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Author: [ADVANCED](#) | Volume Page

Keyword: |



[TOP](#) > [Available Issues](#) > [Table of Contents](#) > [Abstract](#)

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[\[PDF \(196K\)\]](#) [\[References\]](#)

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

[Toshiharu Yokoyama](#)¹⁾ and [Naoko Fujita](#)¹⁾

1) Mitsubishi Chemical Group Science and Technology Research Center Inc.

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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](#)

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