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An infrared study of selective hydrogenation of carboxylic acids to corresponding aldehydes over a ZrO_2 catalyst: pivalic acid to 2,2-dimethylpropanal

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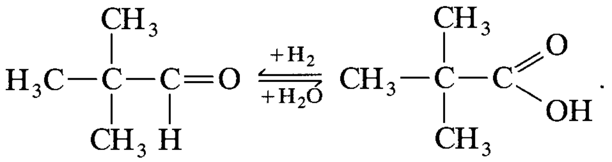
A selective hydrogenation of pivalic acid ($(CH_3)_3C$–COOH) to 2,2-dimethylpropanal ($(CH_3)_3C$–CHO) was studied by infrared spectroscopy. While pivalic acid adsorbed on Cr_2O_3–ZrO_2 as a carboxylate ($(CH_3)_3C$–COO^-) above 303 K and decomposed at 773 K, it was reduced by H_2 at 623 K. The adsorbed aldehyde changed into the carboxylic acid ion species above 523 K via several intermediate species observed below 303 K.

Keywords: ZrO_2; IR spectroscopy; direct reduction

1. Introduction

The selective formation of aldehydes from the corresponding carboxylic acids by H_2 reduction is one of the useful reaction pathways for aldehyde synthesis. Recently, this reaction was achieved as an industrial process by using a modified ZrO_2 catalyst [1–3]. In this process various carboxylic acids are selectively hydrogenated into aldehydes under relatively mild conditions. For example, 2,2-dimethylpropanal (DMP) is produced from 2,2-dimethylpropionic acid (or so called pivalic acid (PA)) and H_2 at 523–673 K with 97% conversion and 99% selectivity [1]. It is noted that further reduction of DMP to the corresponding alcohol is negligible under these reaction conditions. Therefore, it is an interesting subject to examine the structure and the reactivity of the adsorbed species of relevant compounds by infrared spectroscopy. Although there are several reports on hydrogenation mechanisms of small molecules over ZrO_2 [4–18], more complex molecules such as pivalic acid are scarcely studied over modified ZrO_2.

Both ZrO_2 and Cr_2O_3–ZrO_2 (Cr/Zr = 5/100, atomic ratio) show almost the same activity for aldehyde production from carboxylic acids. In this study adsorption and reaction of PA and DMP on Cr_2O_3–ZrO_2 was studied by means of Fourier-transform infrared (FT-IR) spectroscopy in order to reveal the selective reduction mechanism of carboxylic acids to aldehydes over a ZrO_2 catalyst:



$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\underset{H}{C}=O \underset{+H_2O}{\overset{+H_2}{\rightleftharpoons}} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-C\begin{matrix}=O\\ -OH\end{matrix} .$$

2. Experimental

A closed gas circulation system, which is connected to a quartz IR cell, was used. Temperature control of the sample was possible between 100 and 1200 K by using a stainless steel tube for liquid N_2 and an electronic heater equipped around the cell. A Cr_2O_3–ZrO_2 (Cr/Zr = 5/100, atomic ratio) sample was prepared by impregnation of zirconyl hydroxide ($ZrO(OH)_2$) with chromic nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$) and calcination in air at 873 K for 3 h. About 20–30 mg of the sample was pressed into an IR disc of 20 mm in diameter and was placed in the center of the IR cell. Spectra were recorded on a Jasco 7300 FT-IR with a MCT detector at 4 cm^{-1} resolution. Pretreatment of a disc was performed first by O_2 at 773 K overnight followed by evacuation at the same temperature for 30 min. Pivalic acid (Wako Pure Chemical Industries, Ltd. 98 + %) and 2,2-dimethylaldehyde (Wako Pure Chemical Industries, Ltd. 97%) were adsorbed at about 143 K, and spectra were recorded during the warming procedure (2 K s^{-1}). All the spectra of adsorbed species were obtained by taking the ratio of the spectra containing ZrO_2 and adsorbed species and the spectra of ZrO_2 taken at the same temperatures. Hydrogenation of adsorbed pivalic acid was performed by introducing 400 Torr of H_2 (Toyo Oxygen Company, 99.99% purity) at 623 K.

3. Results and discussion

3.1. ADSORPTION OF PIVALIC ACID (PA)

IR spectra of adsorbed PA at various temperatures are shown in fig. 1. PA was introduced below the sample temperature of 200 K and was evacuated to observe only the adsorbed species. The spectra in fig. 1 were taken during

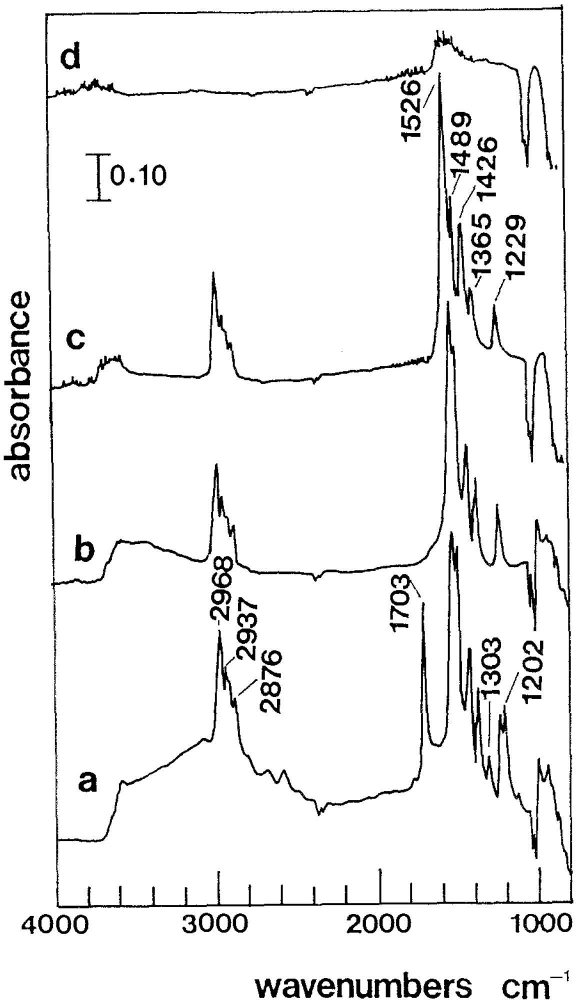


Fig. 1. FT-IR spectra of adsorbed pivalic acid on Cr_2O_3–ZrO_2 at various temperatures; (a) 303 K, (b) 373 K, (c) 673 K and (d) 773 K.

gradual warming procedure in vacuum. At 303 K (a) physically adsorbed PA was observed with the bands at 1703, 1489, 1365, 1303 and 1202 cm^{-1} and in the CH stretching region. The reverse bands between 1100 and 1000 cm^{-1} are assigned to Cr=O stretching modes [19–22]. Another adsorbed species was also observed at 303 K which became obvious at 373 K (b) where the physically adsorbed species was completely desorbed. This species was identified with the bands at 1526, 1489, 1426, 1365 and 1229 cm^{-1} and CH stretching bands. It was stable even at 673 K but disappeared at 773 K. This species is assigned to pivalate ion ($(CH_3)_3C$–COO^-) species which is characterized by intense IR bands at 1526 and 1426 cm^{-1} (asymmetric and symmetric OCO^- stretching bands, respectively) [23–29].

3.2. HYDROGENATION OF PIVALATE ION

The commercial production of DMP from PA and H_2 is performed between 573 and 673 K and at atmospheric pressure [1–3], where pivalate ion is stable on the catalyst surface. Pivalate ion species was formed by introduction of PA and following evacuation at 623 K. Then 400 Torr of H_2 was admitted and circulated through the system at the same sample temperature. The change of the spectra which were taken during the reaction is shown in fig. 2. When pivalate ion existed on Cr_2O_3–ZrO_2 at 673 K under vacuum, it was very stable. On the other hand, when gaseous H_2 existed, decrease of pivalate ion was observed as a function of time. However, only the steady decrease of bands of pivalate ions but no band attributable to the intermediate species was observed during the

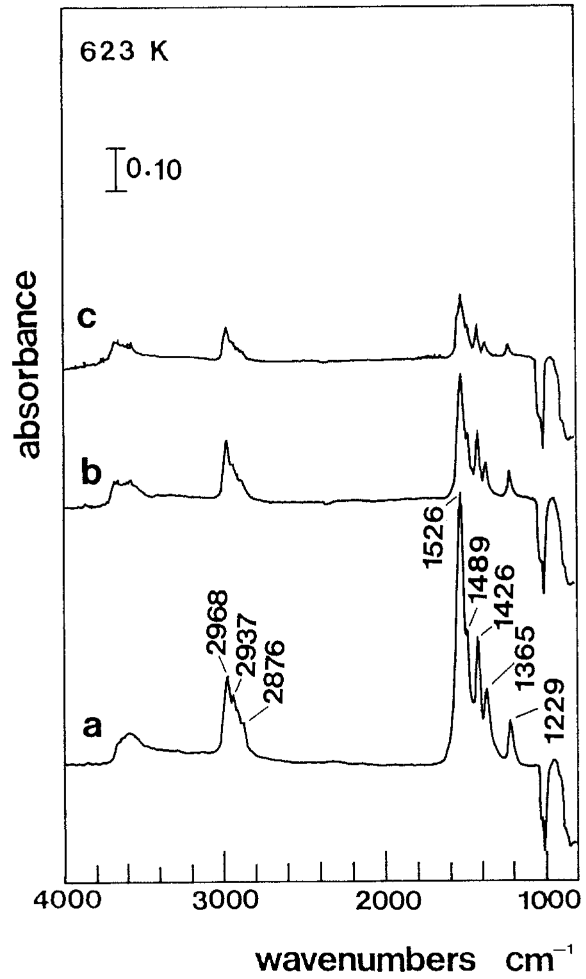


Fig. 2. FT-IR spectra taken during the reaction, $(CH_3)_3C\text{–}COO^-(a)+H_2(g)$ at 623 K; (a) soon after introduction of H_2 (400 Torr) to adsorbed pivalate ion, (b) after 1 h of the reaction and (c) after 3 h.

reaction as shown in fig. 2. Therefore it is considered that the pivalate ion was hydrogenated at 623 K and that produced aldehyde was desorbed rapidly to a gaseous molecule.

3.3. ADSORPTION OF 2,2-DIMETHYLPROPANAL (DMP)

Intermediate species during the reaction were not observed under in situ reaction condition. It is also known that the reverse reaction from aldehydes and H_2O to corresponding carboxylic acids and H_2 proceeds on the used catalyst [20]. Therefore, adsorption of DMP was also studied with the purpose of detecting some unstable intermediate species. DMP was adsorbed at 145 K followed by evacuation at the same temperature. Then the sample was heated gradually. The resulting spectra taken during the heating procedure are shown in figs. 3 and 4. In fig. 3 the IR spectrum of adsorbed DMP at 145 K and that of neat DMP are compared. The CH stretching bands of the $(CH_3)_3C-$ group

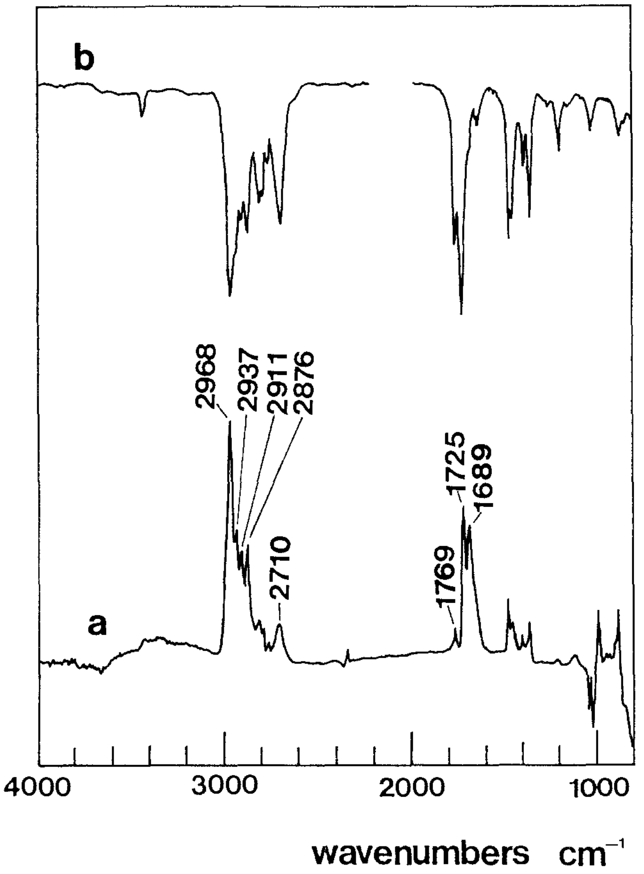


Fig. 3. FT-IR spectra of adsorbed 2,2-dimethylpropanal; (a) neat 2,2-dimethylpropanal and (b) adsorbed species on Cr_2O_3–ZrO_2 at 145 K.

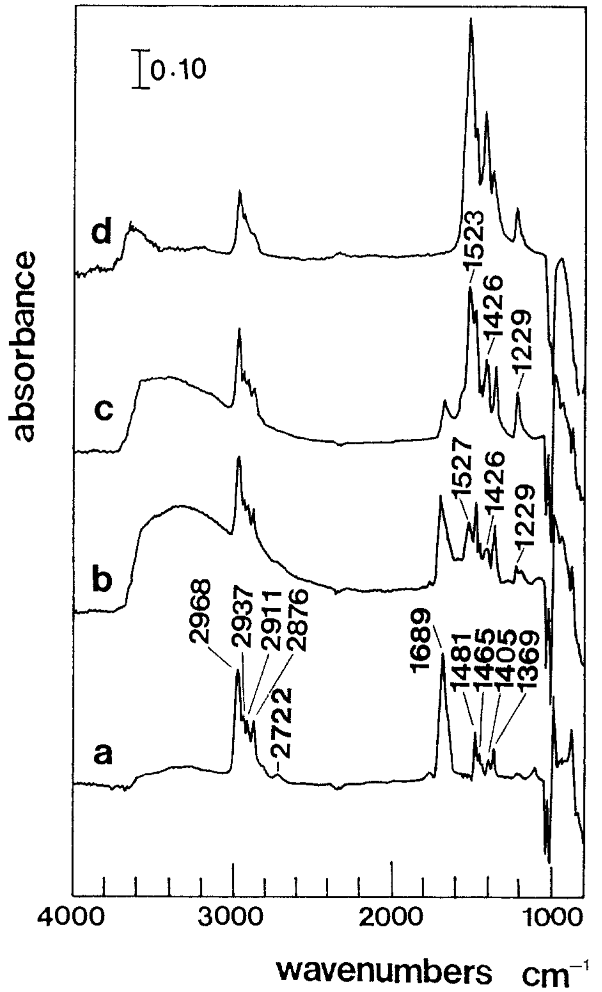
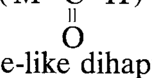
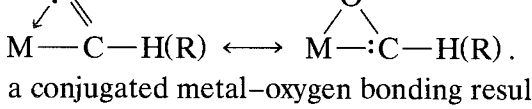


Fig. 4. FT-IR spectra of 2,2-dimethylpropanal adsorbed on Cr_2O_3–ZrO_2 at various temperatures; (a) 173 K, (b) 248 K, (c) 303 K and (d) 673 K.

appear between 3000 and 2850 cm^{-1}, while those of the –CHO group appear below 2850 cm^{-1}. It is noted that, when the two spectra are compared in the CH stretching region, the bands due to the –CHO group were weaker for adsorbed species than for the free molecule. In the C=O stretching region (1800–1600 cm^{-1}) two strong bands were observed at 1769 and 1725 cm^{-1} in fig. 3b. Although the spectral similarity of adsorbed species (fig. 3a) and free molecule (fig. 3b) indicates the existence of physically adsorbed species, an additional strong band was observed at 1689 cm^{-1} in fig. 3a. This band was not found in the spectrum of the free molecule, which suggests the existence of a species other than the physically adsorbed species. When the sample was heated to 173 K, the physically adsorbed species completely disappeared. The disappearance of the physically adsorbed species is confirmed by the disappearance of the characteristic IR bands of aldehyde species at 2710 cm^{-1} (CH stretching) and at 1769 and 1725 cm^{-1} (C=O stretching). At 173 K (fig. 4a) another adsorbed species was still observed with the bands at 2722 cm^{-1} (CH stretching) and 1689 cm^{-1}. This species already existed at 145 K because the band at 1689 cm^{-1} appeared even at 145 K in fig. 3a. The bands assigned to the $(CH_3)_3C-$ group (2800–3000 cm^{-1} and 1350–1500 cm^{-1}) which are common to the physically adsorbed species and the remaining species at 173 K therefore appeared stronger in fig. 3a than the respective bands due to each species. At 248 K a broad band between 3800 and 3000 cm^{-1} assigned to hydrogen-bonded OH group was observed with decrease of the bands due to the adsorbed species at 145 K (2722 and 1689 cm^{-1}) and with appearance of the bands at 1527, 1426 and 1229 cm^{-1}. At 303 K those bands at 1523, 1426 and 1229 cm^{-1} increased in intensity and became dominant at 673 K. The produced species at 673 K is unequivocally assigned to pivalate ion species by the comparison of fig. 4d with fig. 1c. At the same time the species observed at 173 K decreased gradually as the temperature was raised and completely disappeared at 673 K. During the experiment IR spectra were measured under evacuation. Therefore it is considered that the species observed at 173 K transferred to carboxylate ion species. In other words, the species observed at 173 K is regarded as an intermediate species from aldehyde to carboxylate ion species.

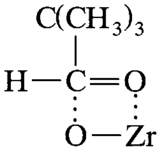
The intermediate species is expected to maintain the CHO group because the CH stretching band was still observed in low frequency region (2722 cm^{-1}) and because increase of OH species due to C–H bond cleavage was not observed. The OH species was formed when this intermediate species changed into pivalate ion as already observed in fig. 4b. The band at 1689 cm^{-1} is regarded as a double bonded C=O stretching band of the –CHO group. The formation of an oxyl species (dioxy-2,2-dimethylpropene) is unlikely because such a species shows CH stretching bands above 2800 cm^{-1} and a strong band due to CH deformation between 1200 and 1000 cm^{-1}. The absorption band of any single bonded C–O should appear between 1200 and 950 cm^{-1} [31].

In transition metal formyl ( $M-\underset{\overset{\|}{O}}{C}-H$) or acyl ( $M-\underset{\overset{\|}{O}}{C}-R$) complexes (M = metal and R = alkyl), a carbene-like dihaptoformyl or dihaptoacyl was proposed [32–35],

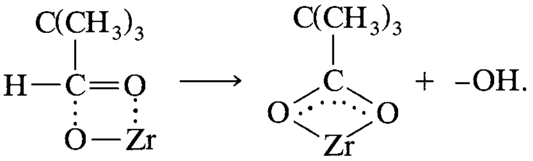


Such a conjugated metal–oxygen bonding results in weakening of the C=O bond. The IR spectra of these compounds exhibit unusually low C–O stretching frequencies for carbonyl compounds. For example C–O stretching bands of acyl Th complexes [33,36] were observed between 1500 and 1460 cm^{-1} and of acyl Zr complexes [32,33] between 1540 and 1510 cm^{-1}. Thus, the observed band of the intermediate species at 1689 cm^{-1} is not considered to be affected by such a resonant structure.

The intermediate species is then postulated to adsorb on the Zr–O site by oxygen interacting with Zr and by carbon interacting with O:



This structure is supported by the fact that the intermediate species changed into pivalate ion and OH species upon heating,



As mentioned above, the reverse reaction, DMP and H_2O to PA and H_2 was observed. Therefore this intermediate species is proposed to be a possible intermediate species of the catalytic reduction of PA to DMP. The role of Cr_2O_3 in the catalyst will be discussed elsewhere [37].

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