

lower (alkyl)ester of a fatty acid comprising combining the fatty acid, a lower alkanol and a catalyst of formula I or II under conditions wherein the catalyst catalyzes the formation of the corresponding lower (alkyl)ester. In a preferred embodiment, the fatty acid is present in an organic or synthetic feedstock such as an animal or vegetable oil that comprises a major portion of glycerol fatty acid esters, such as the mono-, di- and/or tri-esters.

[0018] Preferably the fatty acid portion of the ester or glyceride is derived from a (C_8 - C_{22}) fatty acid, preferably a (C_{10} - C_{18}) fatty acid, which is a saturated alkyl ester that optionally comprises 1-3 $CH=CH$ moieties in the alkyl chain. The (C_1 - C_3) alcohols are preferably methanol, ethanol, propanol or i-propyl alcohol, although higher alkanols such as (C_4 - C_6) alkanols may be useful in some applications. The alcohol is preferably used in a molar excess over the starting material acid and/or ester component of the feedstock, since such esterification/transesterification reactions are highly reversible.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] FIG. 1 depicts general synthetic routes to precursor compounds of formula I, (3, and 7), and 5.

[0020] FIG. 2 depicts synthetic routes to specific precursor compounds of formula I, 11 and 13 and 12.

[0021] FIG. 3 depicts synthetic routes to specific precursors of compounds of formula I and II (15 and 17).

[0022] FIG. 4 depicts a synthetic route to a precursor compound of a compound of formula I (20a) and salt (21a).

[0023] FIG. 5 depicts intermediates useful in the present invention.

[0024] FIG. 6 is a graph depicting the transesterification of soybean oil to methyl soyate in methanol at 25° C. with mesoporous silica supported superbases.

DETAILED DESCRIPTION OF THE INVENTION

[0025] Mesoporous Silicates

[0026] Mesoporous silicates useful in the present method typically have a particle size of about 50 nm to about 1 μ m. In one embodiment, the mesoporous silicates have a particle size of at least about 100 nm, or preferably at least about 200 nm. However, particle size is not critical to the practice of the invention and particulate bodies of larger size can be used in some cases, e.g., to facilitate separations. In another embodiment, the mesoporous silicates have a particle size of less than about 750 nm. As conventionally prepared, they are spherical, but they have also been prepared under conditions that yield other shapes such as rods. The articles of the invention can include mesoporous silicates of any shape, provided the pore structure is suitable for receiving the feedstock, e.g., is uniform and of an appropriate diameter.

[0027] The mesoporous silicate pores typically have a diameter of from about 1-100 nm. In one embodiment of the invention, the pores have a diameter of at least about 2 nm. In other embodiments, the pores have diameters of greater than about 5 nm, or greater than about 10 nm. Typically, the pores have a diameter of less than about 75 nm or less than about 50 nm.

[0028] The mesoporous silicate can be prepared from surfactant micelles of C_{10} - C_{16} alkyl(trialkyl)ammonium salts in water, followed by introduction into the solution of an alkyl orthosilicate, such as tetraethylorthosilicate (TEOS), and one or more functionalized silanes, such as one or more mercaptoalkyl-, chloroalkyl-, aminoalkyl-, carboxy-alkyl-, sulfonylalkyl-, arylalkyl-, alkynyl-, or alkenyl-silanes, wherein the (C_2 - C_{10})alkyl chain is optionally interrupted by $-S-S-$, amido($-C(=O)NR-$), $-O-$, ester($-C(=O)O-$), and the like. The aqueous mixture is stirred at moderate temperatures until the silicate precipitates, after which it is collected and dried. The surfactant "template" is then removed from the pores of the ordered silicate matrix, for example, by refluxing the silicate in aqueous-alcoholic HCl. The remaining solvent can be removed from the pores of the silicate by placing it under high vacuum. The functional groups incorporated onto the surface of the pores can be quantified and used as linker moieties to bind to the functionalized super base, or they can be further modified by attaching terminally-functionalized organic linker moieties that can be reacted with functional groups on Z. The polarity of the interior of the pores can also be adjusted by adding other functionalized silanes to the reaction mixture, including ones comprising non-polar inert groups such as aryl, perfluoroalkyl, alkyl, arylalkyl and the like. The exterior of the silicate matrix can also be functionalized by grafting organic moieties comprising functional groups thereto. These groups can in turn be employed to link the particles to catalytic moieties such as functionalized "superbase" catalysts.

[0029] Superbase-Functionalized Mesoporous Solid Catalysts

[0030] The three commercially available "superbases" of type 1, (1a-1c in FIG. 5) are exceptionally strong nonionic bases with pKa's of ca. 32 in acetonitrile and have superior catalytic activities for a wide variety of reactions including transesterification. See, e.g., U.S. Pat. No. 5,051,533. Their derivatives of type 2a-c are weaker but still very strong bases and catalysts and both types of homogeneous catalysts convert vegetable oils, including soybean oil, to their methyl esters at room temperature. These catalysts deprotonate alcohols to liberate alkoxide ion (the active species in the catalyst system) in concentrations effective for transesterification.

[0031] Compounds of types 1 and 2 lend themselves well to chemically bonding to mesoporous silica surfaces via trialkoxysilyl groups (see 11, 15 and 17). The $Si(OMe)_3$ group linker reacts with up to three SiOH groups in the silica to eliminate MeOH giving robust SiOSi anchors. Precursors 11, 15 and 17 per se homogeneously and efficiently catalyze soybean oil transesterification to soy methyl ester (i.e., 100% conversion of 200 mL of soybean oil in 400 mL of methanol in 24 to 36 h at room temperature using only 0.25 mmol of catalyst). These catalysts are greatly superior to commercially available amine-type nonionic bases or their polymer-mounted forms.

[0032] Intermediates 20a, 5c and 6b, have also been prepared, which are designed to take advantage of the vinyl group for linkage to mesoporous solid supports which comprise a mercaptoalkyl functional group already covalently bound thereto. The mercaptoalkyl groups react with vinyl groups to give strong CSC linkages. Such cata-