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Infrared Study of Hydrogenation of Benzoic Acid to Benzaldehyde on ZrO_2 Catalysts

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The selective hydrogenation of benzoic acid to benzaldehyde on ZrO_2 and Cr_2O_3–ZrO_2 at 523 K was studied by IR spectroscopy. An enhancement of the hydrogenation rate of benzoic acid by Cr_2O_3 doping to ZrO_2 was observed. The main role of Cr_2O_3 was considered to be the step of activating hydrogen. An intermediate species was observed based on the IR bands during a transformation from the adsorbed benzaldehyde to the benzoate at lower temperatures. This is discussed in conjunction with the reaction mechanism of the hydrogenation. The intermediate species was regarded as being the chemisorbed benzaldehyde by an analysis of the observed IR bands.

Recently, a direct formation of aldehydes from carboxylic acids and H_2 has been industrially realized.[1—3] In this process various carboxylic acids are selectively hydrogenated into the corresponding aldehydes over a modified ZrO_2 catalyst under relatively mild conditions. For example, benzaldehyde is produced from benzoic acid and H_2 on the catalyst at between 623 and 673 K with a 98% conversion and a 96% selectivity. One of the characteristic points regarding this process is that a further reduction of the aldehydes to the corresponding alcohols or the decarboxylation reaction are negligible under the reaction conditions. When pure ZrO_2 was used under the same reaction condition, benzaldehyde was produced with a 51% conversion and a 97% selectivity. Cr doping (Cr/Zr=5/100 atomic ratio) enhanced the surface area as well as conversion to 98%.[4] The adsorption and reaction of pivalic acid (2,2-dimethylpropionic acid) and 2,2-dimethylpropanal on a Cr_2O_3–ZrO_2 were previously investigated by means of Fourier-transform infrared (FT-IR) spectroscopy over a wide temperature range.[5] Chemisorbed 2,2-dimethylpropanal was detected during an aldehyde adsorption study at low temperature, which was expected to exist as an intermediate during the hydrogenation reaction. In the present paper, the hydrogenation of a typical aromatic carboxylic acid, benzoic acid, was studied in order to make a comparison with previous studies. The role of Cr_2O_3 in the catalyst is also discussed.

Experimental

An IR cell made of quartz was connected to a closed gas-circulation system. ZrO_2 was obtained by calcination of zirconyl hydroxide ($ZrO(OH)_2$) at 873 K for 3 h. Cr_2O_3–ZrO_2 (Cr/Zr=5/100, atomic ratio) was prepared by the impregnation of zirconium oxide dihydroxide with chromium(III) nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$) and calcination in air at 823 K for 3 h. The BET surface areas of ZrO_2 and Cr_2O_3–ZrO_2 were 49 and 122 $m^2 g^{-1}$, respectively. About 30 mg of the sample was pressed into a self-supporting disc of 20 mm in diameter. The spectra were recorded on a JASCO 7300 Fourier-transform infrared (FT-IR) spectrometer with a MCT detector at 4 cm^{-1} resolution. The IR spectra of the adsorbed species were obtained by subtracting the spectra of ZrO_2 from those of ZrO_2 and the adsorbed species taken at the same temperatures. The bands between 2400 and 2200 cm^{-1} in the IR spectra are due to gaseous CO_2 in the optical path. A pretreatment of both Cr_2O_3–ZrO_2 and ZrO_2 samples was performed in an IR cell by heating in about 100 Torr of oxygen at 773 K for 8 h, followed by evacuation at the same temperature for 30 min. Each sample is designated as Cr–ZrO_2 and ZrO_2, respectively. Both H_2 (Toyo Oxygen Company, 99.9999%) and O_2 (Toyo Oxygen Company, 99.7%) were refined by passing through a liquid-N_2 trap. Benzoic acid (Wako Pure Chemical Industries, Ltd. 99+%) and benzaldehyde (Wako Pure Chemical Industries, Ltd. 99%) were introduced to the sample at vapor pressures without further purification.

Results and Discussion

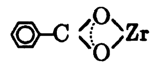
1. Adsorption of Benzoic Acid. The IR spectra of adsorbed benzoic acid on Cr–ZrO_2 are shown in Fig. 1. Benzoic acid was introduced at room temperature followed by evacuation at the same temperature. While the sample was heated gradually under evacuation, the spectra remained unchanged up to 673 K. All of the bands commenced to decrease at 723 K, and completely disappeared at 823 K. In order to assign the observed bands, the IR spectra of silver benzoate,[10] sodium benzoate,[11] and liquid benzoic acid[12] were referred to. In the spectrum of liquid benzoic acid a strong band was observed at around 1690 cm^{-1}, and assigned to the C=O stretching mode of the –COOH group. On the other hand, in spectra of benzoate salts two strong bands were observed at 1550—1520 and 1410—1390 cm^{-1}, which were assigned to the OCO asymmetric stretching and the OCO symmetric stretching modes. These two bands are characteristic for ionic bidentate carboxylate, which is usually represented by the separation of ca. 150 cm^{-1} between the two modes[13,14] (Table 1). Since the spectra of the adsorbed species

Table 1. Assignment of the Benzoate Ion, Benzaldehyde, and Observed Bands[a)]

Assignment[15—17)]	Benzoate ion[17—21)]	Observed species			Benzaldehyde[21—26)]
		Benzoate	Chemisorbed aldehyde	Physisorbed aldehyde	
*C–H str. in-phase	3091—3088				3084-3088
*C–H str.	3067—3073				
*C–H str.	3053—3063	3061	3065	3065	3063—3065
*C–H str.	3036	3032			3035—3040
*C–H str.	3027				3026—3028
C–H str. (–CHO)			2850 br	2817 s 2736 s	2817—2833 s
C=O str. (–CHO)			1681, 1649 vs	1701 vs	1703—1728 vs
*C–*C str.	1600—1605 vs	1600 sh	1602 s	1598 vs	1596—1614 vs
*C–*C str.	1595—1598 vs, sh	1596 s	1582 s	1582 s	1583—1603 s
OCO a-str. (–OCO)	1522—1569 vs	1528 vs			
*C–*C str.	1488—1499 m-w	1497 w	1495 w	1494 m	1491—1496 vw
*C–*C str.	1440—1452 m-vw, sh	1453 vs	1455 m	1455 s	1450—1460 s
OCO s-str.	1391—1421 vs	1435 vs			
C–H bend. (–CHO)					1387—1394 m
*C–*C str., kekule	1305—1318	1309 w	1318 w	1311 m	1308—1314 s
*C–H in-plane bend, in-phase	1272—1282 m-vw		1290 vw	1290 vw	1276—1292 m
*C–C str.	1141—1150 vw	1145 w	1219 s	1204 vs	1202—1206 vs
*C–H in-plane bend.	1178—1187 m-w	1181 w	1174 w	1168 w	1164—1170 m
*C–H in-plane bend.	1148—1159 vw				1158—1160
*C–H in-plane bend.	1065—1072 m-w	1070 w	1068 w	1068 w	1069—1074 sh
*C–H in-plane bend.	1020—1029 m-w, sh	1027 w	1026 w	1026 m	1021—1026 m

a) * represents an aromatic carbon. s, strong; m, medium; w, weak; v, very; sh, shoulder and br, broad.

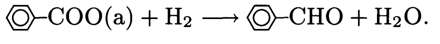
formed by benzoic acid adsorption on Cr–ZrO_2 in Fig. 1 showed two intense bands at 1523 and 1424 cm^{-1}, the observed species on Cr–ZrO_2 could be reasonably assigned to the bidentate carboxylate species,



(1)

Details concerning the assignment are listed in Table 1 along a summary of the observed bands of metal-coordinated benzoic acid ions including adsorbed benzoate on Al_2O_3 formed from benzoic acid[20)] and benzaldehyde[21)] adsorption. The bands at 1592 and 1451 cm^{-1} are attributed to the aromatic group. These two bands became less pronounced as the temperature increased (Fig. 1), probably because of a band broadening of two intense bands of the –OCO group. The adsorption of benzoic acid on ZrO_2 resulted in the same spectral change, depending on the temperatures, as those on Cr–ZrO_2, with the exception of the reverse peaks due to the Cr=O[5—8)] species in the case of Cr–ZrO_2. It is therefore considered that the stability of adsorbed benzoic acid was not affected by the existence of Cr.

2. Hydrogenation of Benzoate. Benzoic acid was introduced to Cr–ZrO_2 at 623 K where the benzoate was sable under evacuation. Then, H_2 (400 Torr, 1 Torr=133.322 Pa) was admitted at the same temperature. This temperature was chosen in order to study the adsorbed species under similar conditions to that of the industrial production of benzaldehyde from benzoic acid and H_2. Figure 2 shows the adsorbed benzoate (a) and the time course of the IR spectra taken during hydrogenation ((b)—(d)). All of the bands, except for those of the OH stretching (3600—3800 cm^{-1}) mode, decreased constantly as the reaction proceeded, and almost disappeared after 30 min. The increase in the IR absorption in the OH stretching region after H_2 admission is not due to the production of H_2O, according to



$$\text{C}_6\text{H}_5\text{–COO(a)} + H_2 \longrightarrow \text{C}_6\text{H}_5\text{–CHO} + H_2O. \quad (2)$$

Since the OH species increased immediately after the introduction of H_2, as shown in (b). Therefore, the increase in the OH species is due to hydrogen adsorption on the benzoate adsorbed-Cr–ZrO_2 surface. The IR spectra taken during hydrogenation of benzoate over ZrO_2 are shown in Fig. 3. It is noticed that the reaction proceeded more slowly over ZrO_2 than over Cr–ZrO_2 (Fig. 2) under the same reaction conditions, although the stability of benzoate under evacuation was not affected by Cr. It is therefore suggested that one of the roles of Cr is to facilitate the activation of H_2.

Both on Cr–ZrO_2 and on ZrO_2 the adsorbed benzoate species reacted with H_2; no intermediate species or product aldehyde were observed at 623 K, as shown in Figs. 2 and 3.

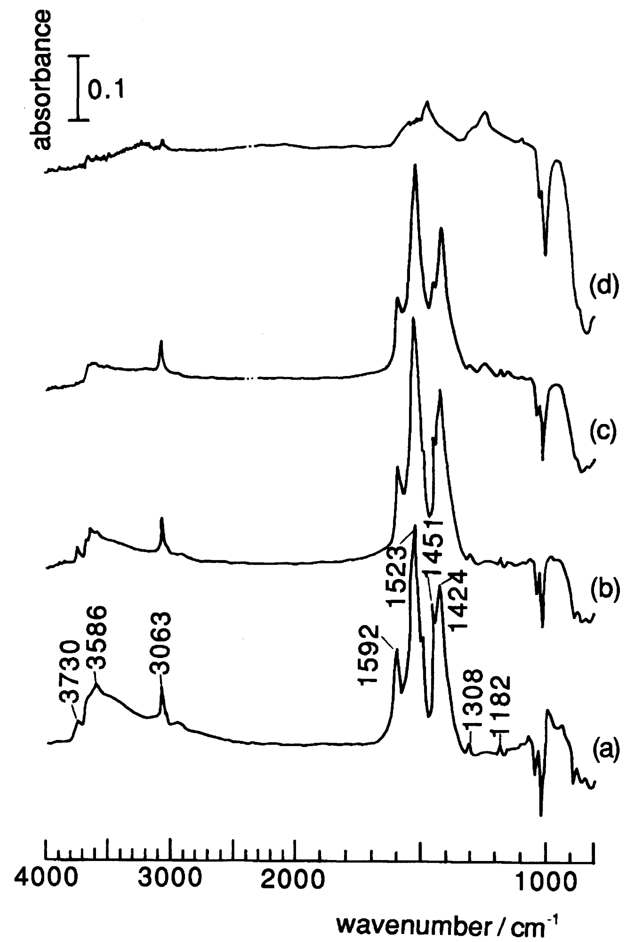


Fig. 1. FT-IR spectra of adsorbed benzoic acid on Cr–ZrO_2 at various temperatures: (a) 473 K, (b) 573 K, (c) 673 K, and (d) 773 K.

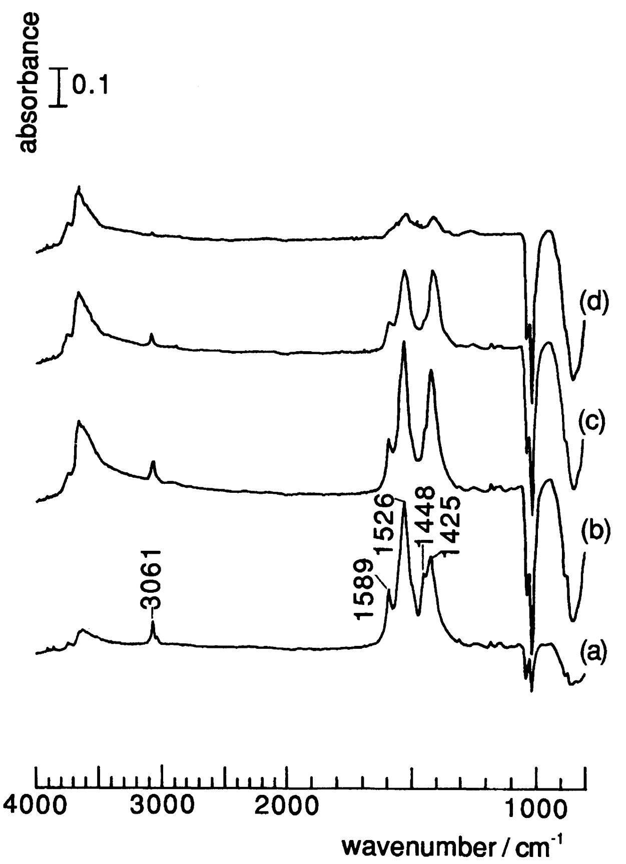


Fig. 2. FT-IR spectra taken during the hydrogenation of benzoate on Cr–ZrO_2 at 623 K: (a) adsorbed benzoate, (b) immediately, (c) 10 min, and (d) 30 min after introduction of H_2 (400 Torr).

3. Adsorption of Benzaldehyde. The reverse reaction from an aldehyde and H_2O to the corresponding carboxylic acid and H_2 was also observed over Cr–ZrO_2.[28] Therefore, the adsorption of benzaldehyde and the transformation on the catalyst were studied by IR spectroscopy. Benzaldehyde was adsorbed on Cr–ZrO_2 and ZrO_2 at about 200 K, followed by evacuation. The sample was then gradually ($2\ \mathrm{K\,s^{-1}}$) heated under evacuation. IR spectra of the adsorbed benzaldehyde on Cr–ZrO_2 are presented in Fig. 4. Heating from 273 K (a) to 373 K (b) caused the disappearance of the bands between 2950 and 2650 $\mathrm{cm^{-1}}$ in the CH stretching region and at 1701, 1311, and 1204 $\mathrm{cm^{-1}}$. These bands were assigned to physically adsorbed benzaldehyde, with reference to the IR and Raman spectra of liquid benzaldehyde[21—26] (see Table 1). The physically adsorbed benzaldehyde desorbed at 373 K.

Above 373 K, several bands at 1681, 1649, and 1219 $\mathrm{cm^{-1}}$ and a weak band in the CH stretching region (ca. 2850 $\mathrm{cm^{-1}}$) decreased. The decrease of these bands in intensity was accompanied by an increase of the bands at 1522 and 1421 $\mathrm{cm^{-1}}$, attributed to the benzoate species; they became dominant at 573 K (d). Since these spectra were taken under evacuation, it is concluded that these bands shown in Fig. 4 (b) were attributed to the precursor species for benzoate formation. Although this intermediate species and the physically adsorbed species coexisted at 273 K, the physically adsorbed species was simply desorbed and did not take part in the production of benzoate.

The structure of the intermediate was then considered based on the observed IR bands. The bands assigned to the intermediate were observed at 3065, 2850, 1681, 1649, 1602, 1582, 1455, 1318, and 1219 $\mathrm{cm^{-1}}$. Among the observed bands, those at 3065, 1602, 1582, 1495, 1455, and 1318 $\mathrm{cm^{-1}}$ are attributed to the absorption bands of the phenyl group (Table 1). Other bands at 2850, 1681, 1649, and 1219 $\mathrm{cm^{-1}}$ are attributed to the aldehyde group. The band at 2850 $\mathrm{cm^{-1}}$ is attributed to the CH stretching mode derived from the CHO group. The bands assigned to aromatic group appear to be sharp, probably due to the absence of a direct interaction with the surface. In Fig. 4, a simultaneous production of the OH species between 3550 and 3600 $\mathrm{cm^{-1}}$ and a decrease in the intermediate were observed. This feature was not observed in case of ZrO_2 in Fig. 5 (discussed below) because of the perturbation

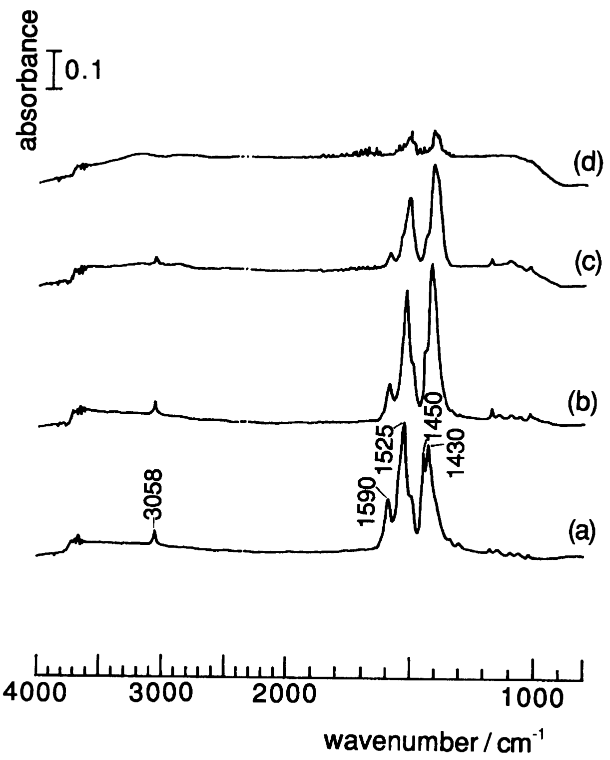
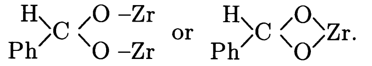


Fig. 3. FT-IR spectra taken during the hydrogenation of benzoate on ZrO_2 at 623 K: (a) adsorbed benzoate, (b) immediately, (c) 30 min, and (d) 120 min after introduction of H_2 (400 Torr).

of the originally existing OH species after a pretreatment. Combining the OH formation and the decrease in the intermediate, it is concluded that the C–H bond of the formyl group in the intermediate species dissociated at the same temperature to the produce benzoate and hydroxyl species. Regarding the structure of the intermediate, the bisoxide species, as described below, is unlikely:


(3)

This is because the bisoxide species should show a strong band due to a CH deformation at between 1200 and 1000 cm^{-1}. Moreover, the IR absorption band of single-bonded C–O should appear at between 1200 and 950 cm^{-1}.[29] Among the absorption bands attributed to the intermediate species, two bands at 1682 and 1649 cm^{-1} are regarded as being the C=O stretching mode based on their peak position. While in the case of free aldehydes, the C=O bands appear at 1700 cm^{-1}, the observed bands appeared in a lower frequency region, suggesting that the C=O bond is weakened via an interaction with the catalyst surface. The slight shift of the C=O stretching band of the intermediate by less than 100 cm^{-1} from physically adsorbed species eliminates the possibility of any resonant structures, such as those proposed in metalloacyls, as described in Eq. 4 or 5.[30]

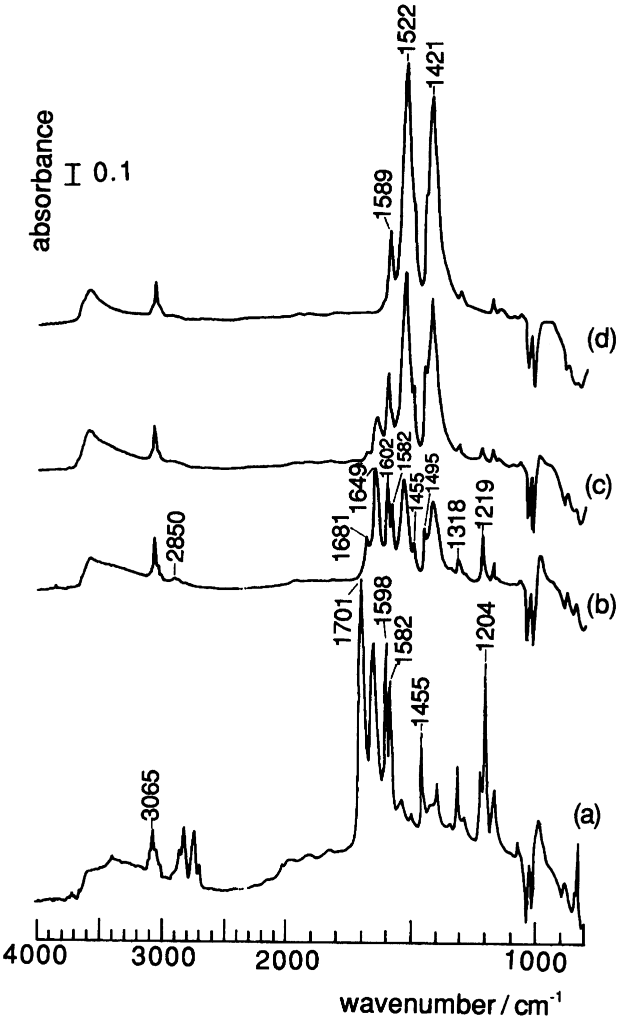
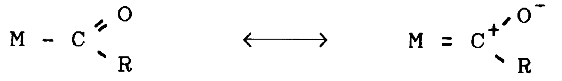
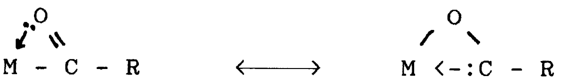
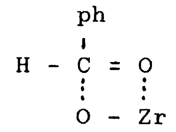


Fig. 4. FT-IR spectra of benzaldehyde adsorbed on Cr–ZrO_2 at various temperatures: (a) 273 K, (b) 373 K, (c) 473 K and (d) 573 K.

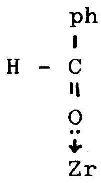

(4)


(5)

In both cases, the C=O stretching bands are shifted by 150—300 cm^{-1} from the free acyl C=O stretching bands. From the observed bands, we therefore propose the structure of the intermediate as follows:


(6)

or


(7)

Taking into account that the intermediate transformed into OH and benzoate with an increase in temperature,

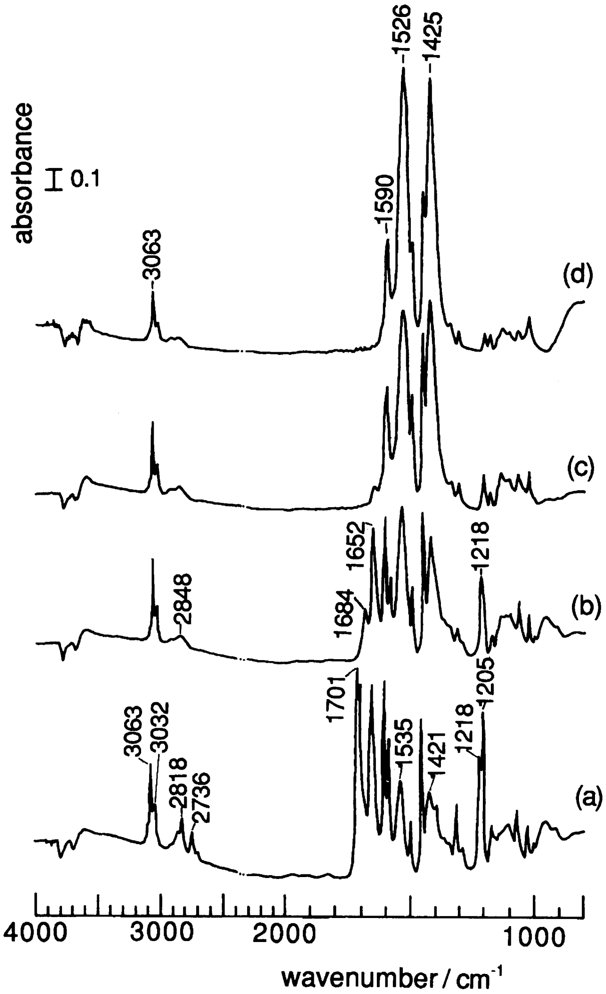


Fig. 5. FT-IR spectra of benzaldehyde adsorbed on ZrO_2 at various temperatures: (a) 273 K, (b) 295 K, (c) 423 K, and (d) 573 K.

structure (6) seems to be preferable. The band at 1218 cm^{-1} is assigned to the ph-C stretching mode.[21—26,29] The appearance of two bands at 1681 and 1649 cm^{-1} may be regarded as being the adsorption of the intermediate species on two different sites.

For a further understanding, the role of the Cr adsorption of aldehyde on ZrO_2 was compared with that on Cr–ZrO_2. Figure 5 shows the IR spectra obtained during the same procedure as those for Fig. 4. At 273 K, the physically adsorbed species and the intermediate were observed. It is also noted that a small amount of the benzoate species (1535 and 1421 cm^{-1}) was already formed at this temperature. The same intermediate as that on Cr–ZrO_2 was observed in Fig. 5 (a) and (b). In addition to the intermediate species (2848, 1684, 1652, and 1218 cm^{-1}), benzoate had already been observed at 295 K. The transformation from the intermediate to the benzoate species was similarly observed on both Cr–ZrO_2 and ZrO_2. The essential property of the catalyst is therefore considered to be based on the nature of ZrO_2. These IR results are in good agreement with the kinetic studies in which the selectivity of benzaldehyde formation is not affected by Cr doping (97% over ZrO_2 and 96% over Cr–ZrO_2 at 623 K), but only conversion is enhanced by Cr from 51 to 98% at 623 K.[1—3]

Summary

It was found that: 1) benzoic acid existed as benzoate species on both ZrO_2 and Cr–ZrO_2; 2) chemisorbed benzaldehyde described as (6) or (7) was formed by benzaldehyde adsorption at low temperature, which was expected to be the intermediate during the catalytic reduction of benzoate species by gaseous H_2; and that 3) the role of the Cr is regarded as being to activate hydrogen, as well as to increase the surface area of the catalyst.

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