

[Regular Paper]

Hydrogenation of Dicarboxylic Acid Diesters to Corresponding Dialdehydes over ZrO₂ Based Catalysts (Part 1) Reactivity of Various Dicarboxylic Acid Diesters

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Dimethyl terephthalate was hydrogenated over ZrO₂ catalyst in the vapor phase to form terephthalaldehydic acid methyl ester and terephthalaldehyde as the major products. The reactivity of the three regioisomers of benzenedicarboxylic acid dimethyl esters to hydrogenation was in the order, terephthalic > isophthalic >> phthalic. The low reactivity of dimethyl phthalate is probably due to the mutual steric hindrance of the two vicinal methoxycarbonyl groups and to catalyst deactivation caused by strong adsorption of the intermediates of dimethyl phthalate on the catalyst surface. Formation of terephthalaldehyde by hydrogenation of terephthalaldehydic acid methyl ester suggested that the hydrogenation reaction of dibasic acid diesters proceeds *via* successive reduction of the ester groups to formyl groups. Alicyclic acid diester dimethyl 1,4-cyclohexanedicarboxylate was also converted into the corresponding mono- and dialdehyde in a similar way. However, aliphatic dibasic acid esters such as dimethyl glutarate and dimethyl adipate were not hydrogenated at all. Modification of ZrO₂ by Cr, In or Zn improved the catalyst activity. Maximum dialdehyde selectivity in the hydrogenation of terephthalaldehydic acid methyl ester reached 72.4% by using Zn modified ZrO₂ catalyst (atomic ratio Zn/Zr = 5/100).

Keywords

Diester, Hydrogenation, Dialdehyde, Zirconia catalyst, Modified zirconia

1. Introduction

Aldehydes are important in both bulk and fine chemical industries and are also key intermediates in the production of compounds with specific structures such as medicines, pesticides and electronic materials^{1)–3)}. Aldehydes can be obtained by several known methods: oxidation of the methyl group attached to an aromatic ring, catalytic hydrogenation of acid chlorides (Rosenmund reduction), and partial oxidation of primary alcohols³⁾. However, these methods also have some disadvantages: necessity for severe reaction conditions, prior preparation of organic halides, requirement of addition of a base or an oxidizing agent, low yields, poor quality, and large amount of waste products.

The development of new “greener” processes has received much attention for the more rational production of organic intermediates using heterogeneous catalysts. We have already succeeded in the development and commercialization of a novel process of aldehyde production based on the direct hydrogenation of carboxylic acids in the vapor phase with Cr–ZrO₂ and

Cr₂O₃ catalysts as shown in Eq. (1)^{4)–6)}. This direct hydrogenation process generates only water as a byproduct and is widely applicable to various types of *monobasic* carboxylic acids, aromatic, alicyclic, aliphatic and even unsaturated aliphatic carboxylic acids, such as 10-undecenoic acid which is converted selectively into 10-undecenal without hydrogenation or migration of the terminal carbon–carbon double bond⁷⁾.



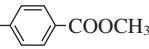
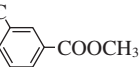
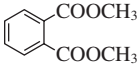
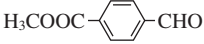
Recently, the liquid-phase direct hydrogenation of carboxylic acids into the corresponding aldehydes was catalyzed by a palladium–phosphane complex in the presence of excess pivalic anhydride⁸⁾. This hydrogenation requires lower reaction temperature but higher hydrogen pressure than our process and can be considered complementary to our hydrogenation process.

We attempted further extension of our hydrogenation process to various *dibasic* carboxylic acid diesters to produce the corresponding monoaldehydes and/or dialdehydes. Only a few methods of hydrogenation of dibasic carboxylic acids or derivatives (acid chlorides, anhydrides and esters) into dialdehydes have been developed. Here we report the range and limitations

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Table 1 Hydrogenation of Aromatic Carboxylic Di- and Monoesters over ZrO₂ and Cr-ZrO₂ Catalyst^{a)}

Substrate	Catalyst	Temperature [°C]	Conversion [%]	Selectivity [%] ^{b)}			
				monoaldehyde	dialdehyde	de-COOCH ₃	phthalide
	ZrO ₂	350	21.6	83.0	13.6	3.4	—
		370	38.5	78.7	13.2	8.1	—
	Cr-ZrO ₂	350	48.6	68.2	14.4	3.7	—
	Cr-ZrO ₂	350	18.4	49.6	6.0	16.7	—
	ZrO ₂	370	50.5	0	0	33.9	55.1
	Cr-ZrO ₂	350	28.7	0	0	23.0	10.0
	ZrO ₂	350	18.1	—	62.5	18.0	—
		370	32.1	—	55.6	25.6	—
	Cr-ZrO ₂	350	42.9	—	61.7	15.8	—

a) Reaction conditions: H₂-GHSV = 1250 h⁻¹, LHSV = 0.22 g·ml·cat.⁻¹·h⁻¹, catalyst volume = 5.0 ml. Calcination temperature: 600°C.

b) Minor byproducts are omitted for clarity.

of the hydrogenation of various types of dibasic carboxylic acid diesters over ZrO₂ or Cr-ZrO₂ catalysts. We also investigated the modification of ZrO₂ catalyst with other metal oxides, the relationship between calcination temperature and catalyst activity, and the determination of the optimal content of additional metal in the modified catalyst.

2. Experimental

2.1. Catalyst Preparation

Zirconia catalyst ZrO₂ was prepared by hydrolysis of ZrOCl₂ in an aqueous solution of NH₄OH to form ZrO(OH)₂ followed by calcination. Modification of ZrO₂ was performed by impregnation of ZrO(OH)₂ with metal nitrate. ZnO was obtained by hydrolysis of Zn(NO₃)₂·6H₂O and further calcination. CeO₂ was prepared by calcination of commercial Ce(OH)₄.

2.2. Hydrogenation

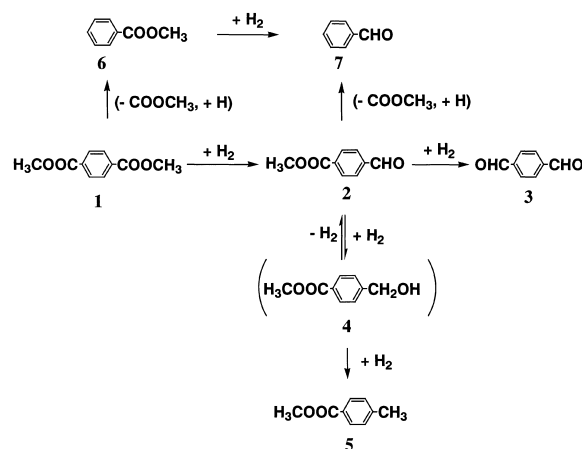
Heterogeneous hydrogenation was performed with a fixed bed reactor consisting of a Pyrex glass tube (19 mm I. D. × 450 mm) filled with 5 ml of the catalyst. The reactant was vaporized by preheating and mixed with hydrogen at atmospheric pressure before introduction to the reactor. The hydrogen flowed through the reactor at H₂-GHSV = 1250 h⁻¹ and reactant at LHSV = 0.22 kg·l·cat.⁻¹·h⁻¹, as standard conditions. The hydrogenation reaction was carried out at 350–380°C. The products were analyzed by gas chromatography (GC).

3. Results and Discussion

3.1. Hydrogenation of Dimethyl Terephthalate

The results of hydrogenation of dimethyl terephthalate **1** and its regioisomers over ZrO₂ or Cr-modified ZrO₂ catalysts are summarized in **Table 1**.

Hydrogenation of dimethyl terephthalate **1** formed



Scheme 1 Possible Reaction Pathways of the Hydrogenation of Dimethyl Terephthalate **1**

terephthalaldehydic acid methyl ester **2** and terephthalaldehyde **3** as the two major products, with *p*-hydroxymethylbenzoic acid methyl ester **4**, *p*-toluic acid methyl ester **5**, methyl benzoate **6**, and benzaldehyde **7** as byproducts. These byproducts were formed by overreduction, demethoxycarbonylation and/or hydrogenolysis of **1**, **2** or the reaction intermediates, as shown in **Scheme 1** that illustrates the possible reaction pathways.

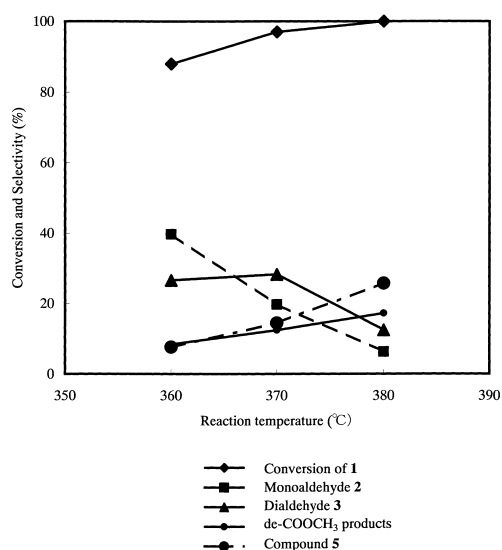
Hydrogenation of dimethyl terephthalate over ZrO₂ catalyst at 350°C formed **2** (83.0% selectivity) with **3** (13.6%) at a conversion of 21.6%. Hydrogenation over Cr-modified ZrO₂ showed higher selectivity for total hydrogenation with slightly lower selectivity for monoaldehyde. The catalyst activity decreased slightly for the initial 2 h, then was maintained almost unchanged. Hydrogenation of monoester **2** under similar conditions afforded dialdehyde **3** in about 60% selectivity with demethoxycarbonylative or hydrogenolysis byproducts

as illustrated in **Table 1**.

The effect of reaction temperature on the hydrogenation of diester **1** over ZrO_2 catalyst is shown in **Fig. 1**. The selectivity for monoaldehyde was reduced and the amount of byproducts increased at higher reaction temperatures. The selectivity of dialdehyde was maximum around 370°C . Based on these results, monoester **2** is considered to be an intermediate in the hydrogenation of diester **1** to dialdehyde **3**.

3.2. Hydrogenation of Regioisomers of Dimethyl Terephthalate

The results of hydrogenation of dimethyl isophthalate and dimethyl phthalate are also described in **Table 1**. Hydrogenation of dimethyl isophthalate formed methyl isophthalaldehyde with lower selectivity and larger amounts of demethoxycarbonylative byproducts compared to **1**. However, hydrogenation of dimethyl phthalate yielded no aldehydic products and the products were dominated by demethoxycarbonylation and overreduction to give phthalide.



Reaction conditions: H_2 -GHSV = 625 h^{-1} , LHSV = $0.10 \text{ kg} \cdot \text{l}^{-1} \cdot \text{cat.}^{-1} \cdot \text{h}^{-1}$.

Fig. 1 Effect of Temperature on the Hydrogenation of Dimethyl Terephthalate **1**

The different reactivities of the three isomers of dimethyl benzendicarboxylates have two possible reasons: steric hindrance of the two methoxycarbonyl groups and different adsorption of the intermediates on the catalyst. In the hydrogenation of dimethyl terephthalate, only one of the two methoxycarbonyl groups interacts easily and weakly on the catalyst to give a formyl group, whereas the other methoxycarbonyl group does not hamper this hydrogenation. In contrast, the *ortho*-substituted methoxycarbonyl groups of dimethyl phthalate mutually hinder the interaction with the catalyst. However, after the dimethyl phthalate molecule is adsorbed onto the ZrO_2 catalyst surface, the adsorption species will be bound strongly to the active site of the catalyst by the two vicinal carboxylate groups and the catalyst will be extremely deactivated. This latter prediction is supported by the following observations. During monoesterification of benzenedicarboxylic acids over alumina catalyst⁹, terephthalic acid was converted to the corresponding monomethyl ester because of the adsorption of only one of the two *para* carboxy groups on the alumina surface. However, phthalic acid was not esterified at all because both *ortho* carboxyl groups interacted at the same time and considerably deactivated the catalyst. Spectroscopic study of the ZrO_2 catalyst during the hydrogenation of benzoic acid into benzaldehyde revealed that benzoic acid was activated as benzoate anion by weak adsorption with the carboxylate group on the catalyst surface^{4,10}. Further investigation of the adsorption species formed during hydrogenation will be reported separately.

3.3. Hydrogenation of Dibasic Alicyclic and Aliphatic Carboxylic Acid Esters

The results of hydrogenation of dibasic alicyclic and aliphatic carboxylic acid esters are summarized in **Table 2**. Dimethyl 1,4-cyclohexanedicarboxylate was hydrogenated over Cr-ZrO_2 to give the corresponding monoaldehyde with a small amount of 1,4-cyclohexanedicarbaldehyde, showing similar high selectivity to dimethyl terephthalate. The reaction has a similar pathway as shown in **Scheme 1**. In contrast, diesters of dibasic aliphatic acids such as dimethyl glutarate and dimethyl adipate were not converted into the corre-

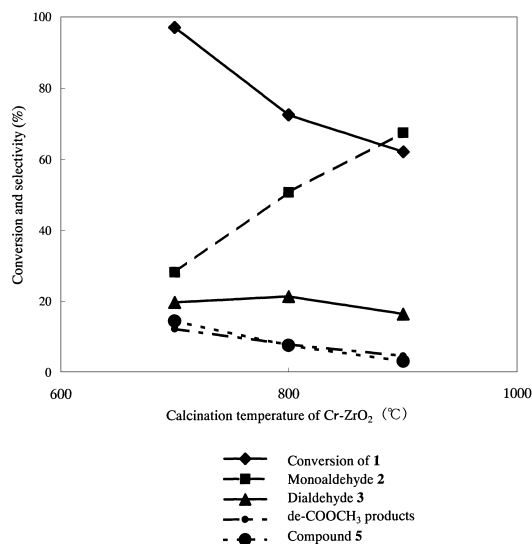
Table 2 Hydrogenation of Dibasic Aliphatic Acid Dimethyl Esters over Cr-ZrO_2 Catalyst^{a)}

Substrate	Catalyst	Temperature [°C]	Conversion [%]	Selectivity [%] ^{c)}	
				monoaldehyde	dialdehyde
<chem>H3COOC-C1=CC=CC=C1-COOCH3</chem>	Cr-ZrO_2	360	24.1	75.1	9.1
<chem>CH3OOC(CH2)4COOCH3</chem> ^{b)}	Cr-ZrO_2	330	74.8	tr	tr
<chem>CH3OOC(CH2)3COOCH3</chem> ^{b)}	Cr-ZrO_2	360	22.0	tr	tr

a) Reaction conditions: H_2 -GHSV = 1250 h^{-1} , LHSV = $0.12 \text{ g} \cdot \text{ml}^{-1} \cdot \text{cat.}^{-1} \cdot \text{h}^{-1}$, catalyst volume = 5.0 ml. Calcination temperature: 700°C .

b) Carbon dioxide (0.1-0.7%) and methane (50 ppm) were also detected in off gas.

c) Minor and/or unidentified products are omitted for clarity.



Reaction conditions: H_2 -GHSV = 625 h^{-1} , LHSV = 0.10 $kg \cdot l^{-1} \cdot cat^{-1} \cdot h^{-1}$, 370°C.

Fig. 2 Effect of Catalyst Calcination Temperature on the Hydrogenation of Dimethyl Terephthalate 1

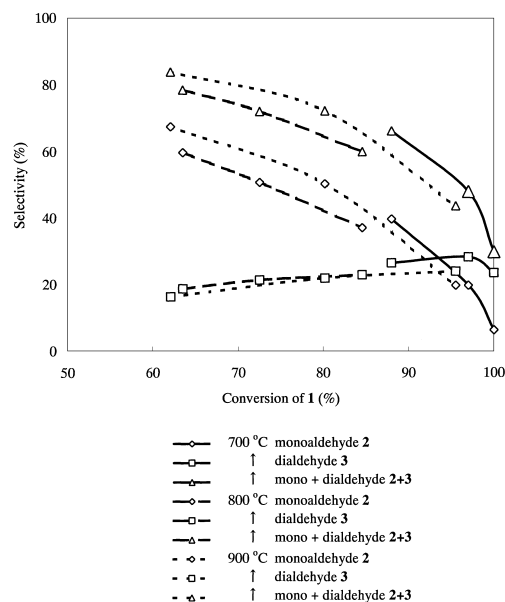
sponding mono- or dialdehydes by hydrogenation. Instead, generation of carbon dioxide and methane were observed by analysis of the off gases. According to the mechanism discussed earlier for the ketonization of *monobasic* carboxylic acids under hydrogenation conditions^{4,5}, the α -CH₂ group of these linear diacid diesters is easily activated on the catalyst surface compared with the α -CH group of 1,4-cyclohexanedicarboxylate, for example, and is also accessible without hindrance to another ester group to form predominantly ketones *via* inter- and/or intramolecular decarboxylative condensation. Carboxylic acids and esters with an α -CH₂ group are known to be converted into ketones in the absence of hydrogen over ZrO₂ catalyst by decarboxylative intramolecular condensation^{11,12}.

3.4. Catalysts

3.4.1. Effect of Catalyst Preparation

The effect of calcination temperature of the Cr-ZrO₂ catalyst on the hydrogenation of dimethyl terephthalate 1 is shown in Fig. 2. The selectivity for monoaldehyde increased with the calcination temperature whereas the catalyst activity decreased. The selectivity for dialdehyde was not significantly affected by the calcination temperature. Conversion-selectivity curves for catalysts calcined at various temperatures are presented in Fig. 3. The total aldehyde selectivity (selectivity for 2 and 3) was almost independent of the calcination temperature in the range of 700-900°C.

The surface area was measured of Cr-ZrO₂ calcined at various temperatures. Higher calcination temperature resulted in abrupt reduction of the surface area of the Cr-ZrO₂ catalyst: surface area was 112, 67, and 26



Reaction conditions: H_2 -GHSV = 625 h^{-1} , LHSV = 0.10 $kg \cdot l^{-1} \cdot cat^{-1} \cdot h^{-1}$.

Fig. 3 Conversion vs. Selectivity Plots of the Hydrogenation of Terephthalaldehydic Acid Monomethyl Ester 2

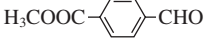
$m^2 \cdot g^{-1}$ for calcination at 600, 700, and 800°C, respectively. Moreover, the X-ray diffraction (XRD) analysis of these catalysts revealed that the crystal structure of ZrO₂ remained monoclinic. Based on these results, the decrease of catalyst activity was caused by the reduction of surface area of the catalyst, whereas the hydrogenation selectivity did not change because the microstructure of the catalyst was not affected.

3.4.2. Effect of Modification of ZrO₂ Catalyst

Improvement of the dialdehyde selectivity is necessary by development of an efficient catalyst that hydrogenates monoaldehydes into dialdehydes more selectively. The results of hydrogenation of monoester 2 over modified ZrO₂ catalysts are summarized in Table 3 and Fig. 4. ZnO and CeO₂ catalysts have high catalytic activity like ZrO₂. Modification of ZrO₂ catalyst with other metals, such as Cr, In, Pb or Zn, affect the hydrogenation activity and selectivity. Modification of ZrO₂ with these metals enlarges the relative surface area of the catalyst and increases the catalyst reactivity⁴. Modification with Cr or In did not affect significantly the selectivity for dialdehyde. Modification with Pb increased the rate of undesirable demethoxycarbonylation. Modification with Zn resulted in some improvement of the dialdehyde selectivity. In addition, modification with Zn or Cr also suppressed demethoxycarbonylation.

The relationship between the Zn content of the modified ZrO₂ catalyst and the hydrogenation products is shown in Fig. 5. The maxima of the conversion and

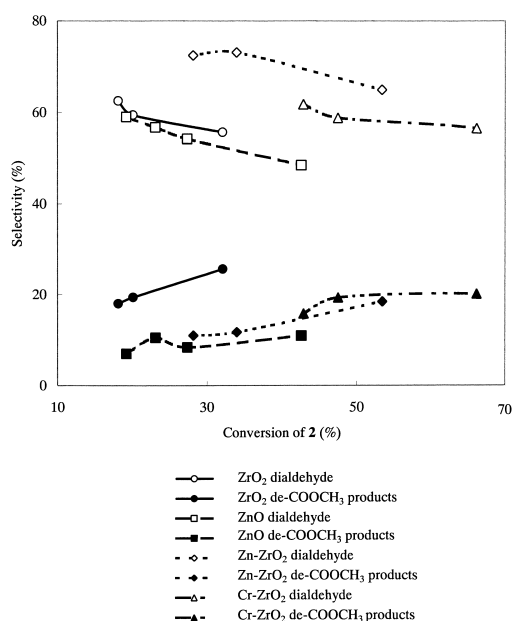
Table 3 Hydrogenation of Terephthalaldehyde Acid Methyl Ester **2** over Modified ZrO₂ Catalyst^{a)}

Substrate	Catalyst ^{b)}	Conversion [%]	Selectivity [%]		
			dialdehyde	de-COOCH ₃ products	5
	ZrO ₂	18.1	62.5	18.0	2.0
	Cr-ZrO ₂ ^{c)}	42.9	61.7	15.8	10.4
	In-ZrO ₂ ^{c)}	35.8	57.6	19.3	7.8
	Pb-ZrO ₂ ^{c)}	34.9	22.3	39.1	12.6
	Zn-ZrO ₂ ^{c)}	28.2	72.4	11.0	4.1
	ZnO	9.2	65.5	8.8	10.5
	CeO ₂	17.6	59.9	9.3	2.2

a) Reaction conditions: H₂-GHSV = 1250 h⁻¹, LHSV = 0.22 g·mL⁻¹·h⁻¹, 350°C.

b) Calcination temperature: 600°C.

c) Metal : Zr = 5 : 100 in atomic ratio.



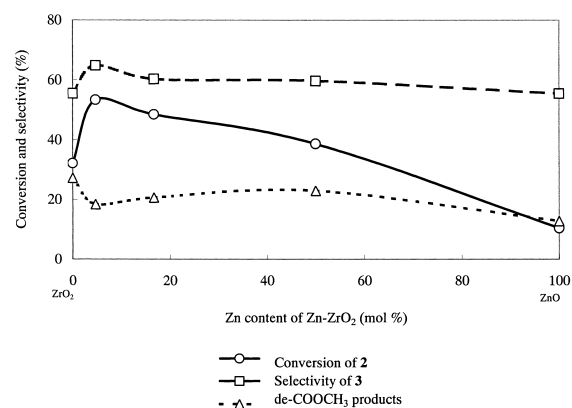
Reaction conditions: H₂-GHSV = 1250 h⁻¹, LHSV = 0.24 kg·l⁻¹·cat.⁻¹·h⁻¹.

Fig. 4 Conversion vs. Selectivity Plots of the Hydrogenation of Monoaldehyde **2**

dialdehyde selectivity were observed at an atomic ratio of Zn/Zr = 5/100. The promotion effects of Zn modified ZrO₂ catalyst on the dialdehyde selectivity can be attributed to degradation of the active sites for demethoxycarbonylation through the synergistic effect of ZnO and ZrO₂, which both catalyze the hydrogenation of aromatic carboxylic acids.

4. Conclusion

Aromatic and alicyclic dibasic acid diesters were hydrogenated over ZrO₂ or Cr-ZrO₂ catalysts in the vapor phase to give the corresponding monoaldehydic acid esters and dialdehydes as the major products. The reactivity of benzenedicarboxylic acid dimethyl



Reaction conditions: H₂-GHSV = 1250 h⁻¹, LHSV = 0.24 kg·l⁻¹·cat.⁻¹·h⁻¹, 370°C.

Fig. 5 Effect of Zn Content of Zn-ZrO₂ on the Hydrogenation of Monoaldehyde **2**

esters was terephthalic > isophthalic >> phthalic (no formation of aldehyde). Aliphatic dibasic acid esters were not hydrogenated to give aldehydes. Modification of ZrO₂ by Cr, In or Zn was effective to improve catalyst activity. These results imply that this hydrogenation process has commercial potential for the production of some types of dialdehydes.

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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1報) 各種ジエステル類の水素化反応性

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ZrO₂ 触媒による各種ジカルボン酸ジエステル類の水素化反応を検討した。芳香族ジエステルであるベンゼンジカルボン酸ジメチルエステル類の反応性はパラ- > メタ-置換体の順で高く、それぞれ対応するモノおよびジアルデヒドに変換された。しかし、オルト置換体であるフタル酸ジメチルの水素化ではアルデヒドは生成しなかった。反応中間生成物として考えられるテレフタルアルデヒド酸メチルは、本反応条件下においてジアルデヒドに変換されることも確認した。以上より、本反応では二個のエステル基が逐次的に水素化を受けることにより進行す

ると推定した。脂環式ジエステルである 1,4-シクロヘキサンジカルボン酸ジメチルは、テレフタル酸ジメチルと同様な水素化反応成績を示した。一方、グルタル酸ジメチルやアジピン酸ジメチルのような脂肪族ジカルボン酸ジエステルの水素化を試みたが、アルデヒド類は生成しなかった。また、ZrO₂ 触媒を Cr, In, Zn 等で修飾することにより、触媒活性が向上した。Zn 修飾触媒 (物質量比 Zn/Zr = 5/100) を用いた場合、テレフタルアルデヒド酸メチルの水素化におけるジアルデヒド選択率は 72.4% に達した。