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PREPARATION OF DIMETHYL
CYCLOHEXANEDICARBOXYLATES

5 This invention pertains to an improved process for
the preparation of dimethyl cyclohexanedicarboxylates by
the hydrogenation of the analogous dimethyl benzenedi-
carboxylate ester. More specifically, the present
invention pertains to an improved process for the
hydrogenation of a dimethyl benzenedicarboxylate ester
10 in the presence of certain, supported palladium
catalysts which permit the use of significantly lower
process pressures.

Dimethyl 1,4-cyclohexanedicarboxylate has been
manufactured for over 30 years as an intermediate in the
15 production of cyclohexanedimethanol which is used
extensively as a monomer in the preparation of conden-
sation polymers, particularly polyesters. Dimethyl
cyclohexanedicarboxylates are valuable chemical
intermediates useful, for example, in the manufacture of
polyester resins used in the formulation of coating
20 compositions.

The manufacture of dimethyl 1,4-cyclohexanedicar-
boxylate and 1,4-cyclohexanedimethanol using dimethyl
terephthalate as the feedstock and a heterogenous mode
25 of operation is described in U.S. Patent 3,334,149.
This process requires the use of high pressures, e.g.,
greater than 346 bars absolute (34,600 kPa), and
utilizes a palladium on alumina catalyst in the
hydrogenation of dimethyl terephthalate to dimethyl
30 1,4-cyclohexanedicarboxylate. The specific palladium on
alumina catalyst contains 0.5 weight percent palladium
deposited on alumina, the crystalline phase of which is
a mixture of bohmite and bohmite. The catalyst is
used in the form of 3 mm chips and exhibits per-
35 formance characteristics.

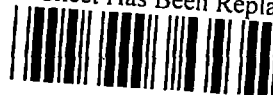
It is apparent that chemical processes which require the use of high pressures such as pressures in excess of 340 bars (34,000 kPa) are inherently expensive due to the increased operating costs and the cost of the apparatus required including the high pressure-rated reactor and the compressors. It has been found, however, that when the hydrogenation of dimethyl terephthalate to dimethyl 1,4-cyclohexanedicarboxylate is carried out at pressures less than 135 bars absolute (13,500 kPa) using the above-described palladium on alumina catalyst, commercially acceptable hydrogenation rates cannot be achieved over an extended period of time. For example, when operating continuously at 125 bars absolute (12,500 kPa) using the above-described catalyst, the process is unstable and the hydrogenation rate typically is not more than approximately 55% of the rates achieved at approximately 410 bars absolute (41,000 kPa) pressure. The reduced hydrogenation rate is due to decreased activity of the palladium catalyst which, we believe, is related to the generation of carbon monoxide during the hydrogenation at lower pressures. It is known that the presence of carbon monoxide in hydrogen gas used in hydrogenation processes is detrimental to such processes. However, the extreme sensitivity of the above-described palladium on alumina catalyst to parts per million (ppm) amounts of carbon monoxide is surprising.

The present invention is concerned with a process whereby dimethyl benzenedicarboxylates may be catalytically hydrogenated to the corresponding dimethyl cyclohexanedicarboxylate using moderate pressures and readily available catalysts. We have discovered that acceptable rates at moderate pressures may be achieved by the use of palladium on alumina catalysts wherein

(1) the dispersion and depth of deposition of the palladium metal are within certain ranges, (2) the alumina is of a particular crystalline phase, and (3) the surface area of the catalyst is within a particular range. The process provided by our invention therefore provides a means for the preparation of a dimethyl cyclohexanedicarboxylate which comprises contacting a dimethyl benzenedicarboxylate with hydrogen at a temperature of 140 to 400°C and a pressure of 10 to 200 bars absolute (1,000 to 20,000 kPa) in the presence of a palladium on alumina catalyst; wherein

- (1) palladium comprises 0.1 to 5.0 weight percent of the catalyst;
- (2) the palladium dispersion is at least 20 percent;
- (3) at least 90 weight percent of the palladium is located on the alumina at a depth less than 200 microns from the surface of the alumina; and
- (4) the crystalline phase of the alumina is alpha, theta, delta, gamma, eta or a mixture thereof.

The minimum temperature at which the process may be carried out is limited by the melting point of the dimethyl benzenedicarboxylate reactant, e.g., 140°C for dimethyl 1,4-benzenedicarboxylate (dimethyl terephthalate). The maximum operating temperature can be as high as 400°C. The process preferably is carried out at a temperature in the range of 140 to 250°C. Although the process may be carried out at pressures in the range of 8 to 690 bars absolute (800 to 69,000 kPa), the present invention permits the achievement of good hydrogenation rates without the use of the high pressures described in the literature. Thus, the preferred pressures are within the range of 50 to 170 bars absolute (5,000 to 17,000 kPa). Although the 1,2-, 1,3- and 1,4-isomers of dimethyl cyclohexanedicar-



boxylate may be prepared by the process of this invention by the hydrogenation of the analogous dimethyl benzenedicarboxylate, the primary usefulness of the process is in the manufacture of the 1,3- and, especially, the 1,4-isomers.

The catalyst used in the present invention is palladium deposited on an alumina support wherein the palladium comprises 0.1 to 5.0, preferably 0.5 to 2.0, weight percent based on the total weight of the catalyst. The dispersion of the palladium on and in the alumina support typically is measured by titration of the surface of the support with carbon monoxide gas and measuring the amount of carbon monoxide adsorbed on the palladium surface. Normally, it is assumed that each surface metal atom will adsorb one molecule of carbon monoxide and thus, the percent of metal exposed may be determined. This percentage is known as the dispersion. See Myasaki, J. Catal., 65, 84 (1980) and "Structure of Metallic Catalysts" by J. R. Anderson, Academic Press, 1975, page 360. The catalysts which are advantageously used in accordance with the present invention have a dispersion percentage of at least 20 percent, preferably at least 30 percent (as determined by carbon monoxide adsorption as described herein).

Another characteristic of the palladium catalyst used in the present invention is that most of the palladium is located on or near the surface of the alumina support. Accordingly, at least 90 weight percent of the palladium is located no deeper than 200 microns, preferably less than 100 microns, from the external surface of the alumina support. As is well-known in the art, depth of impregnation can be determined either visually using optical microscopy or by a line scan technique in a SEM with a palladium

sensitive detector. See, for example, the above-cited "Structure of Metallic Catalysts".

Yet another important characteristic of the catalysts is the crystalline phase of the alumina support which is selected from the alpha, theta, delta, gamma, eta phases or a mixture of such crystalline phases. Alumina of theta, delta or alpha crystalline phases or mixture of such alumina is preferred with theta alumina being especially preferred.

The nitrogen BET surface area of the palladium on alumina catalysts used in the process of our invention is in the range of 20 to 300 square meters per gram (m^2/g) with the range of 30 to 150 m^2/g being preferred. It is well known in the art that BET surface area is a function of crystalline phases and calcination history and should be as high as possible while maintaining the appropriate oxide phase. Catalysts having the characteristics described hereinabove may be prepared according to conventional impregnation or deposition techniques using procedures well known to those skilled in the art. The catalyst may be used in the hydrogenation process in the form of pellets, spheres, extrudates and the like. The particular form is not critical so long as the catalyst form does not lead to excessive channeling of the liquid feed through the reactor, e.g., in continuous operation using a fixed bed of catalyst through which the reactant is passed. Preferably, the surface area:volume ratio of the catalyst is at least 500 and preferably greater than 1500.

The process of the invention may be carried out in a batch, semi-continuous or continuous mode using conventional chemical processing techniques. The preferred mode of operation is a continuous process



wherein a melt of a dimethyl benzenedicarboxylate is passed over and through one or more fixed beds of catalyst in a "trickle bed" manner. Typically, some of the dimethyl cyclohexanedicarboxylate product is recycled to the feed port of the reactor and serves as a solvent for the reactant. Other inert, non-aromatic compounds which are liquid under the operating conditions employed may be used as a solvent. The process may be operated in either an adiabatic or isothermal fashion. In trickle bed operation, the liquid hourly space velocity (LHSV; unit volume reactant fed per hour per unit volume catalyst) of the reactant feed may be in the range of 0.1 to 10 with a preferred range of 0.5 to 5. The LHSV for the total liquid flow (reactant plus solvent) may be in the range of 1 to 30. Hydrogen is fed to the reactor in excess of the stoichiometric quantity and normally is purged from the system. The rate of hydrogen purge is dependent on the temperature and pressure at which the process is operated.

Our novel process is further illustrated by the following examples. All experiments were performed in a trickle bed reactor system comprising a 1.83 meter (6 feet) section of 316 stainless steel pipe having an interior diameter of 2.5 cm (1 inch) and equipped with means for liquid recycle. The catalyst (800 cc) was held in place within the reactor by 100 cc of 1.6 mm (0.0625 inch) 316 stainless steel Penn State packing located above and below the catalyst bed. The temperatures at various points within the catalyst bed were measured by 10 thermocouples which extended through the reactor wall and approximately 3.2 mm into the catalyst. The temperature reported in each example is



the average of these 10 readings. Typical temperature gradients through the bed were less than 10°C.

The procedure generally used in each experiment comprised purging the system with nitrogen and pumping
5 dimethyl 1,4-cyclohexanedicarboxylate (DMCD) through the reactor system at a rate of 5 Kg/hour at 150°C and 70 bars absolute (7,000 kPa) with a 6 L/hour liquid recycle. The feed gas then was switched from nitrogen to hydrogen, the pressure slowly was increased to 125.1
10 bars absolute (12,510 kPa) and, finally, the temperature was increased to the desired reaction temperature. The reaction was commenced by switching the reactor feed from DMCD to 30:70 parts by weight mixture of dimethyl terephthalate and DMCD. Hydrogen was purged from the
15 reactor system at a rate of 8 to 10 L/minute. Carbon monoxide concentrations in the hydrogen purge gas were monitored using a Beckman IR carbon monoxide analyzer. Operating data were recorded when a steady state of operation was achieved, typically 1 to 2 hours from the
20 commencement of the reaction.

The palladium on alumina catalysts employed in the examples are described in Table I wherein % Pd is the weight percent palladium present on the catalyst, BET SA is the BET surface area of the catalyst in m²/g, Pd
25 Disp. is the percent of the palladium which is exposed, Impreg. Depth is the depth in microns of the impregnation of the palladium on and in the support, and

Phase is the crystalline phase of the alumina support.

TABLE I

	<u>Catalyst</u>	<u>% Pd</u>	<u>BET SA</u>	<u>Pd Disp.</u>	<u>Impreg. Depth</u>	<u>Phase</u>
5	A	0.75	42	29	40	Alpha, Theta
10	B	0.50	34	27	62	Alpha, Theta
	C	1.00	107	30	50-100	Alpha, Theta
15	D	0.50	270	32	62	Boehmite
	E	0.75	93	28	400	Theta
	F	0.75	203	-	150	Gamma
20	G	0.75	198	11	<100	Theta

EXAMPLES 1-3 AND COMPARATIVE EXAMPLES 1-4

Dimethyl terephthalate was hydrogenated to DMCD using the catalysts and the procedure described hereinabove. The catalyst and temperature (°C, Temp.) used in each example are set forth in Table II wherein C-1 through C-4 designate the comparative examples, DMT in Product is the weight percent of the product which consists of unconverted dimethyl terephthalate, STY is the space time yield of DMCD in g DMCD per cc catalyst-hour, and CO is the concentration in ppm of carbon monoxide in the hydrogen purge gas.

TABLE II

	<u>Example</u>	<u>Catalyst</u>	<u>Temp.</u>	<u>DMT in Product</u>	<u>STY</u>	<u>CO</u>
5	1	A	177	0.0	1.87	15
	2	B	170	2.2	1.73	16
	3	C	175	0.7	1.82	7
10	C-1	D	173	7.4	1.41	40
	C-2	E	172	6.1	1.49	26
15	C-3	F	170	10.0	1.25	28
	C-4	G	170	>10	<1.25	15

20 The space time yields reported in Table II demonstrate the advantages provided by the present invention utilizing Catalyst A, B or C. The relatively poor performance of Catalysts D, E and F is not completely illustrated by Comparative Examples 1-3 since the gaseous effluent from the reactor was not recycled in the examples reported herein. We have found that in similar experiments in which the gaseous reactor effluent is recycled in a manner analogous to commercial operation, the presence of 37 ppm carbon monoxide in the recycled gas can decrease production rates as much as 15%.

35 The invention has been described in detail with particular reference to preferred embodiments thereof, but it will be understood that variations and modifications can be effected within the spirit and scope of the invention.



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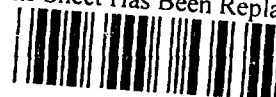
CLAIMS

We claim:

1. Process for the preparation of a dimethyl cyclohexanedicarboxylate which comprises contacting a
5 dimethyl benzenedicarboxylate with hydrogen at a temperature of 140 to 400°C and a pressure of 10 to 200 bars absolute (1,000 to 20,000 kPa) in the presence of a palladium on alumina catalyst; wherein
 - 10 (1) palladium comprises 0.1 to 5.0 weight percent of the catalyst;
 - (2) the palladium dispersion is at least 20 percent;
 - (3) at least 90 weight percent of the palladium is located on the alumina at a depth less than 200 microns from the surface of the alumina; and
 - 15 (4) the crystalline phase of the alumina is alpha, theta, delta, gamma, eta or a mixture thereof.
2. Process according to Claim 1 which comprises contacting a dimethyl benzenedicarboxylate with hydrogen
20 at a temperature of 140 to 400°C and a pressure of 10 to 200 bars absolute (1,000 to 20,000 kPa) in the presence of a palladium on alumina catalyst; wherein
 - (1) palladium comprises 0.5 to 2.0 weight percent of the catalyst;
 - 25 (2) the palladium dispersion is at least 30 percent;
 - (3) at least 90 weight percent of the palladium is located on the alumina at a depth less than 100 microns from the surface of the alumina; and
 - (4) the crystalline phase of the alumina is alpha,
30 theta, delta or a mixture thereof.
3. Process according to Claim 2 wherein a solution of the dimethyl benzenedicarboxylate in dimethyl cyclohexanedicarboxylate is contacted with hydrogen.



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4. Process for the preparation of a dimethyl cyclohexanedicarboxylate which comprises contacting a dimethyl benzenedicarboxylate with hydrogen at a temperature of 140 to 400°C and a pressure of 50 to 170 bars absolute (5,000 to 17,000 kPa) in the presence of a palladium on alumina catalyst; wherein

- (1) palladium comprises 0.1 to 5.0 weight percent of the catalyst;
- (2) the palladium dispersion is at least 20 percent;
- (3) at least 90 weight percent of the palladium is located on the alumina at a depth less than 200 microns from the surface of the alumina; and
- (4) the crystalline phase of the alumina is alpha, theta, delta, gamma, eta or a mixture thereof.

5. Process according to Claim 4 which comprises contacting a dimethyl benzenedicarboxylate with hydrogen at a temperature of 140 to 250°C and a pressure of 50 to 170 bars absolute (5,000 to 17,000 kPa) in the presence of a palladium on alumina catalyst; wherein

- (1) palladium comprises 0.5 to 2.0 weight percent of the catalyst;
- (2) the palladium dispersion is at least 30 percent;
- (3) at least 90 weight percent of the palladium is located on the alumina at a depth less than 100 microns from the surface of the alumina; and
- (4) the crystalline phase of the alumina is alpha, theta, delta or a mixture thereof.

6. Process according to Claim 5 for the preparation of dimethyl 1,4-cyclohexanedicarboxylate wherein a solution of dimethyl 1,4-benzenedicarboxylate in dimethyl 1,4-cyclohexanedicarboxylate is contacted with hydrogen.

7. Process according to Claim 5 for the preparation of dimethyl 1,3-cyclohexanedicarboxylate wherein a solution of dimethyl 1,3-benzenedicarboxylate in dimethyl 1,3-cyclohexanedicarboxylate is contacted with hydrogen.

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8. Process according to Claim 5 for the preparation of dimethyl 1,2-cyclohexanedicarboxylate wherein a solution of dimethyl 1,2-benzenedicarboxylate in dimethyl 1,2-cyclohexanedicarboxylate is contacted with hydrogen.

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PREPARATION OF DIMETHYL
CYCLOHEXANEDICARBOXYLATES

ABSTRACT

Disclosed is a process for the preparation of a dimethyl cyclohexanedicarboxylate by the hydrogenation of the analogous dimethyl benzenedicarboxylate ester in the presence of a class of palladium on alumina catalysts which have a unique combination of characteristics. The use of the catalysts permits the process to be carried out at significantly lower process pressures.

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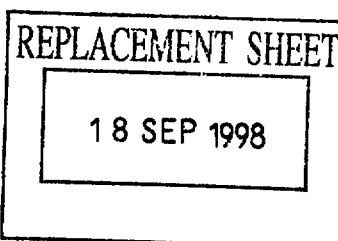
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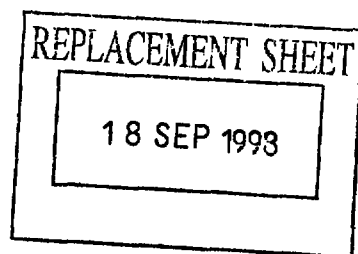
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- (1) the dispersion and depth of deposition of the palladium metal are within certain ranges, (2) the alumina is of a particular crystalline phase, and (3) the surface area of the catalyst is within a particular range. The process provided by our invention therefore provides a means for the preparation of a dimethyl cyclohexanedicarboxylate which comprises contacting a dimethyl benzenedicarboxylate with hydrogen at a temperature of 140 to 400°C and a pressure of 10 to 200 bars absolute (1,000 to 20,000 kPa) in the presence of a palladium on alumina catalyst; wherein
- (1) palladium comprises 0.1 to 5.0 weight percent of the catalyst;
 - (2) the palladium dispersion is at least 20 percent;
 - (3) at least 90 weight percent of the palladium is located on the alumina at a depth less than 200 μm from the surface of the alumina;
 - (4) the crystalline phase of the alumina is alpha, theta, delta or a mixture thereof; and
 - (5) the catalyst has a surface area of 20 to 300 square meters per gram.

The minimum temperature at which the process may be carried out is limited by the melting point of the dimethyl benzenedicarboxylate reactant, e.g., 140°C for dimethyl 1,4-benzenedicarboxylate (dimethyl terephthalate). The maximum operating temperature can be as high as 400°C. The process preferably is carried out at a temperature in the range of 140 to 250°C. Although



the process may be carried out at pressures in the range of 8 to 690 bars absolute (800 to 69,000 kPa), the present invention permits the achievement of good hydrogenation rates without the use of the high pressures described in the literature. Thus, the preferred pressures are within the range of 50 to 170 bars absolute (5,000 to 17,000 kPa). Although the 1,2-, 1,3- and 1,4-isomers of dimethyl cyclohexanedicar-

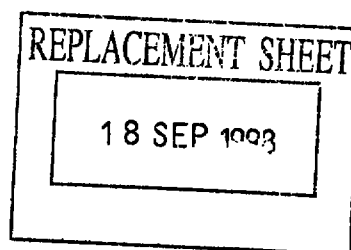


boxylate may be prepared by the process of this invention by the hydrogenation of the analogous dimethyl benzenedicarboxylate, the primary usefulness of the process is in the manufacture of the 1,3- and, especially, the 1,4-isomers.

The catalyst used in the present invention is palladium deposited on an alumina support wherein the palladium comprises 0.1 to 5.0, preferably 0.5 to 2.0, weight percent based on the total weight of the catalyst.

The dispersion of the palladium on and in the alumina support typically is measured by titration of the surface of the support with carbon monoxide gas and measuring the amount of carbon monoxide adsorbed on the palladium surface. Normally, it is assumed that each surface metal atom will adsorb one molecule of carbon monoxide and thus, the percent of metal exposed may be determined. This percentage is known as the dispersion. See Myasaki, J. Catal., 65, 84 (1980) and "Structure of Metallic Catalysts" by J. R. Anderson, Academic Press, 1975, page 360. The catalysts which are advantageously used in accordance with the present invention have a dispersion percentage of at least 20 percent, preferably at least 30 percent (as determined by carbon monoxide adsorption as described herein).

Another characteristic of the palladium catalyst used in the present invention is that most of the palladium is located on or near the surface of the alumina support. Accordingly, at least 90 weight percent of the palladium



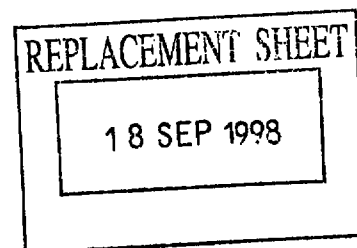
is located no deeper than 200 μm , preferably less than 100 μm , from the external surface of the alumina support. As is well-known in the art, depth of impregnation can be determined either visually using optical microscopy or by
5 a line scan technique in a SEM with a palladium

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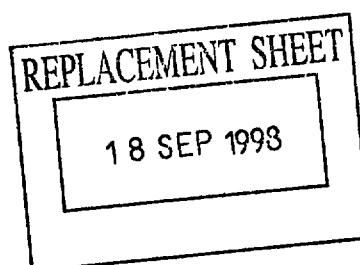
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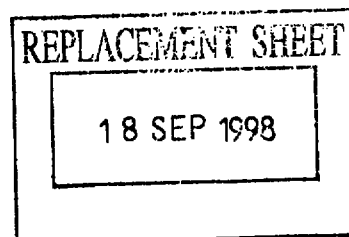
wherein a melt of a dimethyl benzenedicarboxylate is passed over and through one or more fixed beds of catalyst in a "trickle bed" manner. Typically, some of the dimethyl cyclohexanedicarboxylate product is recycled to the feed port of the reactor and serves as a solvent for the reactant. Other inert, non-aromatic compounds which are liquid under the operating conditions employed may be used as a solvent. The process may be operated in either an adiabatic or isothermal fashion. In trickle bed operation, the liquid hourly space velocity (LHSV; unit volume reactant fed per hour per unit volume catalyst) of the reactant feed may be in the range of 0.1 to 10 with a preferred range of 0.5 to 5. The LHSV for the total liquid flow (reactant plus solvent) may be in the range of 1 to 30. Hydrogen is fed to the reactor in excess of the stoichiometric quantity and normally is purged from the system. The rate of hydrogen purge is dependent on the temperature and pressure at which the process is operated.

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points within the catalyst bed were measured by 10 thermocouples which extended through the reactor wall and approximately 3.2 mm into the catalyst. The temperature reported in each example is

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the average of these 10 readings. Typical temperature gradients through the bed were less than 10°C.

The procedure generally used in each experiment comprised purging the system with nitrogen and pumping
5 dimethyl 1,4-cyclohexanedicarboxylate (DMCD) through the reactor system at a rate of 5 Kg/hour at 150°C and 70 bars absolute (7,000 kPa) with a 6 L/hour liquid recycle. The feed gas then was switched from nitrogen to hydrogen, the pressure slowly was increased to 125.1 bars absolute
10 (12,510 kPa) and, finally, the temperature was increased to the desired reaction temperature. The reaction was commenced by switching the reactor feed from DMCD to 30:70 parts by weight mixture of dimethyl terephthalate and DMCD. Hydrogen was purged from the reactor system at a
15 rate of 8 to 10 L/minute. Carbon monoxide concentrations in the hydrogen purge gas were monitored using a Beckman IR carbon monoxide analyzer. Operating data were recorded when a steady state of operation was achieved, typically 1 to 2 hours from the commencement of the reaction.

20 The palladium on alumina catalysts employed in the examples are described in Table I wherein % Pd is the weight percent palladium present on the catalyst, BET SA is the BET surface area of the catalyst in m²/g, Pd Disp. is the percent of the palladium which is exposed, Impreg.
25 Depth is the depth in µm of the impregnation of the palladium on and in the support, and

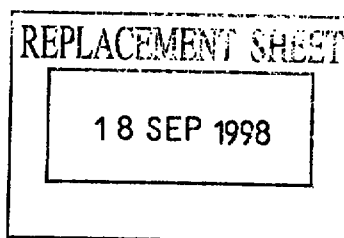
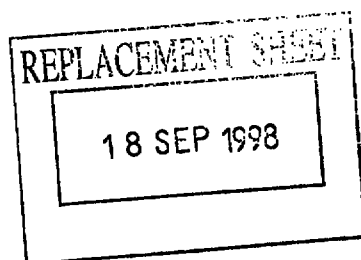


TABLE II

		DMT in				
	<u>Example</u>	<u>Catalyst</u>	<u>Temp.</u>	<u>Product</u>	<u>STY</u>	<u>CO</u>
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	2	B	170	2.2	1.73	16
	3	C	175	0.7	1.82	7
	C-1	D	173	7.4	1.41	40
	C-2	E	172	6.1	1.49	26
10	C-3	F	170	10.0	1.25	28
	C-4	G	170	>10	<1.25	15

The space time yields reported in Table II demonstrate the advantages provided by the present invention utilizing Catalyst A, B or C. The relatively poor performance of Catalysts D, E and F is not completely illustrated by Comparative Examples 1-3 since the gaseous effluent from the reactor was not recycled in the examples reported herein. We have found that in similar experiments in which the gaseous reactor effluent is recycled in a manner analogous to commercial operation, the presence of 37 ppm carbon monoxide in the recycled gas can decrease production rates as much as 15%.

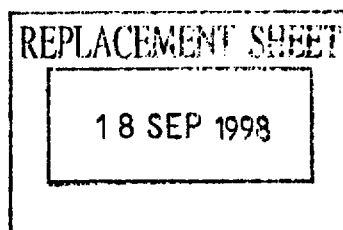




CLAIMS

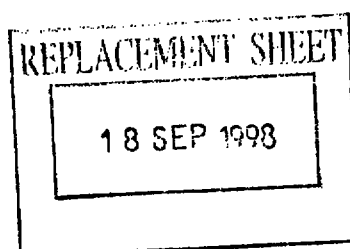
We claim:

1. Process for the preparation of a dimethyl
cyclohexanedicarboxylate which comprises contacting a
5 dimethyl benzenedicarboxylate with hydrogen at a
temperature of 140 to 400°C and a pressure of 10 to 200
bars absolute (1,000 to 20,000 kPa) in the presence of a
palladium on alumina catalyst; wherein
 - 10 (1) palladium comprises 0.1 to 5.0 weight percent of the
catalyst;
 - (2) the palladium dispersion is at least 20 percent;
 - (3) at least 90 weight percent of the palladium is
located on the alumina at a depth less than 200 μ m
from the surface of the alumina; and
 - 15 (4) the crystalline phase of the alumina is alpha, theta,
delta, gamma, eta or a mixture thereof; and
 - (5) the catalyst has a surface area of 20 to 300 square
meters per gram.
- 20 2. Process according to Claim 1 which comprises
contacting a dimethyl benzenedicarboxylate with hydrogen
at a temperature of 140 to 400°C and a pressure of 10 to
200 bars absolute (1,000 to 20,000 kPa) in the presence of
a palladium on alumina catalyst; wherein
 - 25 (1) palladium comprises 0.5 to 2.0 weight percent of the
catalyst;
 - (2) the palladium dispersion is at least 30 percent;





- (3) at least 90 weight percent of the palladium is located on the alumina at a depth less than 100 μ m from the surface of the alumina; and
- (4) the crystalline phase of the alumina is alpha, theta, delta or a mixture thereof; and
- (5) the catalyst has a surface area of 20 to 300 square meters per gram.
3. Process according to Claim 2 wherein a solution of the dimethyl benzenedicarboxylate in dimethyl cyclohexanedicarboxylate is contacted with hydrogen.
4. Process according to Claim 1 wherein the dimethyl benzenedicarboxylate is contacted with hydrogen at a temperature of 140 to 400°C and a pressure of 50 to 170 bars absolute (5,000 to 17,000 kPa).
5. Process according to Claim 2 wherein the dimethyl benzenedicarboxylate is contacted with hydrogen at a temperature of 140 to 400°C and a pressure of 50 to 170 bars absolute (5,000 to 17,000 kPa).
6. Process according to Claim 5 for the preparation of dimethyl 1,4-cyclohexanedicarboxylate wherein a solution of dimethyl 1,4-benzenedicarboxylate in dimethyl 1,4-cyclohexanedicarboxylate is contacted with hydrogen.





7. Process according to Claim 5 for the preparation of dimethyl 1,3-cyclohexanedicarboxylate wherein a solution of dimethyl 1,3-benzenedicarboxylate in dimethyl 1,3-cyclohexanedicarboxylate is contacted with hydrogen.

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8. Process according to Claim 5 for the preparation of dimethyl 1,2-cyclohexanedicarboxylate wherein a solution of dimethyl 1,2-benzenedicarboxylate in dimethyl 1,2-cyclohexanedicarboxylate is contacted with hydrogen.

