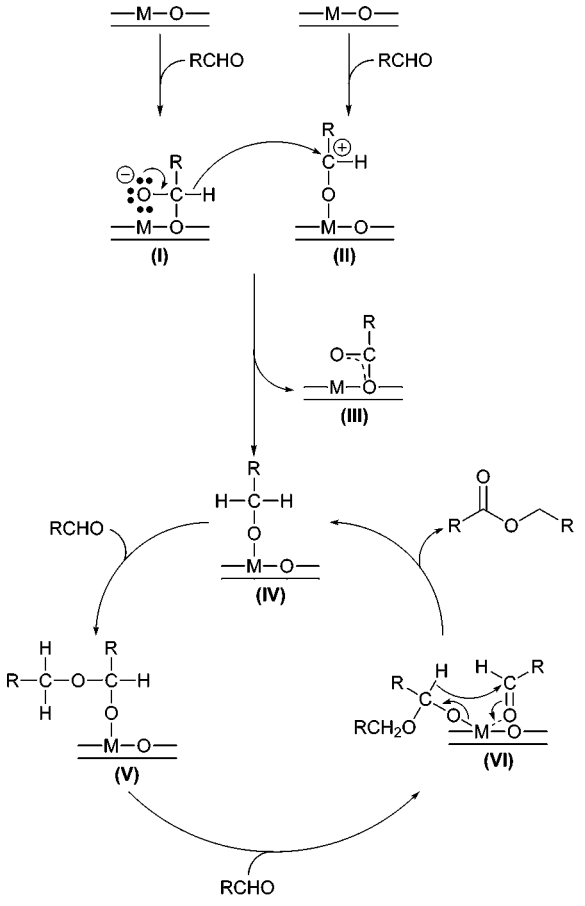
TABLE 5

Activities of Alkaline Earth Oxides in the Mixed Tishchenko Reaction of Cyclopropanecarbaldehyde and Benzaldehyde[a]

Catalyst	Yield[b] (%)			
	Product A	Product B	Product C	Product D
MgO	15	4	6	12
CaO	16	28	13	28
SrO	18	33	22	24
BaO	<1	<1	0	<1

[a] Catalyst, 100 mg; cyclopropanecarbaldehyde, 5 mmol; benzaldehyde, 5 mmol; reaction temperature, 353 K; reaction time, 4 h. Products A, B, C, and D are defined as shown in Scheme 1 ($R^1 = C_3H_5$, $R^2 =$ Ph).

[b] Yield was determined by GC analysis of the resulting solution and was calculated by the decrease in cyclopropanecarbaldehyde and benzaldehyde percentages converted to the corresponding esters.



SCHEME 2. Reaction mechanism of Tishchenko reaction over MgO and CaO proposed by Tanabe and Saito (a). M = Mg or Ca; R = Ph, ^{t}Bu, C_3H_5.

cycle is the nucleophilic addition of the active species (**IV**) to the carbonyl carbon atom of an aldehyde.

The selectivities of three types of the mixed Tishchenko reaction are summarized in Schemes 3, 4, and 5. In these schemes, it is assumed that selectivity is determined by the step of the nucleophilic addition of the active species (**IV**) to the carbonyl carbon atom of an aldehyde to form the intermediate (**V**). In a mixed Tishchenko reaction, four different elementary steps in combinations of two kinds of aldehydes with two kinds of the active species (**IV**) are involved in the nucleophilic addition. The selectivities to four Tishchenko dimers are determined by the relative reaction rates of these four elementary steps, leading to products A, B, C, and D. The relative rates are reflected in the amounts (mol%) of four types of the products. In addition, the reactivities of aldehydes and the active species (**IV**) can be estimated from the amounts (mol%) of four Tishchenko dimers. To take an example from Scheme 4, the reactivity of pivalaldehyde relative to that of cyclopropanecarbaldehyde can be explained by the ratio ([A] + [C])/([B] + [D]). Similarly, the reactivity of the active species of ^{t}BuCH$_2$O–Mg relative to that of $C_3H_5CH_2O$–Mg can be expressed by the ratio ([B] + [C])/([A] + [D]), provided that the surface concentrations are the same for these active species.

From the ratios ([A] + [C])/([B] + [D]) for three different mixed Tishchenko reactions, it is concluded that the relative reactivity of aldehydes toward the active species (**IV**) increases in the order of pivalaldehyde < cyclopropanecarbaldehyde < benzaldehyde, although an exception was observed. The result that cyclopropanecarbaldehyde underwent esterifications faster than benzaldehyde in the mixed Tishchenko reaction of cyclopropanecarbaldehyde and benzaldehyde over MgO is inconsistent with the above reactivity order of aldehydes.

Similarly, from the ratio ([B] + [C])/([A] + [D]), it is concluded that the relative reactivity of the active species (**IV**) toward aldehydes increases in the order of $C_3H_5CH_2O$–Mg < $PhCH_2O$–Mg < ^{t}BuCH$_2$O–Mg.

The selectivities of four Tishchenko dimers would be determined by the relative reactivities of the active species (**IV**) and aldehydes. The relative reactivity should be determined by chemical properties such as molecular structures and charges on the relevant atoms. It is expected that the active species (**IV**) would react faster with the aldehyde having a more positively charged and sterically less-hindered carbonyl carbon atom. The aldehyde, on the other hand, would react faster with the active species (**IV**) having a more negatively charged and sterically less-hindered oxygen atom.

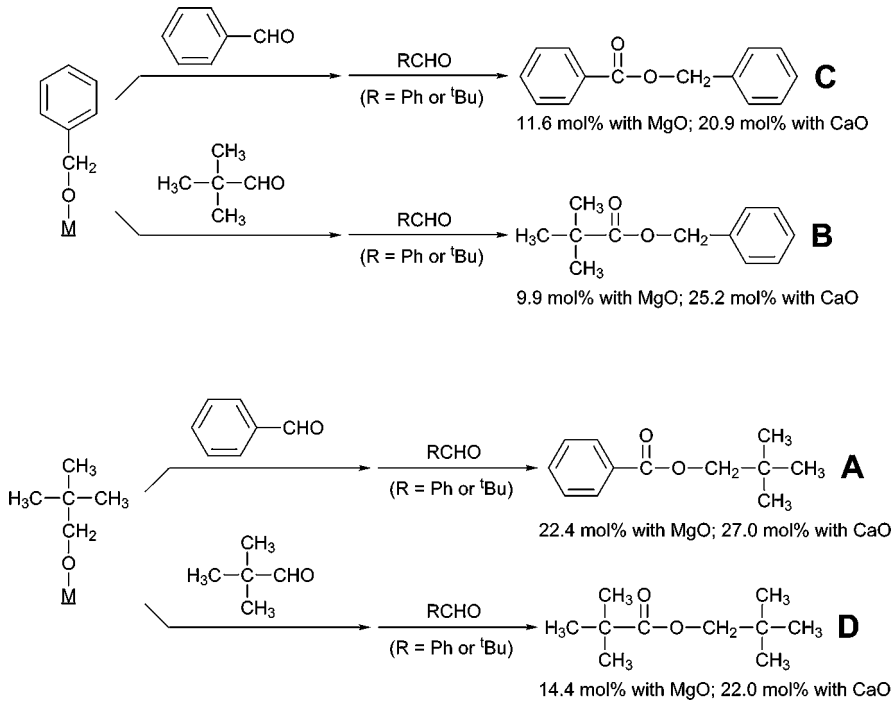
To elucidate the positive charges on the carbonyl carbon atoms of benzaldehyde, pivalaldehyde, and cyclopropanecarbaldehyde, we carried out quantum chemical calculations at the PM3–MO level of theory. The results are given in Table 6. We also calculated the structure parameters and the negative charges on the oxygen atoms of the active species (**IV**) using the cluster model of $(MgO)_9$ shown in Fig. 4. The structure parameters and the negative charges on the oxygen atoms for different active species (**IV**) are given in Tables 7 and 8, respectively.

The positive charges on the carbonyl carbon atoms of the aldehydes increase in the order of pivalaldehyde < cyclopropanecarbaldehyde < benzaldehyde. The molecular structures of the aldehydes estimated by quantum

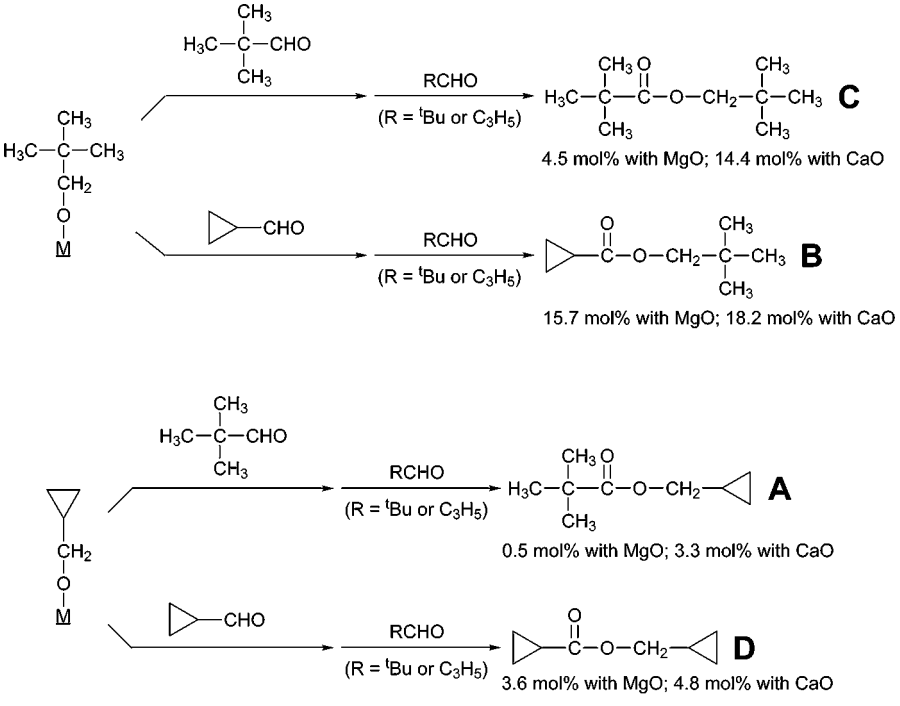
TABLE 6

Charges on Carbonyl Carbon Atoms for Benzaldehyde, Pivalaldehyde, and Cyclopropanecarbaldehyde Calculated at the PM3–MO Level of Theory

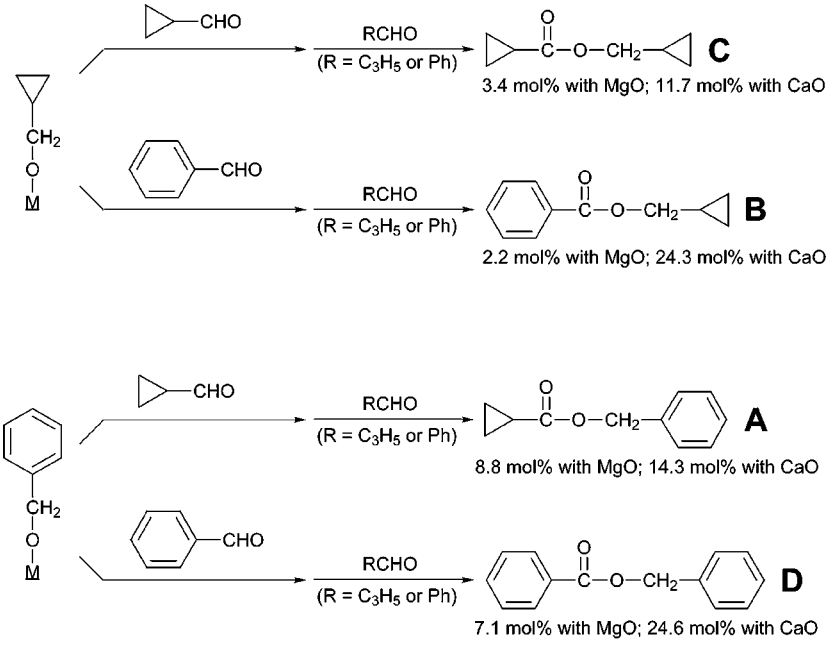
Aldehyde	Calculated charge on carbonyl carbon atom
Benzaldehyde	+0.328
Cyclopropanecarbaldehyde	+0.307
Pivalaldehyde	+0.282



SCHEME 3. Relative reactivity of benzaldehyde and pivalaldehyde for nucleophilic addition of the active species in the mixed Tishchenko reaction of benzaldehyde and pivalaldehyde. M = Mg or Ca. Catalyst, 100 mg; benzaldehyde, 5 mmol; pivalaldehyde, 5 mmol; reaction temperature, 353 K; reaction time, 4 h.



SCHEME 4. Relative reactivity of pivalaldehyde and cyclopropanecarbaldehyde for nucleophilic addition of the active species in the mixed Tishchenko reaction of pivalaldehyde and cyclopropanecarbaldehyde. M = Mg or Ca. Catalyst, 100 mg; pivalaldehyde, 5 mmol; cyclopropanecarbaldehyde, 5 mmol; reaction temperature, 353 K; reaction time, 4 h.



SCHEME 5. Relative reactivity of cyclopropanecarbaldehyde and benzaldehyde for nucleophilic addition of the active species in the mixed Tishchenko reaction of cyclopropanecarbaldehyde and benzaldehyde. M = Mg or Ca. Catalyst, 100 mg; cyclopropanecarbaldehyde, 5 mmol; benzaldehyde, 5 mmol; reaction temperature, 353 K; reaction time, 4 h.

chemical calculations at the PM3–MO level of theory suggest that the steric hindrance around the carbonyl carbon atoms of the aldehydes decreases in the order of pivalaldehyde > cyclopropanecarbaldehyde > benzaldehyde. Thus, it is expected that both electronically and sterically, the relative reactivity of the aldehydes toward the active species (**IV**) increases in the order of pivalaldehyde < cyclopropanecarbaldehyde < benzaldehyde. This order coincides with the observed reactivity of the aldehydes based on the ratios ([A] + [C])/([B] + [D]).

Concerning the reactivity of the active species (**IV**) toward an aldehyde, while the negative charges on the oxygen atoms of the active species are almost the same (Table 8), the steric hindrances around the oxygen atoms of the active species are considerably different (Table 7). Therefore, it is considered that the relative reactivity of the active species (**IV**) toward an aldehyde is determined by the steric hindrance around the oxygen atoms. A long bond distance of r, a large angle of θ, and a small angle of ϕ are favorable for reduction of the steric hindrance around the oxygen atom of the active species. Therefore, we can expect from Table 7 that the relative reactivity of the active species (**IV**)

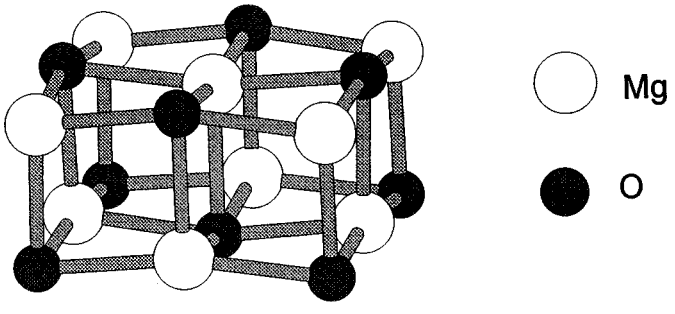
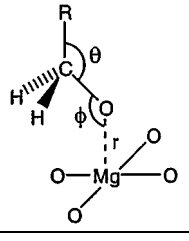


FIG. 4. Cluster model $(MgO)_9$ used in the calculations. The structure was fully optimized at the PM3–MO level of theory. It was assumed that the active species ($PhCH_2O^-$, $^tBuCH_2O^-$, and $C_3H_5CH_2O^-$) are adsorbed on the Mg atom on the center of the first layer.

TABLE 7

Structures of the Active Species Proposed by Quantum Chemical Calculations[a]



R	r (Å)	ϕ (degree)	θ (degree)
Ph–	2.5908	155.6	118.1
C_3H_5–	2.5837	164.9	115.4
^{t}Bu–	2.5965	154.1	118.6

[a] Quantum chemical calculations were carried out at the PM3–MO level of theory. It was assumed that the active species adsorb on the Mg atom on the center of the first layer of the cluster model $(MgO)_9$, which is shown in Fig. 4.

TABLE 8

Charges on Oxgen Atoms for the Active Species Calculated at the PM3–MO Level of Theory [a]

Active species	Calculated charge on oxgen atom
$PhCH_2O$–Mg	−0.146
$^tBuCH_2O$–Mg	−0.146
$C_3H_5CH_2O$–Mg	−0.148

[a] It was assumed that the active species adsorb on the Mg atom on the center of the first layer of the cluster model $(MgO)_9$, which is shown in Fig. 4.

toward an aldehyde increases in the order of $C_3H_5CH_2O$–Mg < $PhCH_2O$–Mg < $^tBuCH_2O$–Mg. This order coincides with the observed reactivity of the active species (**IV**) based on the ratio ([B] + [C])/([A] + [D]). Although we also carried out quantum chemical calculations for elucidation of the adsorption states of the active species on CaO, we failed because of the limitations of the calculation program. However, it seems that our presenting reactivity order of the active species on MgO can also be applied to the active species on CaO, because the surface structure of MgO is considered to be similar to that of CaO. Schemes 3–5 clearly emphasize that the reactivity order of the active species on CaO is in the increasing order of $C_3H_5CH_2O$–Ca < $PhCH_2O$–Ca < $^tBuCH_2O$–Ca. Thus, together with the discussion on the reactivities of aldehydes toward the active species (**IV**), we conclude that the step of the formation of (**V**) from the active species (**IV**) and an aldehyde is the selectivity-determining step in the mixed Tishchenko reaction over MgO and CaO.

For all the reactions, the catalytic activity of CaO is higher than that of MgO. This result should be related to the high reactivity of the active species (**IV**) captured on CaO in comparison with those on MgO. Pauling's electronegativity suggests that acidic sites (metal cation) on CaO are less acidic than those on MgO. The active species (**IV**) on weaker acidic sites are more reactive than those on stronger acidic sites.

Although the basic sites of O^{2-} on MgO and CaO do not participate in the catalytic cycle for the formation of esters, as shown in Scheme 2, they play an important role in the formation of the intermediates (**I**) and (**III**). Thus, the strong basic properties of MgO and CaO are indispensable for the Tishchenko esterifications.

ACKNOWLEDGMENT

This work is supported by a grant-in aid for scientific research from the Ministry of Education, Science, Sports, and Culture, Japan.

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