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(54) **LIQUID PHASE SYNTHESIS OF METHYLENE LACTONES USING NOVEL CATALYST**

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See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

6,232,474 B1 5/2001 Brandenburg et al.
2006/0025605 A1* 2/2006 Hutchenson et al. 549/263
2006/0025607 A1* 2/2006 Hutchenson et al. 549/263
2006/0025608 A1* 2/2006 Hutchenson et al. 549/263
2006/0025611 A1* 2/2006 Hutchenson et al. 549/263
2006/0025612 A1* 2/2006 Hutchenson et al. 549/263

FOREIGN PATENT DOCUMENTS

JP 10298172 * 11/1998

OTHER PUBLICATIONS

machine translation of JP 10298172, paragraph 27-33, May 12, 2006.*
E. P. Barret, L. G. Joyner and P. P. Halenda, J. Amer. Chem. Soc., 73, 373 (1951).

* cited by examiner

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(57) **ABSTRACT**

Process for converting certain lactones to their alpha-methylene derivatives in the liquid phase with both high conversion and selectivity using easily recoverable novel heterogeneous catalysts.

4 Claims, No Drawings

**LIQUID PHASE SYNTHESIS OF
METHYLENE LACTONES USING NOVEL
CATALYST**

CROSS-REFERENCE TO RELATED
APPLICATION

This application claims priority under 35 U.S.C. §119 from U.S. Provisional Application Ser. No. 60/591,498, filed Jul. 27, 2004.

FIELD OF INVENTION

The invention pertains to a method of producing unsubstituted and substituted alpha-methylene lactones by a liquid phase reaction of starting lactones with formaldehyde in the presence of a novel catalyst that provides high selectivity and conversion.

BACKGROUND

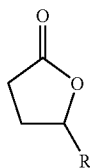
Alpha-methylene-gamma-butyrolactone and methyl alpha-methylene-gamma-butyrolactone are useful monomers in the preparation of both homopolymers and copolymers. In addition, the alpha-methylene-gamma-butyrolactone group is an important structural feature of many sesquiterpenes of biological importance.

U.S. Pat. No. 6,232,474 B1 describes a method for converting certain starting lactones to alpha-methylenelactones using a homogeneous or heterogeneous so-called basic catalyst that can be selected from the metal oxides, hydroxides, carbonates and phosphates, any of which may be supported or unsupported. The preferred reaction is the conversion of gamma-butyrolactone to alpha-methylene-gamma-butyrolactone. The basic catalyst may include additives and promoters to enhance catalyst efficiency. The method involves a reaction between the starting lactone and formaldehyde and may be carried out in a batch mode, optionally using an organic solvent and a phase transfer agent. The method is carried out at a temperature of at least 70° C. and a pressure less than or equal to 2000 psi (13.7 MPa). A problem inherent in the method is that the homogeneous catalysts must be used at high concentration to achieve good yields, but are not easily recycled. On the other hand, the heterogeneous catalysts, while more easily recoverable, do not provide as high conversion and selectivity.

It would be advantageous, therefore, to have a lactone conversion process that not only provides high conversion and selectivity, but also allows for easy catalyst recovery.

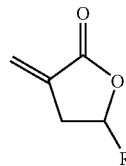
SUMMARY OF THE INVENTION

This need is met by the present invention, which, in its first aspect, is a process for preparing a reaction product comprising an alpha-methylene lactone of the Formula II, said process comprising reacting a lactone of the Formula I with formaldehyde



-continued

II



wherein R is selected from the group consisting of hydrogen, methyl, ethyl, and straight or branched C₃-C₅ alkyl;

at a temperature in the range of from about 100° C. to 300° C. and a pressure in the range of 0.34 MPa to 13.7 MPa in the presence of a catalyst;

said catalyst being made by (or obtainable by) a process comprising:

- (a) contacting (i) porous silica, optionally containing zirconium, with (ii) a solution comprising a solvent and an organic compound of at least one catalytic element selected from the group consisting of potassium, rubidium, and cesium;
- (b) drying the product of step (a) to remove at least a portion of said solvent;
- (c) heating the product of step (b) to a temperature in the range of 350° C. to 550° C. to produce a catalyst precursor; and
- (d) flushing at a preselected flow rate an oxygen-containing gas over said catalyst precursor either during step (c), or after step (c) while the temperature is still in the range of 350° C. to 550° C. to produce a catalyst candidate comprising the at least one catalytic element in an amount from about 0.1% to about 40% by weight of the combined weight of the catalyst candidate and the catalytic element, or the combined weight of the catalyst candidate containing the zirconium and the catalytic element.

In a preferred embodiment, said catalyst is made by (is obtainable by) a process comprising:

- (a) contacting (i) porous silica, optionally containing zirconium, said silica having a pore volume of at least 0.4 cc/gram attributable to pores having a diameter between 65 and 3200 Angstroms, with (ii) a solution comprising a solvent and an organic compound of at least one catalytic element selected from the group consisting of potassium, rubidium, and cesium;
- (b) drying the product of step (a) to remove at least a portion of said solvent;
- (c) heating the product of step (b) to a temperature in the range of 350° C. to 550° C. to produce a catalyst precursor;
- (d) flushing at a preselected flow rate an oxygen-containing gas over said catalyst precursor either during step (c), or after step (c) while the temperature is still in the range of 350° C. to 550° C. to produce a catalyst candidate comprising the at least one catalytic element in an amount from about 0.1% to about 40% by weight of the combined weight of said catalyst candidate and the catalytic element, or the combined weight of the catalyst candidate containing the zirconium and the catalytic element;
- (e) determining by porosimetry whether said catalyst candidate has a pore volume of at least about 0.3 cubic

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centimeters per gram of catalyst attributable to pores having a diameter between 65 and 3200 Angstroms; and

- (f) if said catalyst candidate does not have a pore volume of at least about 0.3 cubic centimeters per gram of catalyst attributable to pores having a diameter between 65 and 3200 Angstroms, repeating, optionally more than once, steps (a) through (e) using in step (d) flow rates successively greater than said preselected flow rate until the catalyst candidate has a pore volume of at least about 0.3 cubic centimeters per gram of catalyst attributable to pores having a diameter between 65 and 3200 Angstroms.

The use of such a catalyst in the conversion of lactones of the Formula I to those of Formula II leads to high conversion and selectivity. Moreover, the catalyst is easily recoverable from the reaction mixture.

DETAILED DESCRIPTION OF THE INVENTION

The following terms generally are abbreviated as follows:

“alpha-methylene-gamma-butyrolactone” is abbreviated MBL;

“gamma-butyrolactone” is abbreviated GBL;

“gamma-valerolactone” is abbreviated GVL;

“alpha-methylene-gamma-valerolactone” is abbreviated MVL;

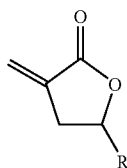
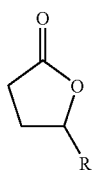
gamma-methyl alpha methylene gamma butyrolactone is abbreviated MeMBL;

“cubic centimeters” is abbreviated as cc or cm³;

“mass spectroscopy” is abbreviated MS; and

“gas chromatography” is abbreviated GC.

The process of the present invention concerns a liquid phase methylenation of lactones of Formula I to yield alpha-methylene lactones of Formula II.



Specifically, lactone of Formula I is reacted with formaldehyde to give a reaction product comprising alpha methylene lactones of Formula II. The substituent —R group is selected from the group consisting of hydrogen, methyl, ethyl, and straight or branched C₃–C₅ alkyl.

In a preferred embodiment the lactone of Formula I is gamma-valerolactone (R is CH₃) and the alpha-methylene lactone of Formula II is alpha-methylene-gamma-valerolactone.

The process of the present invention is carried out in the liquid phase, at a temperature in the range of from about 100° C. to about 300° C. A temperature in the range of from

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about 150° C. to about 250° C. is preferred. A temperature in the range of from about 200° C. to about 225° C. is most preferred.

The reaction can be carried out at pressures ranging from about 0.34 MPa to about 13.7 MPa, with a preferred range of from about 0.68 MPa to about 6.85 MPa. Holdup time and temperature can be selected to achieve desired conversions and selectivities.

The formaldehyde may be supplied to the reaction in the form of an aqueous solution (formalin), a hemiacetal of an alcohol, a low molecular weight polyformaldehyde or formaldehyde trimer (trioxane). Paraformaldehyde is preferred. The use of the trimers and oligomers, however, reduces the need to remove water from the process. Anhydrous formaldehyde can also be used. Hemiacetals work effectively, but require separate steps to release the formaldehyde from the alcohol and to recover and recycle the alcohol.

The catalyst used in the present invention comprises silicon and oxygen that form a matrix (or support) for a catalytic element. The catalytic element is at least one element selected from the group consisting of potassium, rubidium, and cesium. The catalytic element is deposited on or dispersed within the matrix by contacting the matrix with a solution of an organic compound of at least one of these elements. The matrix comprising silicon and oxygen can optionally contain zirconium. The catalytic element should constitute from about 0.1% to about 40% by weight of the combined weight of the starting silica and the added catalytic element (as opposed to the entire compound of which the element is a part).

The preferred catalysts must be porous and preferably have a pore-size distribution such that those pores having a diameter between 65 and 3200 Angstroms provide a pore volume of at least about 0.3 cubic centimeters per gram of the catalyst. Catalysts not meeting this pore volume are still useful in the process of the present invention.

In some cases, reaction conditions may result in a decrease of catalyst efficiency. In these situations it may be useful to periodically reactivate the catalyst. For example, contacting the present catalysts, when activity drops below an acceptable level, with oxygen at elevated temperatures has the effect of reactivating the catalyst. Contact temperatures with oxygen may range from about 225° C. to about 500° C., with temperatures of about 250° C. to about 425° C. being preferred.

Selectivities and yields of product may be influenced by the total holdup time with the catalyst and reaction temperature.

The reaction may be done neat or in the presence of a non-reacting solvent such as toluene, xylenes and dioxane.

Separation and/or purification of the desired products, including MBL or MeMBL, from unreacted starting lactone and/or reaction byproducts may be performed by processes known in the art. A particularly suitable method to recover the desired product is to polymerize MBL in GBL solution, or MeMBL in GVL solution, using standard free-radical polymerization, isolate the polymer by precipitation, and then thermally depolymerize back to MBL or MeMBL, as the case may be, by heating under vacuum. Finally, MBL can be separated from GBL by melt crystallization. Another effective method is liquid-liquid extraction.

Non-limiting reactors suitable for the process of the instant invention include autoclaves, trickle bed, fixed bed and pipeline reactors. The process can be run in either batch or continuous mode as described, for example, in H. Scott Fogler, *Elements of Chemical Reaction Engineering*, 2nd Edition, Prentice-Hall Inc, CA, 1992.

The catalysts of the present invention can be made as follows.

Porous silica powder, such as the material sold by Grace Davison, Inc. (Columbia, Md.), preferably, but not necessarily, with a pore volume of at least 0.4 cc/g attributable to pores having a diameter between 65 and 3200 Angstroms is used as a catalyst matrix. Porosity preferably is determined by mercury porosimetry. The porous silica may contain zirconium. This latter silica is preferred because of its hydrothermal stability.

A suitable way of choosing appropriate starting porous silica for the preferred catalysts of this invention is to eliminate first those silicas that have a mean pore diameter less than 65 Angstroms and porosity less than 0.4 cc/g attributable to pores having diameters between 65 and 3200 Angstroms. Next, a porous silica manufacturer that describes its products in terms of mean pore diameter can be consulted to see if the manufacturer has the underlying data from which the mean pore diameter was calculated. If so, the manufacturer may be able to specify which, if any, of its products have pore volumes of greater than 0.4 Angstroms attributable to pores having diameters between 65 and 3200 Angstroms. These materials preferably should be independently tested by mercury porosimetry to determine that they meet the porosity characteristics of the preferred catalysts by this invention.

Organic compounds such as the carboxylates, such as acetate, propionate, butyrate, and 2-ethylhexanoate, of a catalytic element selected from the group consisting of potassium, rubidium, and cesium is dissolved in aqueous or non-aqueous solvent and contacted with the porous silica. Organic compounds do not include carbonates of the aforesaid catalytic elements. Organic compounds containing acetates are preferred. Other organic anions such as acetylacetonates can be used. One convenient method for introducing the catalytic element into the porous silica is to dissolve a suitable weight of the organic compound of the catalytic element in just enough solvent to equal the volume of the pores of the selected amount of the porous silica. The amount of organic compound should be chosen to provide to the silica from 0.1 wt % to 40 wt % of the element relative to the combined weight of the porous silica plus the element (as opposed to the compound of which the element is a part). This procedure should ensure that the proper amount of the element is present in the final catalyst. The resulting material is allowed to dry, preferably in a nitrogen environment for an extended time. The purpose of the drying is to remove at least a portion of the solvent in which the organic compound is dissolved.

Organic compounds such as the alkoxides can also be used. Organic alkoxides of an element selected from the group consisting of potassium, rubidium, and cesium can contain from one to 20 carbon atoms and preferably 1 to 5 carbon atoms in the alkoxy group. The organic alkoxide should be soluble in the solvent. Most alkoxides can be dissolved in non-aqueous solutions such as ethanol, propanol, or isopropyl alcohol. Subsequent methods for introducing the element and drying are the same.

The dried material is then heated (for example in an alumina boat placed in a tube furnace) at an ambient temperature of 350° C. to 550° C. (The temperature of the catalyst material may be somewhat higher because of exothermic reactions taking place on the material.) A temperature between 450° C. and 550° C. is preferred. Either during the heating or subsequent to it, but at the same temperature, the material must be flushed with an oxygen-containing gas (e.g. air), which is believed to burn off organic residues

formed during the heating step. In a tube furnace, an airflow rate of at least 110 cc/min in a 3 cm diameter tube furnace, which corresponds to a linear velocity of 15.6 cm/min was found to be acceptable. Use of sufficiently high airflow rates is important to produce a high surface area material. In a tube furnace, the material can be heated at a rate of 5° C./min to 120° C., and can be exposed to this temperature for 4 hours. It can be heated subsequently at a rate of 5° C./min to approximately 450° C. and held at this temperature for 16 hours. Other equipment can be used to perform the heating step. Such equipment includes fluidized bed and rotary calcination equipment.

Heating can be accomplished in air or in a combination of an inert gas such as nitrogen, argon, and krypton for parts of the cycle, followed by air. An initial drying step at 120° C. in nitrogen, another inert gas, or air is preferred for a period of 30 minutes to 24 hours. Following this drying step, the catalyst can be heated in air or nitrogen to a temperature of 350° C. to 550° C. For acetate precursors, 450° C. to 550° C. is required. Heating times can range from 30 minutes to 48 hours. The final heating step preferably is performed in air for at least 30 minutes.

Once the catalyst is made as described above, it can be used as is, or if the preferred catalyst is desired, tested to confirm that it has a pore volume of at least about 0.3 cc/g of catalyst attributable to pores having a diameter between about 65 and 3200 Angstroms. (The reason that the porosity of the starting porous silica decreases after treatment is believed to be attributable to the inclusion of the catalytic element into the silica.)

Pore volume may be obtained by a variety of techniques, but preferred techniques are mercury (Hg) and nitrogen porosimetric techniques, with Hg porosimetry being most preferred.

Mercury porosimetry data can be obtained at 414 MPa using, for example, a Micromeritics 1 Model 9420 AutoPore III Instrument (Micromeritics Inc., One Micromeritics Drive, Norcross Ga. 30093-1877). This technique permits one to measure the pore volume and size by forcing mercury to penetrate inside the open porosity. Mercury is used because it behaves as a non-wetting liquid with a large number of materials.

Mercury is forced to enter into the pores by applying a controlled increasing pressure. As a sample holder is filled with mercury under vacuum conditions, mercury surrounds the sample without entering the pores due to the very low residual pressure. During the test, the pressure is increased, and the volume of mercury penetrated is detected by means of a capacitive system. The decreasing volume of mercury in the sample holder represents the pore volume. The penetration pressure is directly related to the pore access size by a well-known mathematical model, expressed by the Washburn equation:

$$D = -4\gamma \cos(\theta) / P_c$$

Where:

γ is surface tension of pure mercury (480 dyne/cm);

θ is contact angle between mercury and the solid (average value 140° C.);

P_c is mercury penetration equilibrated pressure; and

D is pore diameter.

The distribution of pore size, as well as the total porosity, bulk and apparent density and the specific pore volume can be obtained by the relationship between the pressure necessary for penetration (the pore dimension) and the volume of penetrated mercury (pore volume). At each pressure, therefore, a differential volume of Hg can be calculated

which occupies the pores of the solid; this represents the additional Hg volume which is intruded as a consequence of a pressure increase. At lower applied pressure, larger pores are filled with Hg. With increasing applied pressure, smaller pores are occupied up to the smallest pore diameter reasonably measurable by this technique, 65 Angstroms. In this way, a distribution of pore sizes as a function of applied pressure can be obtained.

Pores are assumed to be of a cylindrical shape, as is standard for this technique.

Sample compressibility correction is calculated post priori by determining the volume of samples and pores not yet intruded as a function of applied pressure. The resulting relationship is used to correct the raw intrusion data for sample compression effects.

From the Washburn equation it is clear that the pore size range that can be investigated by mercury porosimetry is directly related to the pressure range.

Alternatively, nitrogen porosimetry may be used. Dinitrogen adsorption/desorption measurements can be performed at 77.3° K. using, for example, Micromeritics ASAP model 2400/2405 porosimeters. Samples can be degassed at 150° C. overnight prior to data collection. Pore volume distributions can be determined using a 27 point desorption isotherm and can be analyzed using the BJH method as discussed in E. P. Barret, L. G. Joyner and P. P. Halenda, *J. Amer. Chem. Soc.*, 73, 373(1951).

In the preferred embodiment of this invention, pores having diameters of 65 Angstroms up to 3200 Angstroms must contribute at least 0.3 cc/g pore volume to the final catalyst. Above 3200 Angstroms, inter-particle pores and void spaces are measured, and are not important for this invention.

If the catalyst possesses the correct porosity, it may be used as the preferred catalyst in the lactone conversion method. If not, it may be necessary to repeat the catalyst synthesis using higher oxygen-containing gas flow rates than were used initially. The process may have to be repeated several times with successively higher gas flow rates until a preferred catalyst with the correct porosity is finally obtained.

COMPARATIVE EXAMPLES

Comparative Catalyst 1 ("CC1")

An example described in U.S. Pat. No. 6,232,474B1 was duplicated. In a 100 ml round bottom flask, 25 ml of solution of 1.86 wt % Ba (as the hydroxide) in H₂O were combined with 5.0 grams of silica (Grace Davison, grade 57, 10-20 mesh). The slurry was stirred at room temperature for 10 minutes. H₂O was removed by rotovac evaporation. The solid was heated at 550° C. for two hours in flowing nitrogen.

Comparative Catalyst 2 ("CC2"): (6.65 wt % Mg, on Davicate® Si 1700, SiO₂ Support)

The same procedure as described in example 1 was used, with the following differences: 12.54 of magnesium acetate was dissolved in 31.40 g of water, which was impregnated into 20 g of Davicat® SiO₂ 1700 powder, which was used as the support.

Comparative Catalyst 3 ("CC3"): (10.5 wt % Ca, on Davicat® Si 1700, SiO₂ Support)

The same procedure as described in example 1 was used, with the following differences: 9.25 g of calcium acetate was dissolved in 31.40 g of water, which was impregnated into 20 g of Davicat® SiO₂ 1700 powder, which was used as the support.

Comparative Catalyst 4 ("CC4"): (20 wt % Sr, on Davicat® Si 1700, SiO₂ Support)

The same procedure as described in example 1 was used, with the following differences: 5.87 g of strontium acetate was dissolved in 15.70 g of water, which was impregnated into 10 g of Davicat® SiO₂ 1700 powder, which was used as the support.

Comparative Catalyst 5 ("CC5"): (2 wt % Li, on Davicat® Si 1700, SiO₂ Support)

The same procedure as described in example 1 was used, with the following differences: 5.97 g of lithium acetate was dissolved in 31.40 g of water, which was impregnated into 20 g of Davicat® SiO₂ 1700 powder, which was used as the support.

EXAMPLES OF THE INVENTION

Catalyst 1 (20% by Weight of Rb, on Davicat® Si 1251; Small Pore Volume Silica)

About 20 g of SiO₂ powder, Davicat® Si 1251 (Grace Davison, Inc., Columbia, Md.) having a pore volume of 0.36 cm³/g was used as support material to make the catalyst support. 8.45 g of rubidium acetate (Aldrich Chemical Co.) was dissolved in enough water to match the pore volume of the Si 1251 support. The amount of water used was approximately 7.2 cm³. The material was allowed to dry for at least 12 hours in a nitrogen environment. Approximately 10 cm³ of the material was loaded into an alumina boat and heated in a tube furnace. The internal diameter of the tube furnace was 10 cm. The airflow rate was greater than 1220 cm³/min, which corresponds to a linear velocity of greater than 15.6 cm/min. Use of this higher airflow is important to produce a high surface area material. The material was heated at a rate of 5° C./min to 120° C., and was exposed to this temperature for 4 hours. It was subsequently heated at a rate of 5° C./min to approximately 450° C. (as measured by a thermocouple placed approximately 0.5 cm over the catalyst bed) and was held at this temperature for 16 hours.

The catalyst produced as described above, while useful in the present invention, has a porosity of less than 0.01 cc/g, and, therefore, is not a preferred catalyst of the present invention.

Catalyst 2 (20% by Weight of Rb on Davicat® Si1700, SiO₂ Support)

The procedure outlined in Example 1 was used with a Davicat® Si1700 support (Grace Davison, Inc., Columbia Md.) instead of Si1251. Davicat® Si 1700 is a SiO₂ powder, and has a greater pore volume than Davicat® 1251 (approximately 1.57 cc/g). Therefore, 31.4 cm³ of water was used, instead of 7.2 cm³ as in Example 1.

Catalyst 3 (20% by Weight of Rb, on Davicat® Si 1405. SiO₂ Support)

The procedure outlined in Example 1 was used with a Davicat® Si1405 support (Grace Davison, Inc., Columbia Md.) instead of Davicat® Si 1251. Davicat® Si 1405 is an SiO₂ powder, which has a greater pore volume than SiO₂ 1251 (approximately 1.10 cc/g). Therefore, 22.0 cm³ of water was used, instead of 7.2 cm³ as in Example 1. The same heating protocol was used as described in example 1, except that a 3 cm diameter tube furnace was used instead of a 10 cm diameter tube furnace. In this tube furnace, an airflow rate of at least 110 cc/min was used, which corresponds to a linear velocity of 15.6 cm/sec.

Catalyst 4 (20% by Weight of Rb, on Davicat® Si 1415. SiO₂ Support)

The procedure outlined in Example 1 was used with a Davicat® Si 1415 support (Grace Davison, Inc., Columbia Md.) instead of Davicat® Si 1251. Davicat® Si 1415 has a greater pore volume than Davicat® Si 1251 (approximately 0.85 cc/g). Therefore, 17.0 cm³ of water was used, instead of 7.2 cm³ as in Example 1.

Catalyst 5 (20% by Weight of Rb, on Davicat® ZrSi4101, Zr—SiO₂ Support)

The same procedure as described in example 1 was used, except for the following differences: 20 g of Davicat® SiZr 4101 support was used, and 8.45 g of rubidium acetate was dissolved in 19.60 g of water and impregnated into the support.

Catalyst 6: (20 wt % Cs, on Davicat® Si 1700, SiO₂ Support)

The same procedure as described in example 1 was used, with the following differences: 7.22 g of cesium acetate was dissolved in 29.0 g of water, which was impregnated into 20 g of Davicat® SiO₂ 1700 powder, which was used as the support.

Catalyst 7 (20% by weight of Cs, on Davicat® Si 1405, SiO₂ Support)

The same procedure as described in example 1 was used, except for the following differences: 20 g of Davicat® Si1405 support was used, and 7.22 g of cesium acetate was dissolved in 19.0 g of water and impregnated into the support.

Catalyst 8: (10.7 wt % K, on Davicat® Si 1415, SiO₂ Support)

The same procedure as described in example 1 was used, with the following differences: 5.74 g of potassium acetate was dissolved in 17.0 g of water, which was impregnated into 20 g of Davicat® Si1415 powder, which was used as the support.

TABLE 1

Mercury Porosimetry Data of Catalysts		
Cat. No.	Composition wt % = (wt Element/(wt Support + wt element) × 100	Pore Volume (cc/g) from pores having diameter of 65 Å or greater
CC1	Ba(OH) ₂ /SiO ₂	0.926
CC2	6.65 wt % Mg/Si 1700	1.11
CC3	10.5 wt % Ca/Si 1700	1.06
CC4	20 wt % Sr/Si 1700	0.843
CC5	2 wt % Li/Si 1700	1.06
1	20% Rb/Si 1251	<0.01
2	20% Rb/Si 1700	1.04
3	20% Rb/Si 1405	0.908
4	20% Rb/Si 1415	0.723
5	20 wt % Rb/ZrSi4101	0.313
6	20 wt % Cs/Si 1700	0.817
7	20 wt % Cs/Si 1405	0.889
8	10.7 wt % K/Si 1415	0.838

Examples of Liquid Phase Reaction

In the following examples, a 2 cc pressure vessel was charged with gamma-valerolactone (100 mg), paraformaldehyde (300 mg), toluene (700 mg, as a solvent) and catalyst (50 mg). Nitrogen was used to pressurize the vessel to 800 psi, which was then heated to 200° C. for 2 hours. The autoclave was then cooled, vented and the liquid analyzed by GC to determine conversion and selectivity.

TABLE 2

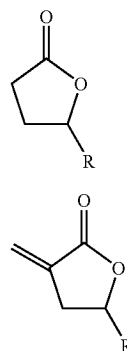
Reaction Data			
Cat No.	Weight % Catalytic Metal/Support	% MeMBL Selectivity	% GVL Conversion
CC1	Ba(OH) ₂ ·8H ₂ O/SiO ₂ /550° C./2 hr	0.0	9.2
CC2	Mg/Si(1700)	0.0	25.3
CC3	20% Ca/Si(1700)	0.0	0.6
CC4	20% Sr/Si(1700)	0.0	3.6
CC5	Li/SiO ₂	19.2	7.2
1	20% Rb/Si(1251)	39.0	69.1
2	20% Rb/Si(1700)	76.8	85.9
3	20% Rb/Si(1405)	70.8	93.2
4	20% Rb/Si(1415)	71.9	88.1
5	20% Rb/Zr/SiO ₂ (4101)	58.9	96.9
6	20% Cs/Si(1700)	55.0	96.0
7	20% Cs/Si(1405)	70.9	92.4
8	K/Si(1415)	69.5	76.4

The comparative examples (i.e., those run with catalysts CC1 through CC5) show that a catalyst made in accordance with U.S. Pat. No. 6,232,474 B1, namely (CC1) shows both poor selectivity and poor activity (low conversion of GVL). The data also show that catalysts made from Mg, Ca, Sr, and Li (CC2 thru CC3) also performed poorly.

In contrast, the examples of the invention show both good selectivity and activity, with larger pore volume (Examples 2 through 8) exhibiting the best overall performance.

What is claimed is:

1. A process for preparing a reaction product comprising an alpha-methylene lactone of the Formula II, said process comprising reacting a lactone of the Formula I with formaldehyde



wherein R is selected from the group consisting of hydrogen, methyl, ethyl, and straight or branched C₃-C₅ alkyl;

at a temperature in the range of from about 100° C. to about 300° C. in the presence of a grafted catalyst; said grafted catalyst being made by a process comprising:

(a) contacting (i) porous silica, optionally containing a first element, said first element being one, two or three members selected from the group consisting of aluminum, zirconium, and titanium, said silica having a pore volume of at least 0.4 cc/g silica attributable to pores having pore diameters between 65 and 3200 Angstroms, with (ii) a solution comprising a solvent and an organic compound of a second element, said second element being one, two, or

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- three members selected from the group consisting of potassium, cesium and rubidium;
- (b) drying the product of step (a) to remove at least a portion of said solvent;
- (c) heating the product of step (b) to a temperature in the range of 350° C. to 550° C. to produce a catalyst precursor;
- (d) flushing at a preselected flow rate an oxygen-containing gas over said catalyst precursor either during step (c), or after step (c) while the temperature is still in the range of 350° C. to 550° C. to produce a catalyst candidate in which the second element is present in said catalyst candidate in an amount from about 0.1% to about 40% by weight of the combined weight of the catalyst and the second element;
- (e) determining by porosimetry whether said catalyst candidate has a pore volume of at least about 0.3 cubic centimeters per gram of catalyst candidate attributable to pores having a diameter between 65 and 3200 Angstroms; and
- (f) if said catalyst candidate does not have a pore volume of at least about 0.3 cubic centimeters per gram of catalyst candidate attributable to pores having a diameter between 65 and 3200 Angstroms, repeating, optionally more than once, steps (a) through (e) using in step (d) flow rates successively greater than said preselected flow rate until the

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- catalyst candidate has a pore volume of at least about 0.3 cubic centimeters per gram of catalyst candidate attributable to pores having a diameter between 65 and 3200 Angstroms;
- (g) contacting the material produced in step (f) with a second solution of zirconium, aluminum or titanium alkoxides dissolved in a second solvent, said alkoxides containing from one to 20 carbon atoms;
- (h) filtering the material of step (g);
- (i) drying the product of step (h) to remove at least a portion of said second solvent;
- (j) heating the product of step (i) to a temperature in the range of 350° C. to 550° C.; and
- (k) flushing at a preselected flow rate an oxygen-containing gas over the product of step (j) either during step (j), or after step (j) while the temperature is still in the range of 350° C. to 550° C. to produce the grafted catalyst.
2. The process of claim 1 wherein the porosimetry is mercury porosimetry.
3. The process of claim 1 wherein R is hydrogen or methyl.
4. The process of claim 1 further comprising separating said alpha methylene lactone from said reaction product.

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