[Regular Paper]

Hydrogenation of Dicarboxylic Acid Diesters to Corresponding Dialdehydes over ZrO2 Based Catalysts (Part 2) Analysis of Catalyst Surface Using Diffuse Reflectance FT-IR and CP/MAS ^{13}C-NMR Spectroscopy

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The adsorption species on ZrO2 or Cr–ZrO2 catalyst in the hydrogenation of dimethyl benzenedicarboxylates as well as benzoic acid were characterized by diffuse reflectance FT-IR and CP/MAS ^{13}C-NMR spectroscopy. Benzoic acid and dimethyl terephthalate were adsorbed as the monocarboxylate species with weak bonding to the catalyst with lower polarization at a carbonyl group similar to that of free benzoic acid. In contrast, dimethyl phthalate was adsorbed only as the dicarboxylate species. Dimethyl isophthalate was adsorbed as both mono- and dicarboxylic species. Formation of dicarboxylate adsorption species will greatly hinder the hydrogenation of dimethyl benzenedicarboxylates. In addition, the methoxycarbonyl group was more favorable for the adsorption to form the carboxylic active species than the formyl group in the interaction of Cr–ZrO2 catalyst with terephthalaldehydic acid methyl ester. A reaction mechanism for the hydrogenation is also proposed.

1. Introduction

Aldehydes are widely recognized as important chemicals in the pharmaceutical, agricultural and fragrance industries[1~3]. We previously established a synthesis method for aldehydes by the direct hydrogenation of the corresponding monobasic carboxylic acids in the vapor phase catalyzed by ZrO2 or Cr2O3. Separately, we reported further application of the hydrogenation process for the production of various dialdehydes from dibasic carboxylic acid diesters under almost the same conditions[4]. The reactivity of the three isomers of dimethyl benzenedicarboxylic acids toward the hydrogenation are quite different. Hydrogenation of dimethyl terephthalate gave mono- and dialdehydes with high selectivity. However, hydrogenation of dimethyl phthalate gave no aldehydic products. Our attempts to explain this reactivity with the pKa values or Hammet's σ value, which represents the degree of polarization at the carboxyl group of the isomers, have failed (for example, pKa$_1$ = 3.54, pKa$_2$ = 4.46, Hammet's σ value = 0.45 for terephthalic acid, pKa$_1$ = 3.70, pKa$_2$ = 4.60, σ value = 0.37 for isophthalic acid).

The adsorption species on metal oxide catalysts in the hydrogenation of monocarboxylic acid have been characterized with fourier transform infrared spectrometer (FT-IR) spectroscopy[5~8]. We found that the adsorbed species on ZrO2 catalyst in the hydrogenation of benzoic acid is the benzoate species, which weakly interacts with the catalyst surface, and catalytic hydrogenation of adsorbed benzoate liberates benzaldehyde[6]. Therefore, the absorbed benzoate species is a key intermediate in the hydrogenation. Few spectroscopic investigations of the catalyst surface in the hydrogenation of dibasic carboxylic acids or diesters are available, although understanding the reaction mechanism will provide useful information for the development of an effective hydrogenation catalyst.

Here we report the spectroscopic analysis of the adsorption species in the hydrogenation of dimethyl benzenedicarboxylates as well as benzoic acid on the ZrO2 or Cr–ZrO2 catalyst using diffuse reflectance FT-IR and CP/MAS ^{13}C-NMR (nuclear magnetic resonance) spectroscopy, which provide more accurate characterization of organic species adsorbed on a solid catalyst[9~15]. A reaction mechanism for the hydrogenation of dimethyl benzenedicarboxylates is also proposed.

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Table 1 Conditions of CP/MAS ^{13}C-NMR Measurement

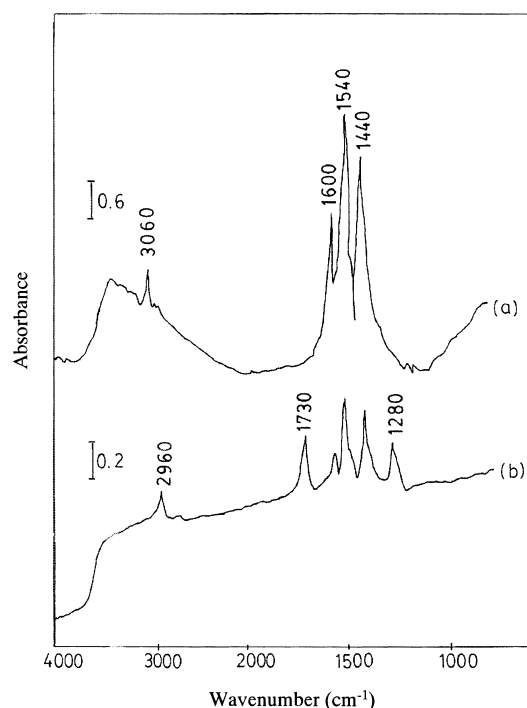|		Adsorbed species	
		Benzoic acid	Dimethyl benzenedicarboxylates
Resonance frequency	[MHz]	50	50
^{1}H $\pi/2$ pulse	[ms]	3.9	4.2
Contact time	[ms]	2	2
Waiting periods		5	5
Number of scans		10,000	10,000
Spinning gas		nitrogen	nitrogen
Spring rate	[kHz]	4.5	4.5

2. Experimental

The apparatus, the catalyst preparation and the experimental procedure of the hydrogenation adopted in this study were essentially the same as those described previously[4]. The used catalyst was prepared as follows. After hydrogenation of benzenedicarboxylic acid esters by ZrO$_2$ or Cr–ZrO$_2$ catalyst at 350°C for 5 h, the catalyst was stood at the same temperature for 1 h under nitrogen flow instead of hydrogen and gaseous ester flow to remove the physical adsorption species, followed by slow cooling to room temperature. Diffuse reflectance FT-IR measurement of the adsorption species on the used catalyst was performed with a Nicolet 740FT-IR. The used catalyst was pulverized and diluted with silicone powder to 10 wt% before the measurement. CP/MAS ^{13}C-NMR spectra of the adsorption species on the used catalyst surface were obtained with a JEOL FX 2000. The measurement conditions are summarized in **Table 1**.

3. Results and Discussion

3. 1. Observation of Adsorbed Species of Benzoic Acid

We first attempted to observe the known benzoate adsorption species in the hydrogenation of benzoic acid to benzaldehyde on ZrO$_2$ catalyst by FT-IR and solid state ^{13}C-NMR. Previous studies have already revealed that the adsorbed benzoate anion on Y$_2$O$_3$/Al$_2$O$_3$[5] and ZrO$_2$[6,7] catalysts is the active species in the hydrogenation of benzoic acid to benzaldehyde based on only IR spectroscopy.

The IR spectrum of the benzoate anion adsorbed on the ZrO$_2$ catalyst is shown in **Fig. 1**(a). The two strong absorption bands at 1540 cm^{-1} and 1440 cm^{-1} are assigned to the OCO asymmetric and symmetric stretching modes of the adsorbed bidentate benzoate species bound to the catalyst as described in Eq. (1). The peak at 1600 cm^{-1} is attributed to the aromatic ring. These results agree well with those of our previous report[7].

(a) adsorption benzoic acid and (b) adsorption dimethyl phthalate.

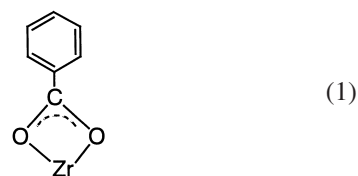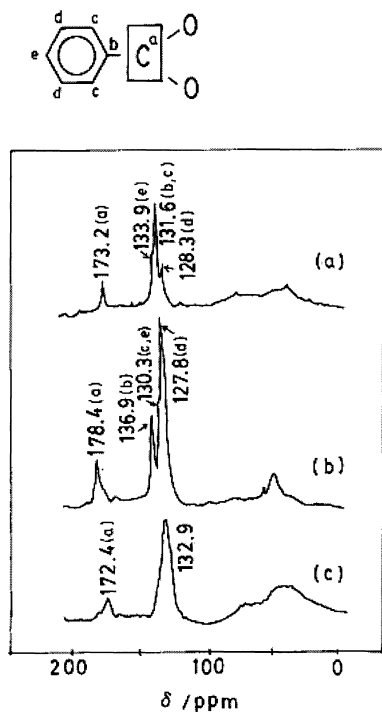Fig. 1 FT-IR Spectra of Adsorption Species on ZrO$_2$ Catalyst

(1)

Figure 2 shows the CP/MAS ^{13}C-NMR spectrum of the benzoic acid (c) adsorbed on the ZrO$_2$ catalyst together with that of benzoic acid (a) and sodium benzoate (b) for comparison. The broadened signal of the C=O carbon atom of benzoate anion adsorbed on the ZrO$_2$ catalyst appeared at 172.4 ppm, which is very close to that of free benzoic acid (173.2 ppm), but not to that of ionic sodium benzoate (178.4 ppm). Therefore, the electron density around the C=O carbon atom of adsorbed benzoate species is similar to that of

(a) benzoic acid, (b) sodium benzoate and (c) adsorption benzoic acid.

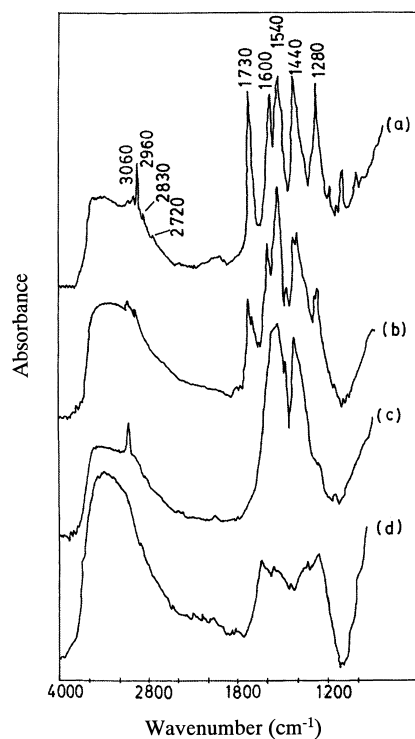Fig. 2　^{13}C-NMR Spectra of Adsorption Species on ZrO$_2$

(a) adsorption dimethyl terephthalate, (b) adsorption dimethyl isophthalate and (c) adsorption dimetyl phthalate; (d) Cr–ZrO$_2$ after H$_2$ reduction at 350°C (background).

Fig. 3　FT-IR Spectra of Adsorption Species on the Cr–ZrO$_2$

free benzoic acid. The peak broadening may be caused by the diverse chemical environments around the adsorbed benzoate. Unfortunately, poor resolution in the region of aromatic carbons prevents further analysis of the benzene ring.

The IR analysis indicated that benzoic acid is adsorbed on the ZrO$_2$ catalyst as the known bidentate benzoate, whereas the ^{13}C-NMR spectrum suggests that polarization of carboxylate anion of the benzoate is not so large, so the adsorbed benzoate will weakly interact with the catalyst. The species weakly adsorbed on the catalyst, among the various types of adsorption benzoate species, is the active species converted into benzaldehyde[7].

3. 2. Determination of Adsorbed Species of Dimethyl Benzenedicarboxylates

Next we tried to observe the catalyst surface used in the hydrogenation of dimethyl benzenedicarboxylates in a similar manner. The FT-IR spectra of the adsorption species on the Cr–ZrO$_2$ catalyst used in the hydrogenation of each isomers of dimethyl benzenedicarboxylate are shown in **Fig. 3**. We previously found that Cr-modified ZrO$_2$ catalyst hydrogenates benzoic acid to benzaldehyde more efficiently than pure ZrO$_2$, because of the considerable enlargement of surface area of the Cr–ZrO$_2$ catalyst and suppression of coke generation to avoid deactivation of the catalyst[6]. The strong absorption peaks arising from C=O and C–O stretching of the ester group of dimethyl terephthalate appeared at 1730 cm^{-1} and 1280 cm^{-1} (**Fig. 3**(a)). Two other strong peaks at 1540 cm^{-1} and 1440 cm^{-1} were assigned to the asymmetric and symmetric OCO stretching modes of the carboxylate anion species adsorbed on the catalyst, similar to those of the adsorbed benzoate as described above. The weak shoulder peak at 2720 cm^{-1} was assigned to an aldehydic C–H stretching mode, indicating formation of a small amount of aldehydes. The two peaks observed at 2830 cm^{-1} and 2960 cm^{-1} are characteristic of the methoxy group directly bound to the catalyst surface[16]. These results indicate that dimethyl terephthalate is adsorbed on the catalyst surface as monocarboxylate anions with an ester or formyl group at the *para* position of the benzene ring as shown in Eq. (2). The surface methoxy group is formed simultaneously by dissociative adsorption of the methoxycarbonyl group of dimethyl terephthalate onto the catalyst.


(2)
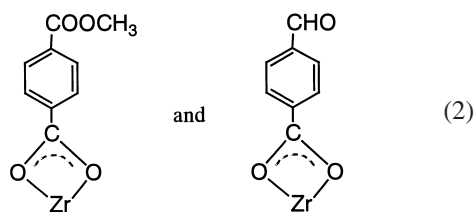
The strong peaks of the adsorbed carboxylate species of dimethyl isophthalate were also observed at 1540 cm^{-1} and 1440 cm^{-1} (**Fig. 3**(b)). However, the absorption of the ester group at 1730 cm^{-1} and 1280 cm^{-1} was somewhat weaker than that of dimethyl terephthalate and no peaks due to aldehydic C–H stretching were observed at around 2720 cm^{-1}. These results suggest that dimethyl isophthalate is adsorbed on the Cr–ZrO$_2$ catalyst as both mono- and dicarboxylate species as shown in Eq. (3).

$$(3)$$
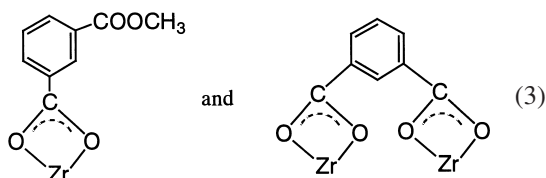
In contrast, only the absorption peaks of adsorbed carboxylate species on the catalyst pretreated with dimethyl phthalate were observed (**Fig. 3**(c)). No peaks due to the free ester group at 1730 cm^{-1} and 1280 cm^{-1} appeared at all. Therefore, dimethyl phthalate is adsorbed on the catalyst surface only as dicarboxylate species (Eq. (4)).

$$(4)$$
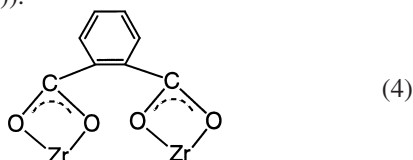
Both ester and formyl groups are adsorbed on the catalyst to form carboxylate species under hydrogenation conditions. Adsorption of benzaldehyde on ZrO$_2$ catalyst forms the same carboxylate anion species as benzoic acid[7]. To compare the reactivity of these two groups toward adsorption, we tried to observe the adsorption species in the hydrogenation of terephthalaldehydic acid methyl ester. **Figure 4**(a) shows the FT-IR spectra of Cr–ZrO$_2$ catalyst reacted with terephthalaldehydic acid methyl ester. Absorption peaks due to the adsorbed carboxylate species (at 1540 cm^{-1} and 1440 cm^{-1}) and the ester or formyl groups (overlapping at 1730 cm^{-1} and 1280 cm^{-1}) were detected. The aldehydic C–H absorption at 2720 cm^{-1} appeared stronger than that of dimethyl terephthalate shown in **Fig. 4**(b). These results indicate that absorption of the ester group on the Cr–ZrO$_2$ catalyst dominates adsorption of the formyl group and so most terephthalaldehydic acid methyl ester is adsorbed on the catalyst as shown in Eq. (5). Presumably greater polarization of the carbon atom of the ester group allowed easier adsorption onto the catalyst despite the larger steric hindrance.
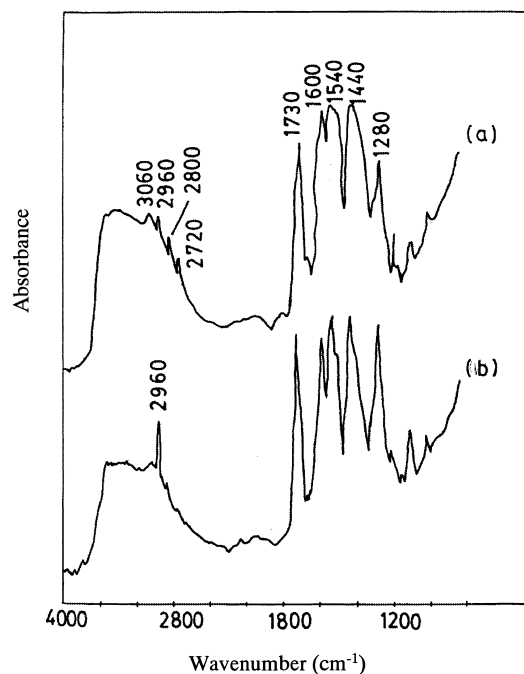
(a) adsorption terephthalaldehydic acid methyl ester and (b) adsorption dimethyl terephthalate.

Fig. 4 FT-IR Spectra of Adsorption Species on the Cr–ZrO$_2$

$$(5)$$
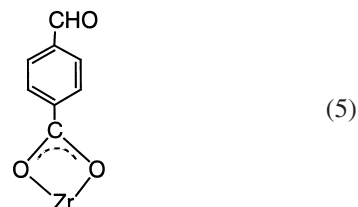
Furthermore, we investigated the solid state NMR analysis of adsorption species derived from the benzenedicarboxylic acid dimethyl esters. In this study, ZrO$_2$ catalyst was employed instead of Cr–ZrO$_2$ because of the paramagnetic character of the Cr atom. The CP/MAS ^{13}C-NMR spectra of adsorption species of dimethyl terephthalate (b) and dimethyl phthalate (c) are presented in **Fig. 5** together with the spectra of solid state dimethyl terephthalate (a) and disodium phthalate (d). Remarkably, the signal of the C=O carbon of free dimethyl terephthalate (166.5 ppm, **Fig. 5**(a)) was split into two peaks (173.0 ppm and 165.2 ppm, **Fig. 5**(b)) after absorption on the catalyst. The signals at 165.2 ppm and 49.5 ppm indicate the presence of free methoxycarbonyl group and the signal at 173.0 ppm was assigned to the COO carbon of the adsorbed carboxylate species (**Fig. 5**(b)). The latter signal is very close to that of adsorbed benzoate (172.9 ppm, **Fig. 2**(c)). These results are in good accordance with those of FT-IR and suggests that one of the two ester groups of dimethyl terephthalate was adsorbed on the catalyst as the monobenzoate anion whereas the
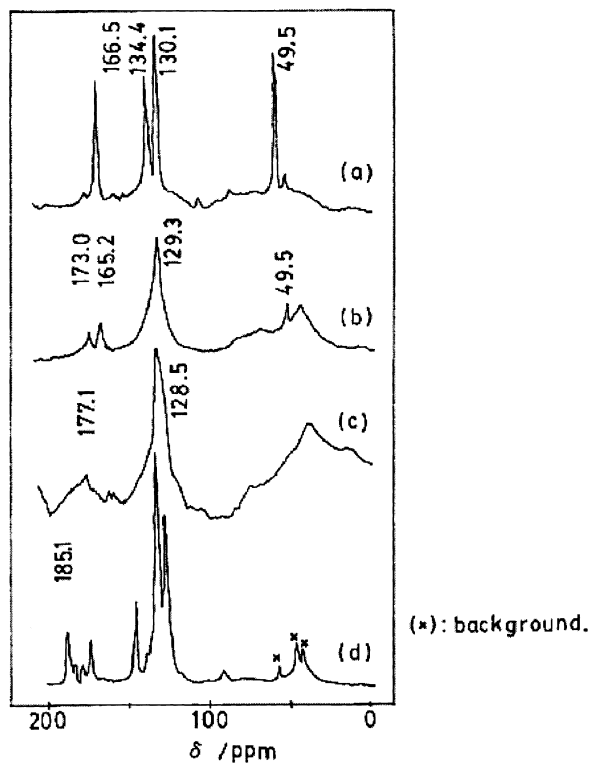
(a) dimethyl terephthalate, (b) adsorption dimethyl terephthalate,
(c) adsorption dimethyl phthalate and (d) disodium phthalate.

Fig. 5　¹³C-NMR Spectra of Adsorption Species on ZrO₂

other ester group at the para position did not interact.

In the case of dimethyl phthalate, no signals of the ester group were observed, and the C=O carbon signal assigned to the adsorbed carboxylate species observed at 177.1 ppm had shifted downfield as compared with that of terephthalate and was somewhat closer to that of disodium phthalate (185.1 ppm). This result suggests that dimethyl phthalate was adsorbed dissociatively onto the ZrO₂ catalyst as a dicarboxylate species, which is highly polarized with strong interaction with the catalyst surface adequate to hinder the hydrogenolysis[17)~19)].

3. 3. Reaction Mechanisms of Dimethyl Benzene-dicarboxylates

We recently reported the reactivity of dimethyl benzenedicarboxylates toward hydrogenation as follows[4)]. Dimethyl terephthalate was hydrogenated to yield the corresponding mono- and dialdehydes, and dimethyl isophthalate gave mono- and dialdehydes with lower selectivity, but dimethyl phthalate yielded no aldehydes at all. The different reactivities of these three isomers of dimethyl benzendicarboxylates may depend on the steric hindrance of the two methoxycarbonyl groups and/or the different adsorption mechanisms of the intermediates affecting catalyst activity. Our present results support the latter reason.

Dimethyl terephthalate was adsorbed onto ZrO₂ or

Cr–ZrO₂ catalyst only as the monocarboxylate which *weakly* interacts with the catalyst and easily reacts further with hydrogen to release aldehyde. Dimethyl terephthalate could form the dicarboxylate absorption species but the IR and NMR analyses provided evidence of exclusive formation of the monocarboxylate species. The reason may be mismatching between the separation of the two carboxyl carbons of terephthalate anion and that of Lewis acid sites on the catalyst or the steric or electronic repulsion between the benzene ring and the catalyst surface. The reactivity of alicyclic dimethyl 1,4-dicyclohexanedicarboxylate was similar to that of dimethyl terephthalate[4)].

In contrast, dimethyl phthalate was adsorbed only as the dicarboxylate, binding strongly to the catalyst with two carboxylate groups. If one of the two ester groups of dimethyl phthalate is adsorbed on a Lewis acid site (Zr⁴⁺) on the ZrO₂ to generate the monocarboxylate species, the other ester group located close to the ZrO₂ surface will immediately interact with another vacant Lewis acid site to form the dicarboxylate species to hinder the hydrogenation. The downfield shift of carbonyl carbon observed by solid state ¹³C-NMR showed that the electron density of the adsorbed dicarboxylate will be closer to that of disodium phthalate which cannot be hydrogenated into aldehydes. Some basic metal oxides such as MgO cannot catalyze the hydrogenation of benzoic acid to benzaldehyde because of the collapse of the MgO catalyst by neutralization forming magnesium benzoate powder[6)]. In addition, the initial interaction of the two ester groups of dimethyl phthalate with the Zr⁴⁺ site will induce localization of positive charge at the carboxyl carbons to facilitate demethoxycarbonylation on the catalyst to form the dicarboxylate adsorption species.

Similar reactivities of benzenedicarboxylates in heterogeneous catalytic reactions have been reported. Although terephthalic acid can be converted into the corresponding monoester or *p*-hydroxybenzaldehyde by selective monoesterification or hydrogenation *via* the monocarboxylate intermediate adsorbed on the alumina catalyst[15)], phthalic acid is adsorbed on the catalyst with two vicinal carboxylate groups to deactivate the catalyst and to hinder further reactions[20)].

The proposed reaction mechanism for the hydrogenation of dimethyl benzenedicarboxylates is illustrated in **Scheme 1**, as we previously suggested for the hydrogenation of benzoic acid[6)]. Dimethyl terephthalate is hydrogenated to give mono- and dialdehydes *via* the pathway shown in the upper part of **Scheme 1**. One of the two ester groups of dimethyl terephthalate is adsorbed dissociatively on ZrO₂ to generate the monocarboxylate active species and the surface methoxy group. After the rate-determining dissociative adsorption of hydrogen onto the ZrO₂ catalyst[21),22)], the adsorbed monocarboxylate species is hydrogenated to
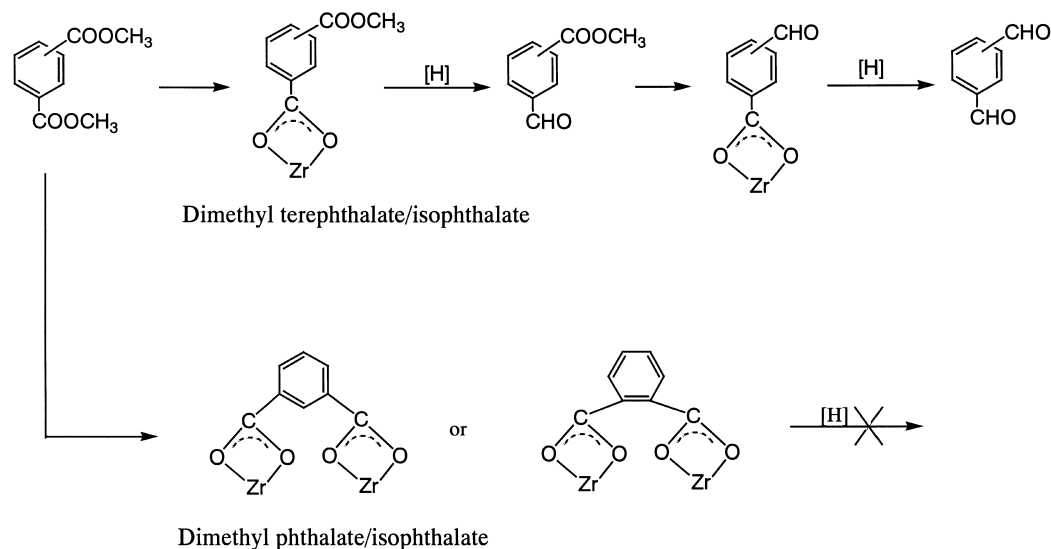
Scheme 1 Proposed Reaction Mechanism

liberate the corresponding aldehyde. The other ester group of the monoaldehyde remaining unreacted can then be hydrogenated to give the dialdehyde. The surface methoxy species generated simultaneously by the dissociative adsorption of the ester group onto the catalyst will be also hydrogenated to methanol and will be partially decomposed to carbon monoxide and methane. On the other hand, dimethyl phthalate reacts with ZrO_2 catalyst *via* the other pathway shown in the lower part of **Scheme 1**. Dimethyl phthalate is adsorbed only as the dicarboxylate with strong binding to the catalyst resulting in retardation of the catalyst activity. Dimethyl isophthalate can react *via* both pathways so that the aldehyde selectivity is lower than that of dimethyl terephthalate. However, the exact features of hydrogen activation on ZrO_2 catalyst in the hydrogenation reaction still remain unclear.

4. Conclusion

The adsorption species on ZrO_2 or $Cr–ZrO_2$ catalyst in the hydrogenation of dimethyl benzenedicarboxy-lates were analyzed by diffuse reflectance FT-IR and CP/MAS ^{13}C-NMR spectroscopy. Dimethyl terephthalate was adsorbed on the catalyst to form the mono-carboxylate species binding weakly to the catalyst. Dimethyl phthalate was adsorbed only as the dicar-boxylate species interacting strongly with the catalyst. Dimethyl isophthalate was absorbed to form both mono- and dicarboxylates. The hydrogenation of dimethyl terephthalate proceeds *via* stepwise reduction of the ester group to form terephthalaldehydic acid methyl ester and terephthalaldehyde. Spectroscopic observations also suggest that the absence of formation of aldehydes in the hydrogenation of dimethyl phtha-late can be attributed to occupation of the active sites on the catalyst surface by dicarboxylate species. In addition, the methoxycarbonyl group was more favor-able than the formyl group for adsorption onto the $Cr–ZrO_2$ catalyst to form the carboxylic active species.

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要　　旨

ZrO₂ 触媒によるジカルボン酸ジエステル類のジアルデヒドへの水素化反応（第 2 報）拡散反射 FT-IR および CP/MAS ¹³C NMR による触媒表面解析

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　ZrO₂ 触媒によるベンゼンジカルボン酸ジエステル類の水素化反応では，テレフタル酸およびイソフタル酸ジエステル類は対応するモノおよびジアルデヒドに変換された。しかし，フタル酸ジメチルはアルデヒド類を与えなかった。この理由を明らかにするため，拡散反射法 FT-IR および CP/MAS ¹³C-NMR による触媒表面吸着種の解析を行った。その結果，テレフタル酸ジメチルからはモノカルボキシレート吸着種が主に観察された。一方，フタル酸ジメチルではジカルボキシレート吸着種のみが触媒表面上に存在した。イソフタル酸ジメチルの場合では，モノおよびジカルボキシレート種の両方の存在が示唆された。このジカルボキシレート型吸着種が生成することにより触媒活性が低下し，本水素化反応のアルデヒド選択性が低下するものと推定した。また，テレフタル酸ジメチルの水素化における中間生成物であるテレフタルアルデヒド酸メチルを触媒に作用させると，メチルエステル基がアルデヒド基に優先して触媒に吸着することが分かった。

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