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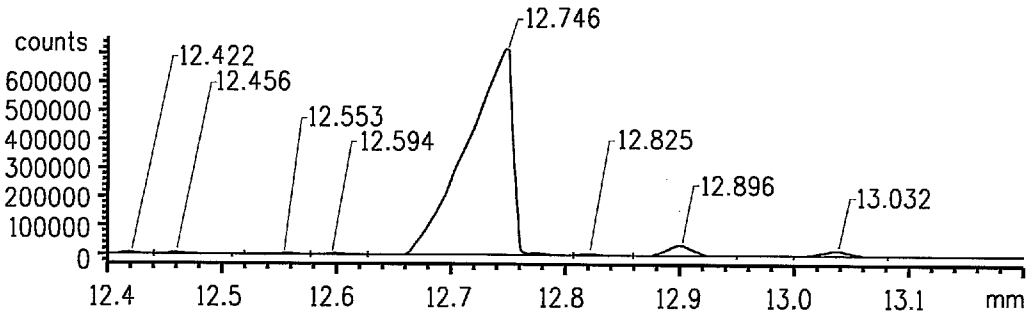
(54) **Title:** OLEFIN ISOMERIZATION



(57) **Abstract:** This invention relates to a process for isomerizing olefins using a porous microcomposite comprising at least one fluorinated sulfonic acid on silica as the catalyst.

WO 2007/050488 A2

TITLE

Olefin Isomerization

FIELD OF THE INVENTION

This invention relates to a process for isomerizing olefins.

BACKGROUND

The isomerization of olefins to internal olefins is an important reaction in the refining industry. Long chain olefins, for example, can be isomerized to the internal olefins, which can be used as precursors to materials used in lubrication.

Various methods for the catalytic isomerization of olefins have been disclosed. For a review of olefin isomerization see, for example, Dunning, H. N. (Ind. Eng. Chem. (1953) 45:551-564). Homogeneous catalysts, while effective, produce highly corrosive media with chemically reactive waste streams. Thus, there has been considerable effort to replace homogeneous catalysts with cost-effective and active solid acid catalysts, which allow for simpler product purification and safer process operation.

U.S. Patent No. 5,849,974 discloses a method for isomerizing olefins using a supported or unsupported nonmetallic sulfonic or perfluorosulfonic acid resin catalyst.

SUMMARY OF THE INVENTION

The present invention provides a method for carrying out isomerization reactions using a porous solid catalyst comprised of at least one fluorinated sulfonic acid on silica.

The present invention relates to a process for making internal olefins comprising forming a reaction mixture comprising (1) at least one α-olefin having from 4 to 25 carbons, and (2) at least one porous microcomposite comprising at least one fluorinated sulfonic acid and silica made by a process comprising the steps of:

(a) contacting, in the presence of water:

(1) at least one silica precursor;

(2) at least one fluorosulfonic acid selected from the group consisting of:

(i) 1,1,2,2-tetrafluoroethanesulfonic acid;

(ii) 1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonic acid;

(iii) 1,1,2-trifluoro-2-(trifluoromethoxy)ethanesulfonic acid;

(iv) 1,1,2-trifluoro-2-(perfluoropropoxy)ethanesulfonic acid;

(v) 1,1,2,3,3,3-hexafluoropropanesulfonic acid; and

(vi) 2-chloro-1,1,2-trifluoroethanesulfonic acid; and

optionally at least one inorganic acid; and

(3) optionally, a non-reacting solvent; to form a mixture;

(b) aging the mixture to form a gelled mixture; and

(c) drying the gelled mixture to remove substantially all water and alcohol, if any, therein.

The present invention also relates to a process for making internal olefins comprising forming a reaction mixture comprising (1) at least one α-olefin having from 4 to 25 carbons, and (2) of at least one porous microcomposite comprising at least one fluorinated sulfonic acid and silica made by a process comprising the steps of:

(a) contacting at least one fluorosulfonic acid selected from the group consisting of:

(i) 1,1,2,2-tetrafluoroethanesulfonic acid;

(ii) 1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonic acid;

(iii) 1,1,2-trifluoro-2-(trifluoromethoxy)ethanesulfonic acid;

(iv) 1,1,2-trifluoro-2-(perfluoropropoxy)ethanesulfonic acid;

(v) 1,1,2,3,3,3-hexafluoropropanesulfonic acid; and

(vi) 2-chloro-1,1,2-trifluoroethanesulfonic acid;

optionally in a non-reacting solvent, with a preformed porous silica support;

(b) allowing sufficient time for at least some of the at least one fluorosulfonic acid to be absorbed by the support to form an acid-impregnated silica; and

(c) drying the acid-impregnated porous silica to remove therefrom substantially all of the non-reacting solvent and water, if any, contained therein.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 is a GC tracing of the products obtained from the isomerization of 1-dodecene using the microcomposite $HCF_2CF_2SO_3H$ (without silica).

Figure 2 is a GC tracing of the products obtained from the isomerization of 1-dodecene using $HCF_2CF_2SO_3H$ on silica.

DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a process for isomerizing α-olefins using as the catalyst a porous microcomposite comprising at least one fluorinated sulfonic acid on silica.

Definitions

In this disclosure a number of terms and abbreviations are used. The following definitions are provided.

By "alkyl" is meant a monovalent radical having the general Formula C_nH_{2n+1}. "Monovalent" means having a valence of one.

By "catalyst" is meant a substance that affects the rate of the reaction but not the reaction equilibrium, and emerges from the process chemically unchanged.

The present invention provides a process for making internal olefins comprising forming a reaction mixture comprising (1) at least one α-olefin having from 4 to 25 carbons, and (2) at least one porous microcomposite comprising at least one fluorinated sulfonic acid and silica made by a process comprising the steps of:

(a) contacting, in the presence of water:

(1) at least one silica precursor;

(2) at least one fluorosulfonic acid selected from the group consisting of:

(i) 1,1,2,2-tetrafluoroethanesulfonic acid;

(ii) 1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonic acid;

(iii) 1,1,2-trifluoro-2-(trifluoromethoxy)ethanesulfonic acid;

(iv) 1,1,2-trifluoro-2-(perfluoropropoxy)ethanesulfonic acid;

(v) 1,1,2,3,3,3-hexafluoropropanesulfonic acid; and

(vi) 2-chloro-1,1,2-trifluoroethanesulfonic acid; and

optionally at least one inorganic acid; and

(3) optionally, a non-reacting solvent; to form a mixture;

(b) aging the mixture to form a gelled mixture; and

(c) drying the gelled mixture to remove substantially all water and alcohol, if any, therein.

The α-olefin starting material comprises from about four carbons to about twenty-five carbons. In a more specific embodiment, the α-olefin starting material may comprise from about 12 carbons to about 18 carbons. The starting material may comprise either linear or branched olefins, however preferably the starting material will comprise greater than 60 mol% linear α-olefin. The starting material may also comprise from about 10 mol% to about 35 mol% branched α-olefin, from about 0 mol% to about 10 mol% linear internal olefin, and/or from about 0 mol% to about 10 mol% branched internal olefin. The olefin starting material may also be admixed with one or more inert hydrocarbons, such as paraffins, cycloparaffins, or aromatics, however preferably, the olefin starting material comprises at least 90% by weight of olefins.

Preparation of the porous microcomposite

The term "silica precursor" refers to a silicon and oxygen-containing compound capable of forming silica in the presence of water. For example, it is well known that a range of silicon alkoxides of the Formula $Si(OR)_4$, wherein R is $-CH_3$, $-C_2H_5$, or C3 to C6 straight-chain or branched alkyl, can be hydrolyzed and condensed to form a silica network. A silica network is a known concept in the art and is described in Brinker, C. J.

and G. W. Scherer, Sol-Gel Science (Academic Press, NY, 1990). Preferably R is methyl or ethyl. Such precursors include tetramethoxysilane (tetramethyl orthosilicate), tetraethoxysilane (tetraethyl orthosilicate), tetrapropoxysilane, tetrabutoxysilane. Also included, as a silica precursor is silicon tetrachloride. Further silica precursors comprise organically modified silica, for example, $CH_3Si(OCH_3)_3$, $PhSi(OCH_3)_3$ where Ph is phenyl, and $(CH_3)_2Si(OCH_3)_2$. Other silica precursors include metal silicates, such as potassium silicate, sodium silicate, and lithium silicate. Potassium, sodium, or lithium ions can be removed using a cation exchange resin, such as DOWEX® (Dow Chemical, Midland, Mich.), that generates polysilicic acid which gels upon aging and drying.

An inorganic acid or a fluorinated sulfonic acid selected from the group consisting of 1,1,2,2-tetrafluoroethanesulfonic acid, 1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonic acid, 1,1,2-trifluoro-2-(trifluoromethoxy)ethanesulfonic acid, 1,1,2-trifluoro-2-(perfluoropropoxy)ethanesulfonic acid, 1,1,2,3,3,3-hexafluoropropanesulfonic acid, and 2-chloro-1,1,2-trifluoroethanesulfonic acid may be used to hydrolyze silicon alkoxides or organically modified silicon alkoxides. Suitable inorganic acids include hydrochloric acid, sulfuric acid, and nitric acid.

The at least one fluorinated sulfonic acid may be synthesized as described in the following references: U.S. Patent No. 2,403,207, Rice, *et al.* (Inorg. Chem., 1991, 30:4635-4638), Coffman, *et al.* (J. Org. Chem., 1949, 14:747-753 and Koshar, *et al.* (J. Am. Chem. Soc. (1953) 75:4595-4596), and can be used in either hydrated or anhydrous forms.

The non-reacting solvent may be a lower aliphatic alcohol such as methanol, 1-propanol, 2-propanol, and *n*-butanol. Other suitable solvents include acetonitrile, diethyl ether, dimethyl formamide, dimethylsulfoxide, nitromethane, tetrahydrofuran and acetone.

Aging of the mixture may be carried out under air. Alternatively, the mixture may be aged under a flowing, non-reactive gas such as argon, nitrogen or helium, or under a vacuum. The temperature for aging of the mixture may be from about 15°C to about 150°C. Gelation of the mixture

will be dependent on a number of factors such as the amount of water present, temperature, solvent, concentrations, and the acid or acids used. See Brinker, C. J. and G. W. Scherer, *supra*, pages 518-523 for a discussion of silica gel formation.

Drying of the gelled mixture to remove substantially all remaining water and/or alcohol can be carried out as described for aging. The gelled mixture is preferably dried under an inert gas such as nitrogen at a temperature from about 50 °C to about 150 °C.

The microcomposite of the present invention exists as a particulate solid that is glass-like in nature, typically 0.1 to 4 millimeters in size and structurally hard, similar to dried silica gels. The porous nature of the material is evident from the high surface areas measured for these glass-like pieces. Typical pore diameters are in the range of about 0.5 to about 75 nanometers; preferably the pore diameters are in the range of about 0.5 to about 25 nanometers. The weight percentage of fluorinated sulfonic acid relative to silica is from about 0.1% to about 90%, that is, acid is about 0.1% to 90%, silica is about 99.9% to 10%. Optionally, the hard glass-like product can be comminuted, such as by grinding with a pestle and mortar.

In another embodiment, the porous microcomposite used in the isomerization reaction is prepared from a preformed silica support. Thus, the present invention also provides a process for making internal olefins comprising forming a reaction mixture comprising (1) at least one α-olefin having from 4 to 25 carbons, and (2) of at least one porous microcomposite comprising at least one fluorinated sulfonic acid and silica made by a process comprising the steps of:

(a) contacting at least one fluorosulfonic acid selected from the group consisting of:

(i) 1,1,2,2-tetrafluoroethanesulfonic acid;

(ii) 1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonic acid;

(iii) 1,1,2-trifluoro-2-(trifluoromethoxy)ethanesulfonic acid;

(iv) 1,1,2-trifluoro-2-(perfluoropropoxy)ethanesulfonic acid;

(v) 1,1,2,3,3,3-hexafluoropropanesulfonic acid; and

(vi) 2-chloro-1,1,2-trifluoroethanesulfonic acid;

optionally in a non-reacting solvent, with a preformed porous silica support;

(b) allowing sufficient time for at least some of the at least one fluorosulfonic acid to be absorbed by the support to form an acid-impregnated silica; and

(c) drying the acid-impregnated porous silica to remove therefrom substantially all of the non-reacting solvent and water, if any, contained therein.

The preformed porous silica support may be obtained commercially from, for example, PQ Corporation (Valley Forge, PA), W.R. Grace (Baltimore, MD) or Aldrich (St. Louis, MO). An example is Silica Gel Beads (2-3 millimeter amorphous silicon dioxide beads) from PQ Corporation.

The non-reacting solvent may be a lower aliphatic alcohol such as methanol, 1-propanol, 2-propanol, and n-butanol. Other suitable solvents include acetonitrile, diethyl ether, dimethyl formamide, dimethylsulfoxide, nitromethane, tetrahydrofuran and acetone.

Drying of the acid-impregnated porous silica may be carried out under air. Alternatively, the acid-impregnated porous silica may be aged under a flowing, non-reactive gas such as argon, nitrogen or helium, or under a vacuum. The temperature for drying is from about 15 °C to about 150 °C. Preferably the acid-impregnated porous silica is dried under an inert gas such as nitrogen at a temperature from about 50 °C to about 150 °C.

The weight percentage of fluorinated sulfonic acid relative to silica is from about 0.1% to about 90%; the weight percent of the fluorinated sulfonic acid will depend on the pore volume of the preformed support.

It is believed that the highly porous structure of the microcomposite comprises a continuous silicon oxide phase that absorbs the highly dispersed fluorinated sulfonic acid catalyst within and throughout a

connected network of porous channels. The porous nature of the material can be readily demonstrated, for example, by solvent absorption. The microcomposite can be observed to emit bubbles, which are evolved due to the displacement of the air from within the porous network.

The porous microcomposite is used in the isomerization reaction at a concentration of from about 0.1% to about 20% by weight of the total weight of the α-olefin(s) at the start of the reaction. In a more specific embodiment, the porous microcomposite is used at a concentration of from about 0.1% to about 10% by weight of the total weight of the α-olefin(s) at the start of the reaction. In an even more specific embodiment, the porous microcomposite is used at a concentration of from about 0.1% to about 5% by weight of the total weight of the α-olefin(s) at the start of the reaction.

The isomerization reaction is preferably carried out at a temperature of from about 50°C to about 175°C. In a more specific embodiment, the reaction is carried out at a temperature of from about 50°C to about 120°C.

The isomerization reaction is preferably carried out under an inert atmosphere, such as nitrogen, argon or helium. The reaction may be performed at atmospheric pressure, or at pressures above atmospheric pressure.

The time for the reaction will depend on many factors, such as the reactants, reaction conditions and reactor. One skilled in the art will know to adjust the time for the reaction to achieve optimal isomerization of the α-olefins.

The process of the present invention may be carried out in batch, sequential batch (i.e., a series of batch reactors) or in continuous mode in any of the equipment customarily employed for continuous process (see for example, H.S. Fogler, Elementary Chemical Reaction Engineering, Prentice-Hall, Inc., N.J., USA).

The isomerization product(s) may be recovered from the porous microcomposite by any suitable method known to those skilled in the art,

including decantation. The porous microcomposite may be reused in subsequent reactions.

EXAMPLES

General Materials and Methods

The following abbreviations are used:

Milliliter is abbreviated ml; gram is abbreviated g; Centigrade is abbreviated C; meter is abbreviated m; cubic centimeter is abbreviated cc; nanometer is abbreviated nm; gas chromatography is abbreviated GC; tetramethyl orthosilicate is abbreviated TMOS, tetraethyl orthosilicate is abbreviated TEOS; weight percent is abbreviated wt%.

Acetonitrile, oleum (20% SO_3), sodium sulfite (Na_2SO_3, 98%), and acetone were obtained from Acros (Hampton, NH). Potassium metabisulfite ($K_2S_2O_5$, 99%), was obtained from Mallinckrodt Laboratory Chemicals (Phillipsburg, NJ). Tetramethyl orthosilicate, tetraethyl orthosilicate HCl, *p*-xylene, potassium sulfite hydrate ($KHSO_3 \bullet xH_2O$, 95%), sodium bisulfite ($NaHSO_3$), diethyl ether, trifluoromethanesulfonic acid and 1-dodecene were obtained from Aldrich (St. Louis, MO). Sulfuric acid was obtained from EMD Chemicals, Inc. (Gibbstown, NJ). Perfluoro(ethyl vinyl ether), perfluoro(methyl vinyl ether), hexafluoropropene and tetrafluoroethylene were obtained from DuPont Fluoroproducts (Wilmington, DE). 1,1,2,2-Tetrafluoro-2-(pentafluoroethoxy)sulfonate was obtained from SynQuest Laboratories, Inc. (Alachua, FL).

Preparation of Fluorosulfonic Acid Precursors

(A) Synthesis of potassium 1,1,2,2-tetrafluoroethanesulfonate (TFES-K):

A 1-gallon Hastelloy® C276 reaction vessel was charged with a solution of potassium sulfite hydrate (176 g, 1.0 mol), potassium metabisulfite (610 g, 2.8 mol) and deionized water (2000 ml). The pH of this solution was 5.8. The vessel was cooled to 18°C, evacuated to 0.10 MPa, and purged with nitrogen. The evacuate/purge cycle was repeated two more times. To the vessel was then added tetrafluoroethylene (TFE,

66 g), and it was heated to 100°C at which time the inside pressure was 1.14 MPa. The reaction temperature was increased to 125°C and kept there for 3 hr. As the TFE pressure decreased due to the reaction, more TFE was added in small aliquots (20-30 g each) to maintain operating pressure roughly between 1.14 and 1.48 MPa. Once 500 g (5.0 mol) of TFE had been fed after the initial 66 g precharge, the vessel was vented and cooled to 25°C. The pH of the clear light yellow reaction solution was 10-11. This solution was buffered to pH 7 through the addition of potassium metabisulfite (16 g).

The water was removed *in vacuo* on a rotary evaporator to produce a wet solid. The solid was then placed in a freeze dryer (Virtis Freezemobile 35xl; Gardiner, NY) for 72 hr to reduce the water content to approximately 1.5 wt% (1387 g crude material). The theoretical mass of total solids was 1351 g. The mass balance was very close to ideal and the isolated solid had slightly higher mass due to moisture. This added freeze drying step had the advantage of producing a free-flowing white powder whereas treatment in a vacuum oven resulted in a soapy solid cake that was very difficult to remove and had to be chipped and broken out of the flask.

The crude TFES-K can be further purified and isolated by extraction with reagent grade acetone, filtration, and drying.

^{19}F NMR (D_2O) δ -122.0 (dt, J_{FH} = 6 Hz, J_{FF} = 6 Hz, 2F); -136.1 (dt, J_{FH} = 53 Hz, 2F).

^{1}H NMR (D_2O) δ 6.4 (tt, J_{FH} = 53 Hz, J_{FH} = 6 Hz, 1H).

% Water by Karl-Fisher titration: 580 ppm.

Analytical calculation for $C_2HO_3F_4SK$: C, 10.9: H, 0.5: N, 0.0

Experimental results: C, 11.1: H, 0.7: N, 0.2.

Mp (DSC): 242°C.

TGA (air): 10% wt. loss @ 367°C, 50% wt. loss @ 375°C.

TGA (N_2): 10% wt. loss @ 363°C, 50% wt. loss @ 375°C.

(B) Synthesis of potassium-1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonate (TPES-K):

A 1-gallon Hastelloy® C276 reaction vessel was charged with a solution of potassium sulfite hydrate (88 g, 0.56 mol), potassium metabisulfite (340 g, 1.53 mol) and deionized water (2000 ml). The vessel was cooled to 7°C, evacuated to 0.05 MPa, and purged with nitrogen. The evacuate/purge cycle was repeated two more times. To the vessel was then added perfluoro(ethyl vinyl ether) (PEVE, 600 g, 2.78 mol), and it was heated to 125°C at which time the inside pressure was 2.31 MPa. The reaction temperature was maintained at 125°C for 10 hr. The pressure dropped to 0.26 MPa at which point the vessel was vented and cooled to 25°C. The crude reaction product was a white crystalline precipitate with a colorless aqueous layer (pH = 7) above it.

The ^{19}F NMR spectrum of the white solid showed pure desired product, while the spectrum of the aqueous layer showed a small but detectable amount of a fluorinated impurity. The desired isomer is less soluble in water so it precipitated in isomerically pure form.

The product slurry was suction filtered through a fritted glass funnel, and the wet cake was dried in a vacuum oven (60°C, 0.01 MPa) for 48 hr. The product was obtained as off-white crystals (904 g, 97% yield).

^{19}F NMR (D_2O) δ -86.5 (s, 3F); -89.2, -91.3 (subsplit ABq, J_{FF} = 147 Hz, 2F);

-119.3, -121.2 (subsplit ABq, J_{FF} = 258 Hz, 2F); -144.3 (dm, J_{FH} = 53 Hz, 1F).

^1H NMR (D_2O) δ 6.7 (dm, J_{FH} = 53 Hz, 1H).

Mp (DSC) 263°C.

Analytical calculation for $C_4HO_4F_8SK$: C, 14.3: H, 0.3 Experimental results: C, 14.1: H, 0.3.

TGA (air): 10% wt. loss @ 359°C, 50% wt. loss @ 367°C.

TGA (N_2): 10% wt. loss @ 362°C, 50% wt. loss @ 374°C.

(C) Synthesis of potassium-1,1,2-trifluoro-2-(trifluoromethoxy)ethanesulfonate (TTES-K)

A 1-gallon Hastelloy® C276 reaction vessel was charged with a solution of potassium sulfite hydrate (114 g, 0.72 mol), potassium metabisulfite (440 g, 1.98 mol) and deionized water (2000 ml). The pH of this solution was 5.8. The vessel was cooled to -35°C, evacuated to 0.08 MPa, and purged with nitrogen. The evacuate/purge cycle was repeated two more times. To the vessel was then added perfluoro(methyl vinyl ether) (PMVE, 600 g, 3.61 mol) and it was heated to 125°C at which time the inside pressure was 3.29 MPa. The reaction temperature was maintained at 125°C for 6 hr. The pressure dropped to 0.27 MPa at which point the vessel was vented and cooled to 25°C. Once cooled, a white crystalline precipitate of the desired product formed leaving a colorless clear aqueous solution above it (pH = 7).

The ^{19}F NMR spectrum of the white solid showed pure desired product, while the spectrum of the aqueous layer showed a small but detectable amount of a fluorinated impurity.

The solution was suction filtered through a fritted glass funnel for 6 hr to remove most of the water. The wet cake was then dried in a vacuum oven at 0.01 MPa and 50°C for 48 hr. This gave 854 g (83% yield) of a white powder. The final product was isomerically pure (by ^{19}F and ^{1}H NMR) since the undesired isomer remained in the water during filtration.

^{19}F NMR (D_2O) δ -59.9 (d, J_{FH} = 4 Hz, 3F); -119.6, -120.2 (subsplit ABq, J = 260 Hz, 2F); -144.9 (dm, J_{FH} = 53 Hz, 1F).

^{1}H NMR (D_2O) δ 6.6 (dm, J_{FH} = 53 Hz, 1H).

% Water by Karl-Fisher titration: 71 ppm.

Analytical calculation for $C_3HF_6SO_4K$: C, 12.6: H, 0.4: N, 0.0

Experimental results: C, 12.6: H, 0.0: N, 0.1.

Mp (DSC) 257°C.

TGA (air): 10% wt. loss @ 343°C, 50% wt. loss @ 358°C.

TGA (N_2): 10% wt. loss @ 341°C, 50% wt. loss @ 357°C.

(D) Synthesis of sodium 1,1,2,3,3,3-hexafluoropropanesulfonate (HFPS-Na)

A 1-gallon Hastelloy® C reaction vessel was charged with a solution of anhydrous sodium sulfite (25 g, 0.20 mol), sodium bisulfite 73 g, (0.70 mol) and of deionized water (400 ml). The pH of this solution was 5.7. The vessel was cooled to 4°C, evacuated to 0.08 MPa, and then charged with hexafluoropropene (HFP, 120 g, 0.8 mol, 0.43 MPa). The vessel was heated with agitation to 120°C and kept there for 3 hr. The pressure rose to a maximum of 1.83 MPa and then dropped down to 0.27 MPa within 30 minutes. At the end, the vessel was cooled and the remaining HFP was vented, and the reactor was purged with nitrogen. The final solution had a pH of 7.3.

The water was removed *in vacuo* on a rotary evaporator to produce a wet solid. The solid was then placed in a vacuum oven (0.02 MPa, 140°C, 48 hr) to produce 219 g of white solid which contained approximately 1 wt% water. The theoretical mass of total solids was 217 g.

The crude HFPS-Na can be further purified and isolated by extraction with reagent grade acetone, filtration, and drying.

^{19}F NMR (D_2O) δ -74.5 (m, 3F); -113.1, -120.4 (ABq, J = 264 Hz, 2F); -211.6 (dm, 1F).

^{1}H NMR (D_2O) δ 5.8 (dm, J_{FH} = 43 Hz, 1H).

Mp (DSC) 126°C.

TGA (air): 10% wt. loss @ 326°C, 50% wt. loss @ 446°C.

TGA (N_2): 10% wt. loss @ 322°C, 50% wt. loss @ 449°C.

Preparation of Catalysts From the Corresponding Anions

(E) Synthesis of 1,1,2,2-tetrafluoroethanesulfonic acid (TFESA)

A 100 ml round bottomed flask with a sidearm and equipped with a digital thermometer and magnetic stirr bar was placed in an ice bath under positive nitrogen pressure. To the flask was added 50 g crude TFES-K (from synthesis (A) above), 30 g of concentrated sulfuric acid (95-98%)

and 78 g oleum (20 wt% SO_3) while stirring. The amount of oleum was chosen such that there would be a slight excess of SO_3 after the SO_3 reacted with and removed the water in the sulfuric acid and the crude TFES-K. The mixing caused a small exotherm, which was controlled by the ice bath. Once the exotherm was over, a distillation head with a water condenser was placed on the flask, and the flask was heated under nitrogen behind a safety shield. The pressure was slowly reduced using a PTFE membrane vacuum pump (Buchi V-500, Buchi Analytical, Inc., Wilmington, DE) in steps of 100 Torr (13 kPa) in order to avoid foaming. A dry-ice trap was placed between the distillation apparatus and the pump to collect any excess SO_3. When the pot temperature reached 120°C and the pressure was held at 20-30 Torr (2.7-4.0 kPa) a colorless liquid started to reflux which distilled at 110°C and 31 Torr (4.1 kPa). A forerun of lower-boiling impurity (2.0 g) was obtained before collecting 28 g of the desired colorless acid, TFESA.

It was calculated that approximately 39.8 g TFES-K was present in the 50 g of impure TFES-K. Thus, the 28 g of product is an 85% yield of TFESA from TFES-K, as well as an 85% overall yield from TFE. Analysis gave the following results: 19F NMR (CD_3OD) -125.2 (dt, $^3J_{FH}$ = 6 Hz, $^3J_{FF}$ = 8Hz, 2F); -137.6 (dt, $^2J_{FH}$ = 53 Hz, 2F). 1H NMR (CD3OD). 6.3 (tt, $^3J_{FH}$ = 6 Hz, $^2J_{FH}$ = 53 Hz, 1H).

(F) Synthesis of 1,1,2,3,3,3-hexafluoropropanesulfonic acid (HFPSA)

A 100 ml round bottomed flask with a sidearm and equipped with a digital thermometer and magnetic stirr bar was placed in an ice bath under positive nitrogen pressure. To the flask was added 50 g crude sodium hexafluoropropanesulfonate (HFPS-Na) (from synthesis (D) above), 30 g of concentrated sulfuric acid (95-98%) and 58.5 g oleum (20 wt% SO_3) while stirring.

The amount of oleum was chosen such that there would be a slight excess of SO_3 after the SO_3 reacted with and removed the water in the sulfuric acid and the crude HFPSA. The mixing caused a small exotherm, which was controlled by the ice bath. Once the exotherm was over, a

distillation head with a water condenser was placed on the flask, and the flask was heated under nitrogen behind a safety shield. The pressure was slowly reduced using a PTFE membrane vacuum pump in steps of 100 Torr (13 kPa) in order to avoid foaming. A dry-ice trap was placed between the distillation apparatus and the pump to collect any excess SO_3. When the pot temperature reached 100°C and the pressure was held at 20-30 Torr (2.7-4 kPa) a colorless liquid started to reflux and later distilled at 118°C and 23 Torr (3.1 kPa). A forerun of lower-boiling impurity (1.5 g) was obtained before collecting 36.0 g of the desired acid, hexafluoropropanesulfonic acid (HFPSA).

It was calculated that approximately 44 g HFPS-Na was present in 50 g of impure HFPS-Na. Thus, the 36.0 g of HFPSA product was an 89% yield from HFPS-Na, as well as an 84% overall yield from HFP.

^{19}F NMR (D_2O) -74.5m, 3F); -113.1, -120.4 (ABq, J = 264 Hz, 2F); -211.6 (dm, 1F).

^{1}H NMR (D_2O) 5.8 (dm, $2J_{FH}$ = 43 Hz, 1H).

(G) Synthesis of 2-chloro-1,1,2-trifluoroethanesulfonic acid

A 1-gallon Hastelloy® C276 reaction vessel was charged with a solution of 240 g sodium bisulfite hydrate ($NaHSO_3 \cdot H_2O$, 95%), 128 g sodium metabisulfite ($Na_2S_2O_5$, 99%) and 800 ml of deionized water. The vessel was cooled to 18°C, evacuated to 0 kPa, and purged with nitrogen. The evacuate/purge cycle was repeated two more times. To the vessel was then added 233 g of chlorotrifluoroethylene in 50 g amounts until the last 33 g at a temperature of 125°C which time the inside pressure is 250 psi (1.83 MPa). The reaction temperature was maintained at 125°C for 3 hr., and then cooled to room temperature. The water was removed *in vacuo* on a rotary evaporator to produce a yellow/white solid which contained in part the sodium salt, $CClHFCF_2SO_3H$. To 160 g of the yellow/white solid was added 250 ml of 98% sulfuric acid in a round bottomed flask. The mixture was heated and the acid monohydrate was distilled under vacuum at 119-120°C (0.8 mm Hg (107 Pa)). Thionyl

chloride (70 ml) was then added to the acid monohydrate under a nitrogen atmosphere; the mixture was heated at 50°C for one hour, and the excess thionyl chloride was removed under vacuum. The acid was removed by distillation under vacuum to give pure $HClCFCF_2SO_3H$, as shown by NMR.

Synthesis of porous microcomposites useful for the invention.

(H) Preparation of microcomposite of TFESA and silica

Tetramethyl orthosilicate (4 g), water (4.7 g), and 0.04 M HCl (0.05 g) were stirred together for 15 minutes to hydrolyze the tetraalkoxide. $HCF_2CF_2SO_3H$ (0.5 g) was then added, and the mixture was stirred for several hours. The resulting gel was left to dry in air in an uncovered beaker at room temperature for four days. Drying of the composite was completed in a 100°C vacuum oven for 48 hours. The surface area, pore volume and pore diameter were determined by the Brunauer-Emmett-Teller (BET; see C. N. Satterfield, Heterogeneous Catalysis in Industrial Practice, 2nd Edition,1991, McGraw-Hill, Inc., NY, pages 134-139) method to be 565 m^2/g, 0.32 cc/g and 2.3 nm.

(I) Preparation of microcomposite of TFESA and silica - Slow Drying

Tetramethyl orthosilicate (16 g), water (18.8 g) and 0.04 M HCl (0.2 g) were stirred together for 15 minutes to hydrolyze the tetraalkoxide. $HCF_2CF_2SO_3H$ (2 g) was then added, and the mixture was stirred in a loosely capped jar for 72 hours to gel. The resulting gel was dried slowly in a 75°C nitrogen oven (still in a loosely capped jar) for 7 days. Drying of the composite was completed in a 100°C vacuum oven for 48 hours. The surface area, pore volume and pore diameter were determined to be 584 m^2/g, 0.39 cc/g and 2.7 nm, respectively.

(J) Preparation of microcomposite of TFESA and silica - Rapid Drying

Tetramethyl orthosilicate (8 g), water (9.4 g) and 0.04 M HCl (0.1 g) were stirred together for 15 minutes to hydrolyze the tetraalkoxide. $HCF_2CF_2SO_3H$ (1 g) was then added; the mixture was stirred for 1 minute

to mix and then placed immediately in a 90°C oven, in an open beaker under a nitrogen stream for 48 hours. Drying of the composite was completed in a 100°C vacuum oven for 72 hours. The surface area, pore volume and pore diameter were determined by BET to be 506 m^2/g, 0.29 cc/g and 2.3 nm respectively.

(K) Preparation of microcomposite of TFESA and silica

Tetramethyl orthosilicate (4 g), water (4.7 g) and 0.04 M HCl (0.05 g) were stirred together for 15 minutes to hydrolyze the tetraalkoxide. $HCF_2CF_2SO_3H$ (1.59 g) was then added, and the mixture was stirred to gel (less than about two hours). The resulting gel was left to dry in air in an uncovered beaker at room temperature for four days. Drying of the composite was completed in a 100°C vacuum oven for 48 hours. The composite comprised approximately 50% by weight of the acid relative to the weight of the silica. The surface area, pore volume and pore diameter were determined by BET to be 597 m^2/g, 0.42 cc/g and 2.8 nm, respectively.

(L) Preparation of microcomposite of TFESA and silica

Tetramethyl orthosilicate (8 g), water (9.4 g) and 0.04 M HCl (0.1 g) were stirred together for 15 minutes to hydrolyze the tetraalkoxide. $HCF_2CF_2SO_3H$ (0.45 g) was then added, and the mixture was stirred to gel (less than about two hours). The resulting gel was left to dry in air in an uncovered beaker at room temperature for four days. Drying of the composite was completed in a 100°C vacuum oven for 48 hours. The composite comprised approximately 12.5% by weight of the acid relative to the weight of the silica. The surface area, pore volume and pore diameter were determined by BET to be 576 m^2/g, 0.25 cc/g and 1.4 nm, respectively.

(M) Preparation of microcomposite of TFESA and silica

Tetramethyl orthosilicate (16 g), water (18.8 g) and 0.04 M HCl (0.2 g) were stirred together for 15 minutes to hydrolyze the tetraalkoxide. $HCF_2CF_2SO_3H$ (0.33 g) was then added, and the mixture was stirred to gel (less than about two hours). The resulting gel was left to dry in air in an uncovered beaker at room temperature for four days. Drying of the composite was completed in a 100°C vacuum oven for 48 hours. The composite comprised approximately 5% by weight of the acid relative to the weight of the silica. The surface area, pore volume and pore diameter were determined by BET to be 571 m^2/g, 0.24 cc/g and 1.4 nm, respectively.

(N) Preparation of microcomposite of TFESA and silica

Tetramethyl orthosilicate (2g), water (2.35 g) and 0.04 M HCl (0.025 g) were stirred together for 15 minutes to hydrolyze the tetraalkoxide. $HCF_2CF_2SO_3H$ (2.37 g) was then added, and the mixture was stirred to gel (less than about 20 seconds). The resulting gel was left to dry in air in an uncovered beaker at room temperature for three days and then in a 70°C oven under nitrogen for 24 hours. Drying of the composite was completed in a 100°C vacuum oven for 24 hours. The composite comprised approximately 75% by weight of the acid relative to the weight of the silica.

(O) Preparation of microcomposite of TFESA and silica

Tetraethyl orthosilicate (14 g), water (12 g) and 1 M HCl (0.1 g) were stirred together for 2 hours to hydrolyze the tetraalkoxide. $HCF_2CF_2SO_3H$ (1 g) was then added, and the mixture was stirred in an open beaker to gel (less than about two hours). The resulting gel was left to dry in air in an uncovered beaker at room temperature for 48 hours. Drying of the composite was completed in a 100°C vacuum oven for 24 hours. The surface area, pore volume and pore diameter were determined by BET to be 342 m^2/g, 0.16 cc/g and 1.9 nm, respectively.

(P) Preparation of microcomposite of HFPSA and silica

Tetramethyl orthosilicate (8 g), water (9.4 g) and 0.04 M HCl (0.1 g) were stirred together for 15 minutes to hydrolyze the tetraalkoxide. $CF_3HCFCF_2SO_3H$ (1 g) was then added, and the mixture was stirred to gel (less than about two hours). The resulting gel was left to dry in air in an uncovered beaker at room temperature. Drying of the composite was completed in a 100°C vacuum oven.

(Q) Preparation of 2-chloro-1,1,2-trifluoroethanesulfonic acid

Tetramethyl orthosilicate (8 g), water (9.4 g) and 0.04 M HCl (0.1 g) were stirred together for 15 minutes to hydrolyze the tetraalkoxide. $HCFClCF_2SO_3H$ (1 g) was then added, and the mixture was stirred to gel (less than about two hours). The resulting gel was left to dry in air in an uncovered beaker at room temperature. Drying of the composite was completed in a 100°C vacuum oven.

(R) Preparation of a microcomposite of $HCF_2CF_2SO_3H{\cdot}H_2O$ on a preformed support

$HCF_2CF_2SO_3H{\cdot}H_2O$ (50 g) was added to 125 of diethyl ether. This mixture was added to 140 g of a spherical silica support (Silica Gel beads, 2-3 mm amorphous silicon dioxide beads, PQ Corporation, Valley Forge, PA) in a larger glass bottle. The bottle and contents were gently shaken for twenty minutes. The material was dried using a roto-vap at 35°C under vacuum for 2 hours.

(S) Preparation of a microcomposite of CF_3SO_3H (triflic acid) on a pre-formed support (Comparative Example)

CF_3SO_3H (5.1 g) was added to 16.7 g of diethyl ether. This mixture was added to 16 g of a spherical silica support (Silica Gel beads, 2-3 mm amorphous silicon dioxide beads, PQ Corporation, Valley Forge, PA) in a larger glass bottle. The bottle and contents were gently shaken for twenty

minutes. The material was dried using a roto-vap at 35°C under vacuum for 2 hours.

Examples 1 to 5 illustrate the use of microcomposites of the invention in isomerization reactions.

Example 1: Isomerization of 1-dodecene using $HCF_2CF_2SO_3H$ (Comparative Example)

In a nitrogen atmosphere, the acid catalyst $HCF_2CF_2SO_3H$ (0.5 g) was loaded into a dried Schlenk flask, followed by the addition of anhydrous 1-dodecene (15 ml). The flask was set up under a nitrogen blanket and stirred vigorously at 100°C for 2 hours. GC analysis of the products at 2 hours showed that <5% of the 1-dodecene was isomerized (see Figure 1).

Example 2: Isomerization of 1-dodecene using the microcomposite $HCF_2CF_2SO_3H$ on silica

The acid catalyst $HCF_2CF_2SO_3H$ supported on silica (24 wt% acid) was ground to a fine powder with a pestle and mortar. The finely ground powder (0.5 g) was then weighed into a vial, dried at 150°C under vacuum for at least four hours, and cooled under vacuum before transfer into a nitrogen atmosphere. The catalyst was loaded into a dried Schlenk flask, followed by the addition of anhydrous 1-dodecene (15 ml). The flask was set up under a nitrogen blanket and stirred vigorously at 100°C for 2 hours. GC analysis of the products at 2 hours showed that >80% of the 1-dodecene was isomerized (see Figure 2).

Example 3: Isomerization of 1-dodecene using the microcomposite $CF_3HCFCF_2SO_3H$ on silica

The acid catalyst $CF_3HCFCF_2SO_3H$ supported on silica was ground to a fine powder with a pestle and mortar. The finely ground powder (0.5 g) was then weighed into a vial, dried at 150°C under vacuum for at least four hours, and cooled under vacuum before transfer into a nitrogen

atmosphere. The catalyst was loaded into a dried Schlenk flask, followed by the addition of anhydrous 1-dodecene (15 ml). The flask was set up under a nitrogen blanket and stirred vigorously at 100°C for 2 hours. GC analysis of the products at 2 hours showed that >80% of the 1-dodecene was isomerized.

Example 4: Isomerization of 1-dodecene using the microcomposite $HCFClCF_2SO_3H$ on silica

The acid catalyst $HCFClCF_2SO_3H$ supported on silica was ground to a fine powder with a pestle and mortar. The finely ground powder (0.5 g) was then weighed into a vial, dried at 150°C under vacuum for at least four hours, and cooled under vacuum before transfer into a nitrogen atmosphere. The catalyst was loaded into a dried Schlenk flask, followed by the addition of anhydrous 1-dodecene (15 ml). The flask was set up under a nitrogen blanket and stirred vigorously at 100°C for 2 hours. GC analysis of the products at 2 hours showed that >80% of the 1-dodecene was isomerized.

Example 5: Isomerization of 1-dodecene using the microcomposite $HCF_2CF_2SO_3H$ on silica; large scale reaction

The acid catalyst $HCF_2CF_2SO_3H$ on silica was ground to a fine powder with a pestle and mortar. The finely ground powder (0.5 g) was then weighed into a vial, dried at 150°C under vacuum for at least four hours, and cooled under vacuum before transfer into a nitrogen atmosphere. The catalyst was loaded into a dried Schlenk flask, followed by the addition of anhydrous 1-dodecene (150 ml). The flask was set up under a nitrogen blanket and stirred vigorously at 100°C for 2 hours. GC analysis of the products at 7 hours showed that >95% of the 1-dodecene was isomerized.

CLAIMS

1. A process for making internal olefins comprising forming a reaction mixture comprising (1) at least one α-olefin having from 4 to 25 carbons, and (2) at least one porous microcomposite comprising at least one fluorinated sulfonic acid and silica made by a process comprising the steps of:

(a) contacting, in the presence of water:

(1) at least one silica precursor;

(2) at least one fluorosulfonic acid selected from the group consisting of:

(i) 1,1,2,2-tetrafluoroethanesulfonic acid;

(ii) 1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonic acid;

(iii) 1,1,2-trifluoro-2-(trifluoromethoxy)ethanesulfonic acid;

(iv) 1,1,2-trifluoro-2-(perfluoropropoxy)ethanesulfonic acid;

(v) 1,1,2,3,3,3-hexafluoropropanesulfonic acid; and

(vi) 2-chloro-1,1,2-trifluoroethanesulfonic acid;

optionally at least one inorganic acid; and

(3) optionally, a non-reacting solvent; to form a mixture;

(b) aging the mixture to form a gelled mixture; and

(c) drying the gelled mixture to remove substantially all water and non-reacting solvent, if any, therein.

2. The process of Claim 1 wherein the silica precursor is selected from the group consisting of:

(i) silicon alkoxides of the Formula $Si(OR)_4$, wherein R is $-CH_3$, $-C_2H_5$, or C3 to C6 straight-chain or branched alkyl;

(ii) silicon tetrachloride;

(iii) $CH_3Si(OCH_3)_3$;

(iv) $PhSi(OCH_3)_3$, where Ph is phenyl;

(v) $(CH_3)_2Si(OCH_3)_2$;and

(vi) polysilicic acid.

3. The process of Claim 1 wherein the inorganic acid is selected from the group consisting of hydrochloric acid, sulfuric acid and nitric acid.

4. The process of Claim 1 wherein the porous microcomposite is used at a concentration of from about 0.1% to about 20% by weight of the weight of the α-olefin(s) at the start of the reaction.

5. The process of Claim 1 further comprising heating said reaction mixture to a temperature of about 50°C to about 175°C.

6. The process of Claim 1 wherein the reaction is carried out under an inert atmosphere at atmospheric pressure.

7. The process of Claim 6 wherein the inert atmosphere is nitrogen, helium or argon.

8. A process for making internal olefins comprising forming a reaction mixture comprising (1) at least one α-olefin having from 4 to 25 carbons, and (2) of at least one porous microcomposite comprising at least one fluorinated sulfonic acid and silica made by a process comprising the steps of:

(a) contacting at least one fluorosulfonic acid selected from the group consisting of:

(i) 1,1,2,2-tetrafluoroethanesulfonic acid;

(ii) 1,1,2-trifluoro-2-(perfluoroethoxy)ethanesulfonic acid;

(iii) 1,1,2-trifluoro-2-(trifluoromethoxy)ethanesulfonic acid;

(iv) 1,1,2-trifluoro-2-(perfluoropropoxy)ethanesulfonic acid;

(v) 1,1,2,3,3,3-hexafluoropropanesulfonic acid; and

(vi) 2-chloro-1,1,2-trifluoroethanesulfonic acid;

optionally in a non-reacting solvent, with a preformed porous silica support; and

(b) drying the acid-impregnated porous silica to remove therefrom substantially all of the non-reacting solvent and water, if any, contained therein.

9. The process of Claim 1 wherein the silica precursor is selected from the group consisting of:

(i) silicon alkoxides of the Formula $Si(OR)_4$, wherein R is $-CH_3$, $-C_2H_5$, or C3 to C6 straight-chain or branched alkyl;

(ii) silicon tetrachloride;

(iii) $CH_3Si(OCH_3)_3$;

(iv) $PhSi(OCH_3)_3$, where Ph is phenyl;

(v) $(CH_3)_2Si(OCH_3)_2$;and

(vi) polysilicic acid.

10. The process of Claim 8 wherein the porous microcomposite is used at a concentration of from about 0.1% to about 20% by weight of the weight of the α-olefin(s) at the start of the reaction.

11. The process of Claim 8 further comprising heating said reaction mixture to a temperature of about 50°C to about 175°C.

12. The process of Claim 8 wherein the reaction is carried out under an inert atmosphere at atmospheric pressure.

13. The process of Claim 11 wherein the inert atmosphere is nitrogen, helium or argon.

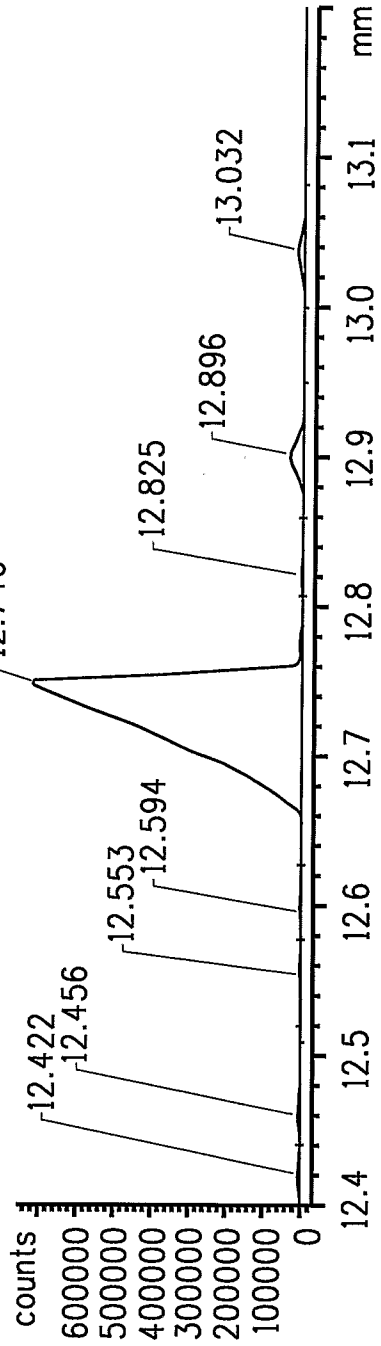

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FIG. 1

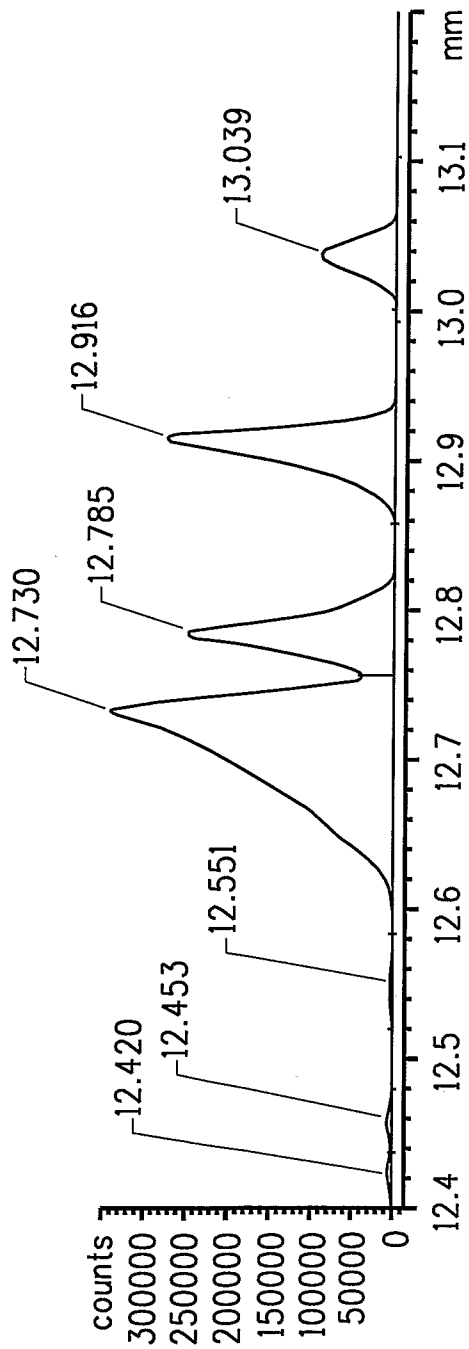
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FIG. 2