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An *In Situ* Study of Methyl Benzoate and Benzoic Acid Reduction on Yttrium Oxide by Infrared Spectroscopic Flow Reactor

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The reduction of methyl benzoate and benzoic acid on a Y_2O_3 catalyst under hydrogen has been examined by using an infrared spectroscopic flow reactor at 250–450°C. The formation and reduction of surface benzoate was monitored by infrared spectroscopy. Surface methoxide was also observed during the methyl benzoate reaction. The experimental evidence indicates that the benzoic acid and benzoate esters are reduced to benzaldehyde via the surface benzoate. The hydrogen is transferred from the gas phase to the final product by surface hydroxyl groups.

INTRODUCTION

The reduction mechanism of benzoate ester and benzoic acid on the surface of metal oxides has not been reported before in the literature. In a previous paper (*1*) it was reported that the benzoate ions formed on the surface of different metal oxides have different desorption rates. Recently, we have examined the behavior of benzoate ions on the surface of yttrium oxide (Y_2O_3) in more detail by a flow-through infrared (ir) spectroscopic technique (*1*). Both methyl benzoate (MB) and benzoic acid were used as reactants in this work. A reduction mechanism via the surface benzoate is proposed in this paper. We have also demonstrated that the *in situ* ir spectroscopic technique with a properly designed cell (*1*) can be used to obtain dynamic data for high-temperature catalysis.

EXPERIMENTAL

The unsupported Y_2O_3 catalyst was prepared by evaporation of an aqueous yttrium nitrate solution. The catalyst was calcined at 450°C in air for 2–3 hr. The supported catalyst was prepared by similar procedures. The loading of Y_2O_3 on α-alumina support (Norton SA 5102, $\frac{1}{16}$-in. pellets) was 21–24%. The catalysts were ground into powder and each catalyst was pressed into a 1-cm-diameter wafer for studying reactions in the ir spectroscopic flow reactor. All the ir data given in this paper were obtained from one unsupported catalyst wafer which contained 9 mg of Y_2O_3. The infrared transmittance of this wafer was about 30% at 2000 cm^{-1}.

A gas chromatograph was connected to the ir reactor for analyzing the vapor-phase composition after it emerged from the reaction vessel. All the ir spectra shown in this paper are ratios of spectra taken before and after certain conditions were changed. These ratioed spectra represent the net surface changes that occurred during the experiment. The downward ir bands in all the figures, except Fig. 10, are due to the formation of new species. The upward bands are due to the loss of surface groups.

The ir spectra with 4-cm^{-1} resolution were recorded by using a Fourier transform ir spectrometer (Digilab FTS-10) which was equipped with a HgCdTe detector. Ten to fifty scans per spectrum were recorded.

The catalyst wafer was heated in the ir reactor with air at 430°C for 30 min. The air was switched to hydrogen for 30 min before the experiment. The temperature of the reactor was then dropped to the desired reaction temperature and the background ir spectrum was recorded. The liquid reactant methyl benzoate was introduced to the ir

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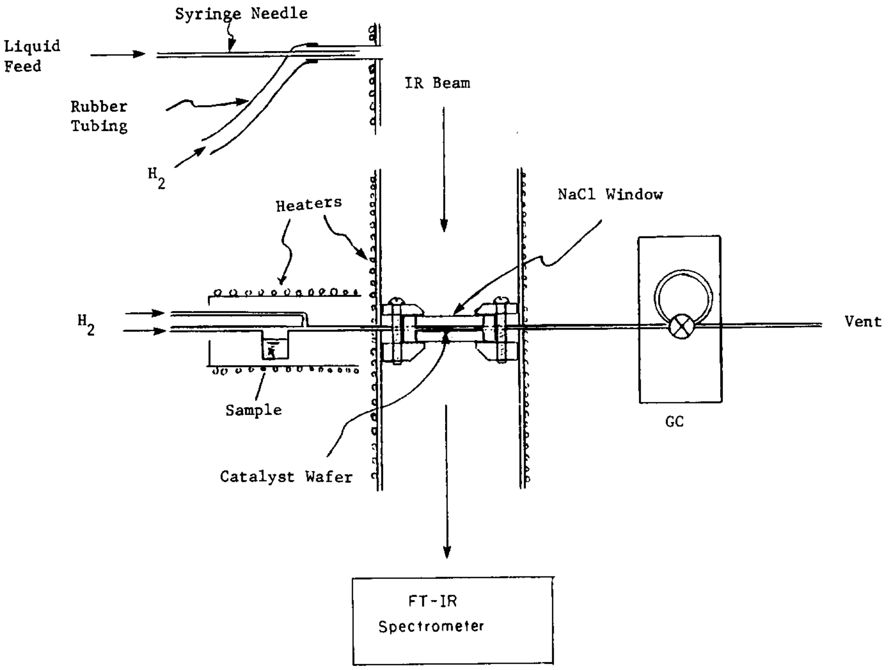


FIG. 1. Block diagram of experimental setup and the ir flow reactor.

reactor through a syringe pump. The liquid reactant was evaporated at the tip of the syringe needle and the vapor was carried into the cell by a hydrogen stream. The solid reactant benzoic acid was introduced by a vapor saturator (Fig. 1). After the organic reactant was fed to the reactor, both the ir spectra of the catalyst and the vapor-phase composition were monitored at 3- to 10-min intervals.

The hydrogen flow rate was kept at 5 cm^3/min and the methyl benzoate feed rate was 1–0.05 μl/min. The diluted organic vapor in the 0.5-mm optical path reactor showed negligible contribution to the observed ir spectra of the surface species.

A 20-cm^3 tubular plug flow reactor was also used to study the catalyst in a 10- to 20-g scale. The reaction conditions for this reactor are given below. Only supported Y_2O_3 catalyst was examined in this reactor.

RESULTS AND DISCUSSION

Spectra (A) and (B) in Fig. 2 show the removal of water and surface hydroxyl when the Y_2O_3 wafer was heated to 350°C in the stream of helium as indicated by the loss of the 1650-cm^{-1} band and the broad OH band in the region 3200–3600 cm^{-1}. Above 350°C, severe decomposition of carbonate was observed (spectrum (C) in Fig. 2). This carbonate was reformed when CO_2 was passed through the reactor even at 430°C (spectrum (D) in Fig. 2). The original carbonate was presumably formed during the calcination in air. The formation of this carbonate was always accompanied by the loss in intensity of ir bands in the regions 3660 cm^{-1} (sharp) and 3600–3200 cm^{-1} (broad). Decomposition of this carbonate was much faster when hydrogen rather than helium was passed through the cell (Fig. 3). Carbon monoxide was detected during the first minute of desorption in hydrogen. The surface OH groups were recovered after the removal of carbonate. These data indicate that the formation of carbonate at high temperature is on the hydroxyl site.

The observed surface carbonate has ir absorptions at 855, 1050, 1360, and 1500 cm^{-1}. It is consistent with the unidentate structure as assigned by Fujita *et al.* (*2*).

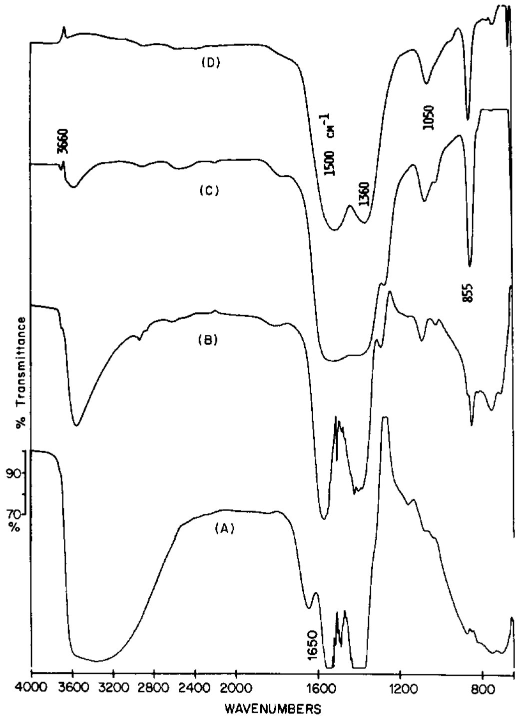


FIG. 2. The ratioed ir spectra during the heating of a Y_2O_3 wafer in the ir flow reactor. The sample was heated for about 15 min at each temperature: (A) room temperature/250°C; (B) 250°C/350°C; (C) 350°C/450°C; (D) CO_2 treated/H_2 treated at 430°C.

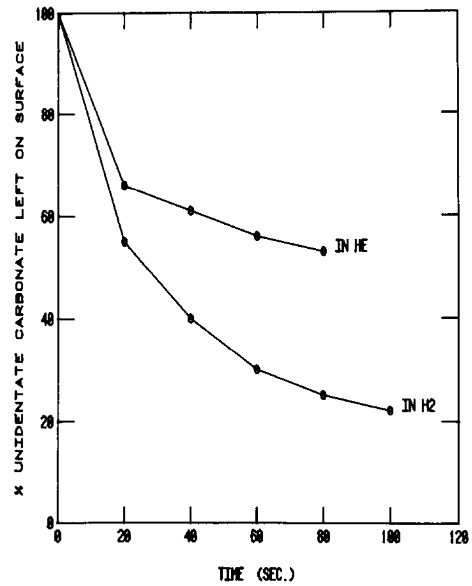
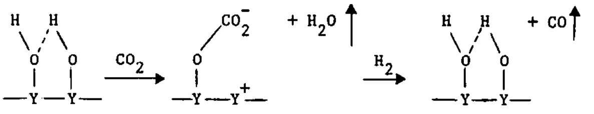


FIG. 3. Desorption of the unidentate carbonate at 380°C in the flow of 5 cm³/min H_2 and He. The unidentate carbonate on the surface was measured from the ir intensity change of the 855-cm^{-1} band.

The loss and gain of ir intensity at 3660 cm^{-1} and 3600–3200 cm^{-1} may be explained by the following reactions:



When both CO_2 and H_2 were passed over the Y_2O_3 catalyst at 380°C in the ir cell, about 20% conversion of CO_2 to CO was observed. Water was not analyzed because the gas chromatograph used in this work was not equipped to analyze water. If as much H_2O as CO is formed, then the above reactions may represent the water gas conversion on Y_2O_3. The formate ion has been observed as the intermediate for water gas conversion on zinc oxide, magnesia, and alumina by others (*3*).

The BET surface area of the Y_2O_3 sample was measured at two different degassing temperatures. The measured surface area was 40 m²/g when the sample was degassed at 200°C. After degassing at 400°C, the apparent surface area increased to 75 m²/g. The decomposition of carbonate can generate more available surface.

After the surface of the Y_2O_3 was activated in hydrogen at 430°C, the temperature was reduced to 270°C and methyl benzoate was fed slowly (0.05 μl/min) with the flow of hydrogen (5 cm³/min). Both the ir spectra of the catalyst in action and the vapor-phase composition change were recorded.

Figure 4 shows the ir spectra of the surface species which are formed during the

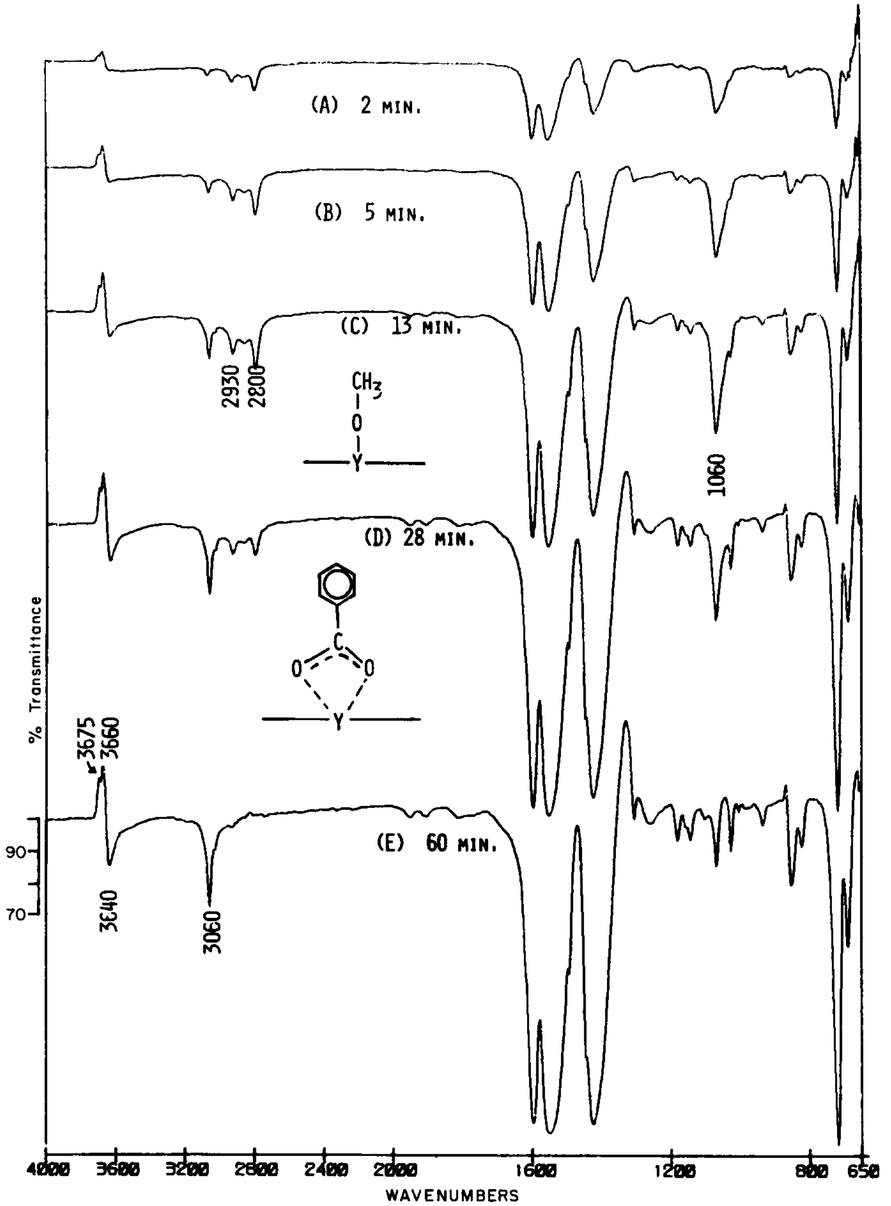
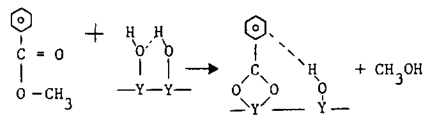


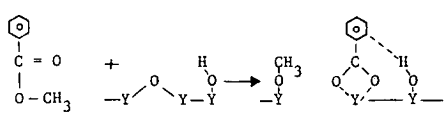
FIG. 4. Infrared spectra of the Y_2O_3 surface changes during the first hour of reaction of MB in H_2 at 270°C. Spectra (A), (B), (C), (D), and (E) were recorded at 2, 5, 13, 28, and 60 min after the reaction started. These are spectra ratioed against a spectrum taken at time zero to show the net change of the catalyst surface.

induction period of this reaction. The ir bands at 1060, 2800, and 2930 cm^{-1} are assigned, respectively, as C–O (ν_{C-O}), symmetric CH_3 (s-ν_{CH}), and antisymmetric CH_3 (a-ν_{CH}) stretching modes of methoxide groups on the catalyst surface. This surface methoxide has a stronger s-ν_{CH} band than a-ν_{CH} band. On the other hand, methanol has a stronger a-ν_{CH} adsorption than s-ν_{CH}. The ν_{C-O} frequency in Fig. 4 is also 25 cm^{-1} higher than the same band in methanol. All these spectral changes are consistent with the formation of methoxide. (For example, the ir intensity of the s-ν_{CH} mode of sodium methoxide is much stronger than that of a-ν_{CH}, and the ν_{C-O} frequency is about 35 cm^{-1} higher than the same band in methanol.) All the other bands, except for the bands in the region 3700–3500 cm^{-1}, are due to benzoate ions formed on the surface (surface benzoate). The change of ir spectra from (A) to (E) in Fig. 4 indicates that the population of surface benzoate increases with time. On the other hand, the surface methoxide increases to a maximum and then decreases quickly. Clearly, both benzoate and methoxide are formed on the fresh catalyst surface initially. The strongly bonded surface benzoates gradually occupy all the available sites and the weakly adsorbed methoxides lose their places on the surface.

Figure 4 also shows the loss of surface OH bands at 3670 and 3660 cm^{-1} and the formation of surface -OH at 3640 cm^{-1} during the formation of surface benzoate. This surface benzoate seems to occupy the similar hydroxyl site as observed for unidentate carbonate via the following reaction:



These reactions can account for the loss of the 3660-cm^{-1} band and the formation of the 3640-cm^{-1} band. The 3640-cm^{-1} band may be attributed to the OH group involved in the very weak interaction with the benzoate and this will be discussed later. However, the loss of hydrogen-bonded -OH was not clearly observed in the region 3200–3500 cm^{-1} in Fig. 4E. The following scheme is another possible explanation:



Here, only a single OH group is involved and the methanol evolved later.

The changes of vapor-phase composition, as monitored by GC, and the ir absorbances of the surface methoxide (2800 cm^{-1}) and surface benzoate (3060 cm^{-1}) are plotted in Fig. 5. During the first 50 min of reaction, the fresh catalyst surface generated a relatively high concentration of methanol (MeOH) but no benzaldehyde (BA). The desorption of surface methoxide caused the production of methanol to reach a maximum and then decreased quickly to an equilibrium state when the surface was covered with benzoate. At this point, the production of benzaldehyde, toluene (Tol), and benzene (BZ) began.

The data indicate that the methanol is produced quickly when a methyl benzoate molecule hits the catalyst surface. This process may not involve the step of methoxide formation on the surface. However, if the sites are available, the methoxide will be formed as observed by ir. The mechanism of this reaction may be expressed by the following steps:

$$\begin{array}{llll}
\mathrm{MB} & + \text{ Surface Sites} & \rightarrow & \mathrm{MB}_{(S)}, \\
\mathrm{H_2} & + \text{ Surface Sites} & \rightarrow & 2\mathrm{H}_{(S)}, \\
\mathrm{MB}_{(S)} + & \mathrm{H}_{(S)} & \rightarrow & \mathrm{B}_{(S)} + \mathrm{MeOH}_{(g)}, \\
\mathrm{MB}_{(S)} & & \rightarrow & \mathrm{B}_{(S)} + \mathrm{M}_{(S)}, \\
\mathrm{M}_{(S)} + & \mathrm{H}_{(S)} & \rightarrow & \mathrm{MeOH}_{(g)}, \\
\mathrm{B}_{(S)} + & \mathrm{H}_{(S)} & \xrightarrow{\text{slow}} & \text{Benzaldehyde}_{(g)}.
\end{array}$$

The subscripts (g) and (S) in the above equations indicate gaseous and adsorbed species, respectively. The surface benzoate and methoxide are represented by $B_{(S)}$ and $M_{(S)}$, respectively.

Benzene and toluene were two by-products of this surface reaction (Table 1). However, they were produced by different pathways. When the methyl benzoate feed rate was changed from 0.05 to 0.6 μl/min at 380°C, there was an immediate response of an increase in benzaldehyde and methanol production, and a decrease of toluene production, but very little change was observed for benzene production. This implies that the benzene is produced from a stable surface species at a very slow rate.

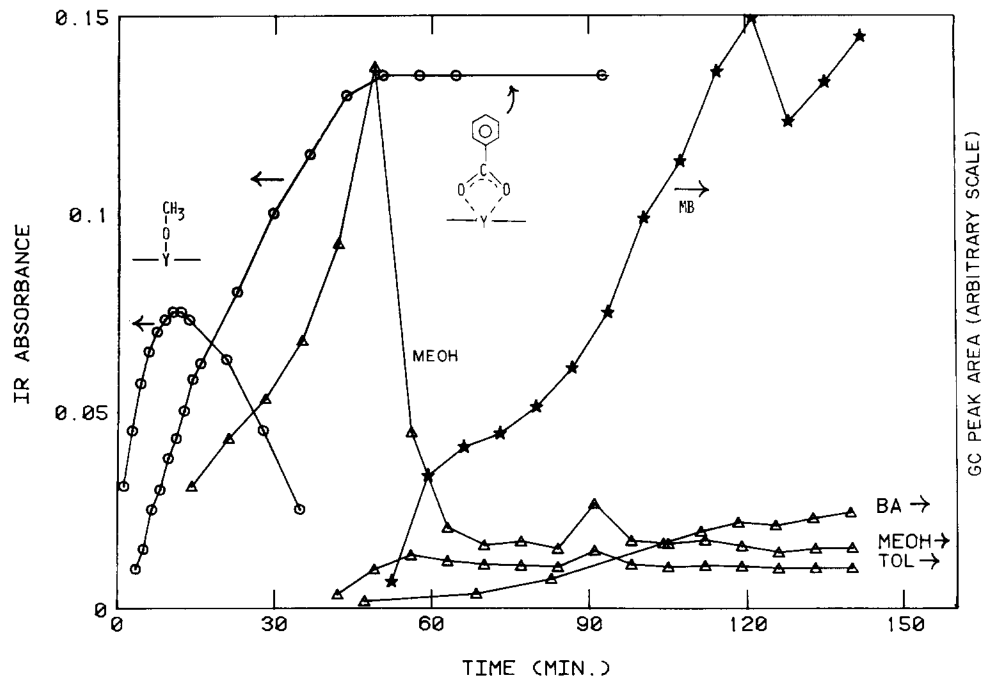


FIG. 5. The vapor-phase composition changes as monitored by GC during the same experiment as shown in Fig. 4. The GC peak area changes of methyl benzoate (MB), benzaldehyde (BA), methanol (MeOH), and toluene (Tol) used in this figure were sealed arbitrarily to fit in the graph. The ir absorbances at 2800 cm^{-1} for surface methoxide and 3060 cm^{-1} for surface benzoate were also plotted in this figure.

But this stable surface species has a relatively high population which can sustain the production of the significant amount of benzene (Table 1). As will be shown later in this paper, the benzene may be produced from the decarboxylation of the strongly bonded benzoate which accounts for most of the observed surface benzoate. On the other hand, the benzaldehyde is produced from the similar surface benzoate which is bonded to a weaker site and can be desorbed quickly in hydrogen.

The data given above can still not preclude that the benzaldehyde is produced from a very small number of sites which have a very fast production rate. During the induction period of the reaction, the benzaldehyde may be readsorbed by the open surface to form benzoate. The number of such fast sites can be below the detection limit of the ir and the observed surface benzoate is not the intermediate of benzaldehyde. If this hypothesis is true, then the benzaldehyde production should stop as soon as the methyl benzoate is removed from the vapor phase in the reaction. The ir reactor system used in this work has a very small volume, and the organic vapor in the system can be purged out within 30 sec. Figure 6 shows the desorption of surface benzoate in the flow of 5 cm^3/min hydrogen at 380°C. The methanol and methyl benzoate were not detected in the effluent 3 min after the methyl benzoate was stopped. Benzaldehyde and other by-products desorbed for a long period of time. Such desorption correlated to the observed decrease of surface benzoate (Fig. 6). This observation supports the mechanism that the benzaldehyde is produced from the observed surface benzoate.

Figure 7 shows the results of a similar desorption experiment at a higher temperature (430°C). The desorption of all the components was faster as expected. However,

TABLE 1

Reduction of Methyl Benzoate and Benzoic Acid over 21% Y_2O_3/Al_2O_3 at an H_2 GHSV[a] of 625 liters/liter-hr

Feed	LVSV[b]	Time (hr)	Temperature (°C)	Conversion (%)	Selectivity (wt%) Benzene	Toluene	Benzaldehyde	Benzyl alcohol	Recovery of theoretical Methanol (%)
Methyl benzoate	92.5	20.0	370	40.4	1.0	1.0	88.4	2.4	~90
Benzoic acid	70.0	18.8	440	91.0	2.0	0.4	96.2		
	56.7	65.8	435	72.4	0.8	0.4	92.1		

[a] GHSV = flow of hydrogen in liters per liters of catalyst per hour measured at 25°C and 1 atm.

[b] LHSV = flow of liquid feed in grams per liter of catalyst per hour.

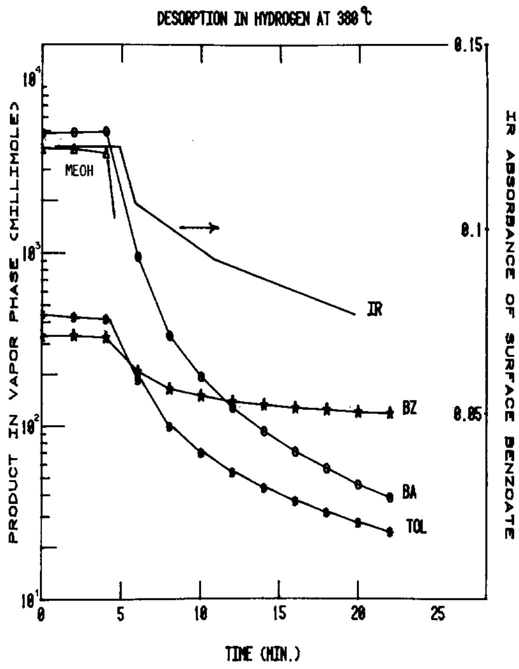


FIG. 6. Desorption of benzoate on Y_2O_3 in the flow of 5 cm^3/min H_2 at 380°C. BA, BZ, and Tol represent the amount of benzaldehyde, benzene, and toluene in 2 cm^3 of the gaseous effluent. They are expressed in log scale. The ir curve represents the absorbance of the benzoate band at 3060 cm^{-1} as measured by ir.

the benzene production increased during the first 8 min. This phenomenon is reproducible and no proper explanation can be made with the data available at this point.

When the reaction was run with a relatively high methyl benzoate (MB) feed rate, an increased MB/H_2 ratio did not affect the production rates of all products because all the surface sites were saturated. Increased temperatures can increase the rates as expected. The apparent activation energies for methanol, benzaldehyde, benzene, and toluene, determined under such a saturation condition, are 12.7, 12.7, 14.3, and 10.2 kcal/mole, respectively. The actual activation energy for methanol production may be lower than 12.7 kcal/mole since it is not a slow step as discussed before. The activation energies for methanol and benzaldehyde have the same value because the production of methanol is restricted by the production rate of benzaldehyde.

When hydrogen was switched to helium during the methyl benzoate reaction at 430°C, the production of methanol, benzaldehyde, and toluene almost ceased. However, the production of benzene continued at a lower rate. When the desorption of surface benzoate was performed in the flow of helium, only small amounts of surface benzoate were desorbed (Fig. 8). Such a difference is similar to that observed for unidentate carbonate as discussed before (Fig. 3). Obviously, the interaction of hydrogen and surface benzoate is necessary to desorb the weakly bonded benzoate into benzaldehyde. The experimental results discussed below indicate that this interaction is most likely through the surface OH group.

An H/D exchange experiment was performed by simply switching H_2 flow to D_2 during the heating of Y_2O_3 in the range 200–450°C. The exchange of surface OH to OD was instantaneous (Fig. 9A). The amount of OH exchanged, as indicated by the loss of ir intensity in the region 3660 to 3500 cm^{-1}, was invariant to temperature. Obviously, the gas-phase H_2 forms a very fast equilibrium with the surface OH groups. The interaction between surface benzoate and surface OH groups as observed in Fig. 4 provides a pathway to transfer the H_2 in gas phase to final products.

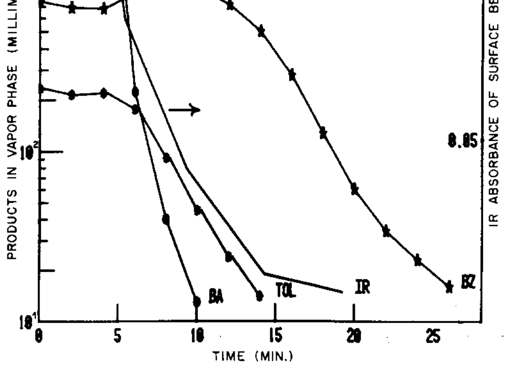


FIG. 7. Results of the desorption experiment under the same condition as Fig. 6 except that a higher temperature (430°C) was used.

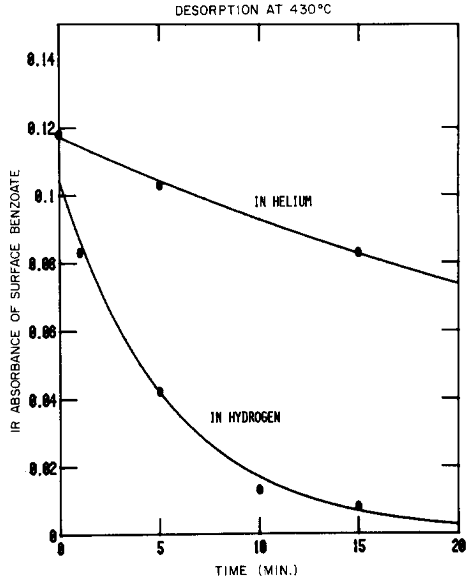


FIG. 8. Desorption of surface benzoate at 430°C in the flow of H_2 and He (5 cm^3/min). The concentration of surface benzoate was measured by monitoring the 3060-cm^{-1} ir band.

Figures 9B and C show the methyl benzoate reaction on the surface of deuterated Y_2O_3. The interaction between surface OD and surface benzoate is similar to that observed for OH (Fig. 4). The hydrogen on surface methoxide did not exchange with the deuterium as indicated by the $-CH_3$ bands at 2930 and 2800 cm^{-1} in Fig. 9B. Part of the ring hydrogen on surface benzoate was exchanged as shown by the 2260-cm^{-1} band in Fig. 9C.

During this discussion, the words "strong site" and "weak site" are used to differentiate the surface benzoates which produced benzene and benzaldehyde, respectively. A closer examination of the ir spectra recorded (Fig. 10) during the desorption in hydrogen and in helium at 430°C shows evidence of an observable difference between these two types of sites. In Fig. 10,

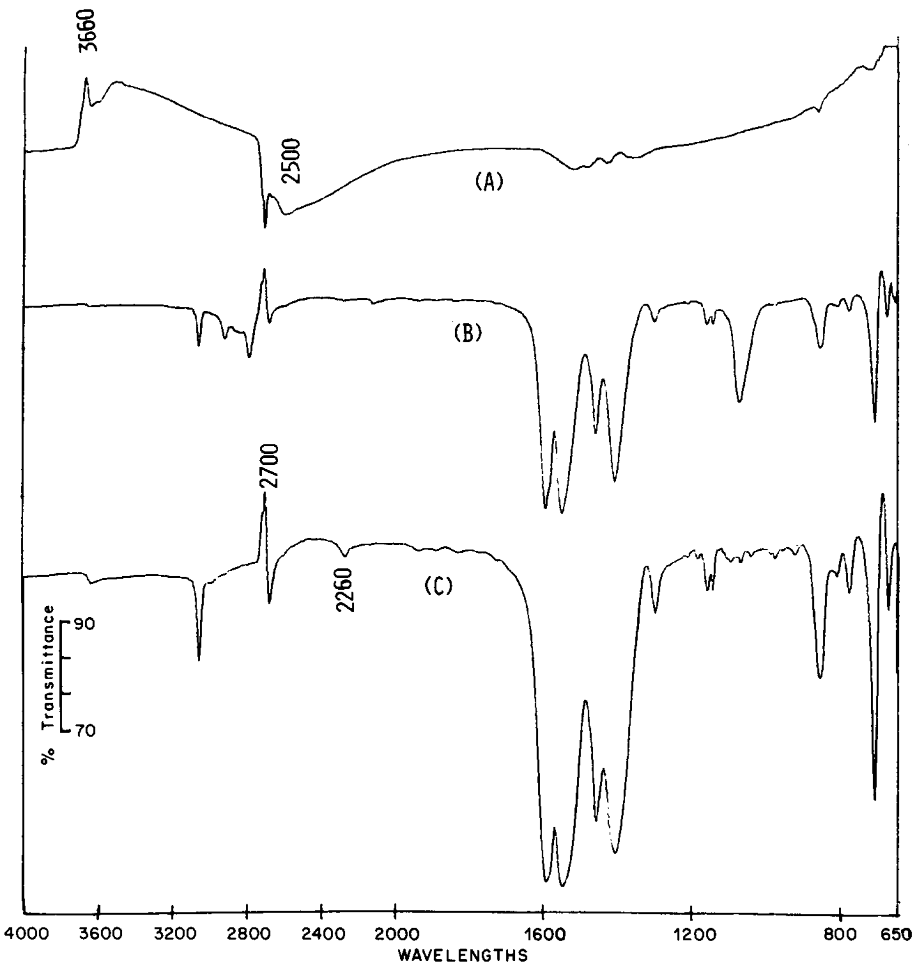
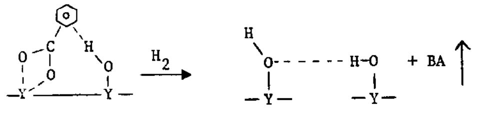


FIG. 9. (A) The ratioed ir spectrum of Y_2O_3 before and after the D_2/H_2 exchange at 300°C. (B), (C) Infrared spectra of the surface change 5 and 30 min after the MB was introduced over the deuterated Y_2O_3 at 300°C.

the percentage transmittance scale in the region 4000–2000 cm^{-1} was expanded for an easier examination of the spectra. All the spectra were expanded by the same factor so that the comparison of the change in ir intensities can be made visually.

Figures 8 and 10 show that about 90% of the surface benzoate was desorbed within 15 min in hydrogen. However, the desorption of surface benzoate in the first 5 min was accompanied by the formation of the surface OH as indicated by the 3660-cm^{-1} band in Figs. 10A and B. The benzoate which was desorbed within the first minutes, presumably the weakly bonded benzoate, showed a much stronger ir absorption for the band at 720 cm^{-1} (Fig. 10A). This absorption band is due to the ring-puckering mode of the surface benzoate. The interaction between surface OH and the π electron in the benzene ring is presumably the cause of such intensity enhancement. The following reactions may be used to describe the desorption of benzoate on this site:



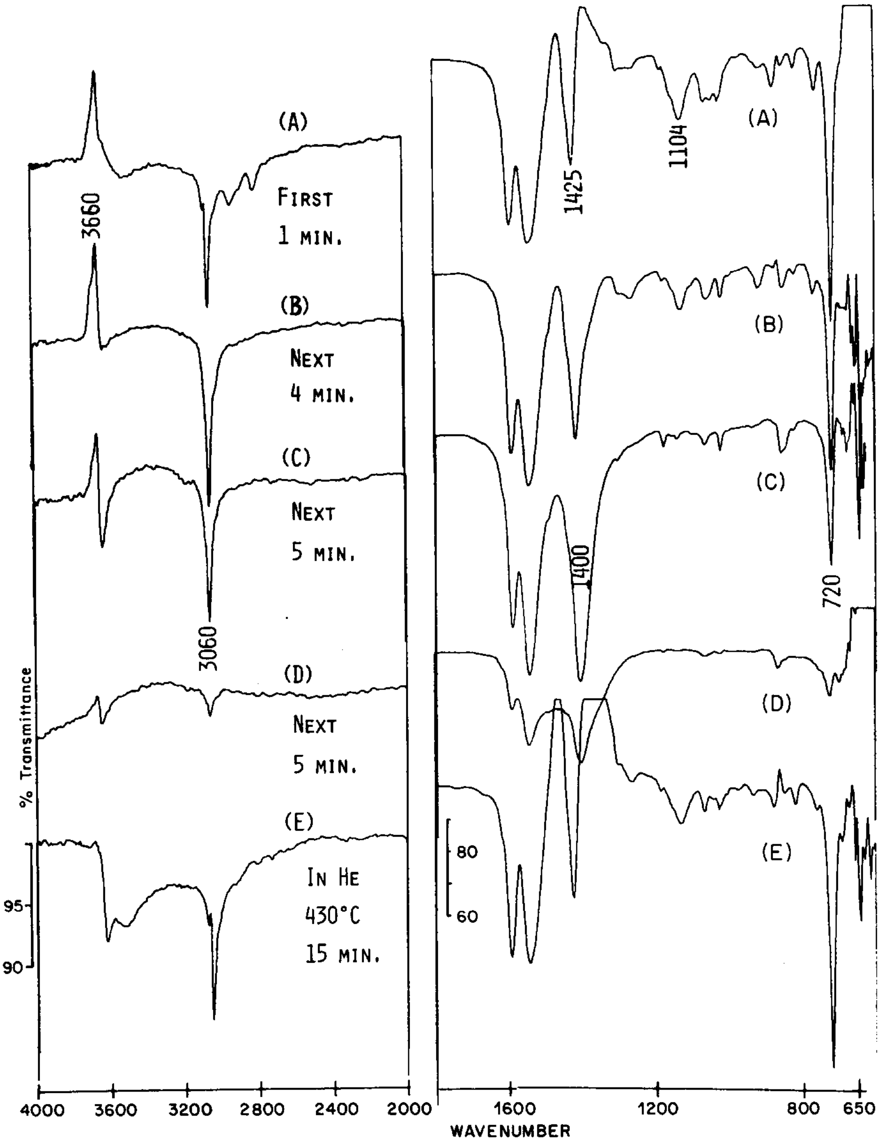
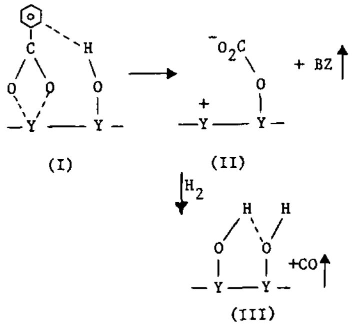


FIG. 10. (A)–(D) Infrared spectra of the surface change during the benzoate desorption in H_2. (E) Infrared spectrum of surface change during the benzoate desorption in helium. The desorption temperature was 430°C. They are ratioed spectra before and after the time interval as specified in the figure. For example, the ratio of the spectra which were recorded at 5 and 10 min respectively after desorption started is shown in spectrum (C). The downward bands and upward bands represent the loss and gain of surface groups respectively during this 5-min period.

The net spectral change is the loss of surface benzoate and gain of ir absorption at 3660 cm^{-1} as indicated in Figs. 10A and B. The hydrogen bonded OH groups may have similar frequency after the desorption and show little net change in the ratioed spectra.

The interaction between the OH and the strongly bonded benzoate is probably weaker and has an OH stretching frequency at 3640 cm^{-1}. At this site, the decarboxylation may proceed by the following steps:



Carbon monoxide was observed during the reaction of methyl benzoate on Y_2O_3.

The symmetric $-CO_2$ stretching ($s\text{-}\nu_{CO_2}$) frequency of the surface benzoate at 1425 cm^{-1} (Fig. 10A) shifted to 1400 cm^{-1} during the desorption (Fig. 10C). But the asymmetric $-CO_2$ stretching ($a\text{-}\nu_{CO_2}$) at 1550 cm^{-1} and the ring stretching mode at 1600 cm^{-1} did not change in position; they, of course, lost intensity. The higher $s\text{-}\nu_{CO_2}$ frequency of the easily desorbed species indicates the presence of a stronger C–O bond in this benzoate ion and weaker bonding between benzoate ion and the surface Y^+. This is more evidence to support the presence of weak and strong sites of attachment.

The reduction of CO_2 by H_2 was also tested when the Y_2O_3 surface was covered with benzoate. Unlike the free catalyst surface, the covered surface produced very little CO. The high CO_2-to-CO conversion resumed after the surface benzoate was removed by air oxidation. This indicates that the surface benzoate and unidentate carbonate are either formed on the same site, or occupy two different types of sites which are very close to each other and hinder one another.

Spectrum (E) in Fig. 10 is the net ir spectral change after desorption of surface benzoate at 430°C in helium flow for 15 min. The loss of a small amount of surface benzoate was accompanied by the loss of OH as indicated by ir bands at 3630 and 3500 cm^{-1}. Without hydrogen, the decarboxylation process stopped at step II in the reactions shown above. The carbonate left on the surface can be observed by the formation of ir bands at 1480 and 1380 cm^{-1} in Fig. 10E.

On the basis of the mechanism given above, one can predicate that any compound which can form surface benzoate with a fast desorption rate in hydrogen can be reduced to benzaldehyde. We have found that benzoic acid and benzyl alcohol form surface benzoate easily on many oxides. This has also been observed by others (*4*). Our subsequent experiment using both the ir flow reactor and 20-cm^3 plug flow reactor proved that the benzoic acid can be reduced on Y_2O_3 at a very high yield (Table 1). The ir spectrum of the surface benzoate formed from the benzoic acid is identical to that formed from methyl benzoate. No methoxide was observed from benzoic acid reaction as expected.

CONCLUSIONS

The benzoate ion on the surface of Y_2O_3 is the intermediate species for the reduction of benzoic acid and benzoate esters to benzaldehyde. The hydrogen is transferred to the final products via surface hydroxyl groups.

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