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(54) **Title**: METHODS FOR CATALYST SEPARATION AND RECOVERY

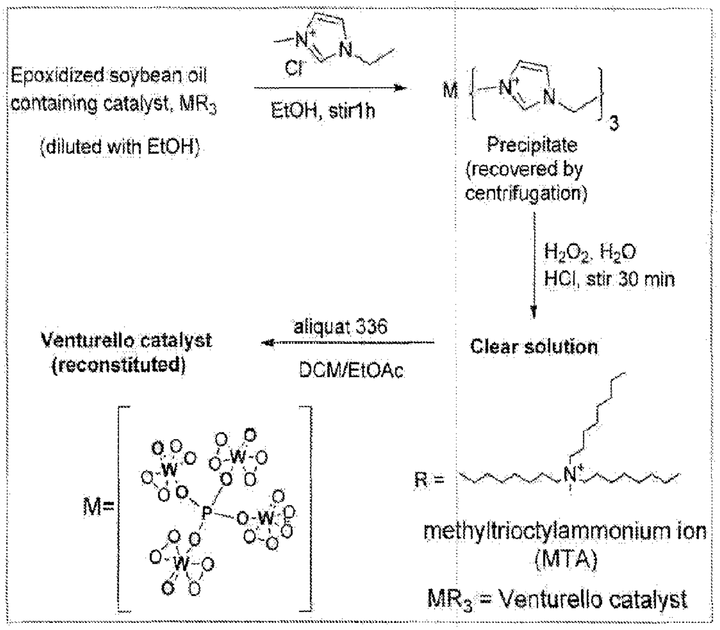

Fig. 1: Catalyst Separation by Complexation Followed by Precipitation and Catalyst Reconstitution

[Continued on next page]

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(57) Abstract: Disclosed herein are methods of separating a catalyst from a product mixture. Methods of reconstituting a catalyst are further disclosed. The present invention is also directed towards methods of recovering a catalyst from a product mixture.

TITLE

METHODS FOR CATALYST SEPARATION AND RECOVERY

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to the U.S. Provisional Patent Application No. 62/281,454, filed January 21, 2016, the contents of the entirety of which are incorporated by this reference.

TECHNICAL FIELD

[0002] The present invention relates generally to catalysts. The present disclosure is further directed to methods of separating a catalyst from a product mixture. The present disclosure is also directed to methods of reconstituting a catalyst. Additionally, the present disclosure is directed to methods of recovering a catalyst from a product mixture.

BACKGROUND OF THE INVENTION

[0003] Methods of epoxidation of vegetable oils are well known. For example, US Patent Application US 2006/0020062 A1 to Bloom discloses that epoxidation of soybean and linseed oils is well known in the art, is performed on a commercial scale, and commonly is achieved by using a strong catalyst, oxidant, and carboxylic acid.[1] Epoxidized vegetable oils have a wide range of utility, including uses as plasticizers and stabilizers in certain polymers.[2]

[0004] Heterogeneous systems for epoxidation are well known. For example, "Metal-catalyzed Epoxidations of Alkenes with Hydrogen Peroxide" discloses several typical heterogeneous systems, such as mineral-type catalysts including zeolites and hydrotalcites.[3] Additionally, heterogeneous systems may be constructed by attaching homogeneous catalysts to solid supports.[4] While heterogeneous systems have the advantage of easy catalyst recovery, these systems suffer from drawbacks such as limitations in the kinds of epoxides which can be produced and reduced activity relative to homogeneous catalysts.[5]

[0005] Homogeneous systems for epoxidation are also well known. For example, "Metal-catalyzed Epoxidations of Alkenes with Hydrogen Peroxide" discloses several kinds of soluble metal oxides, including the Venturello epoxidation catalyst and the Noyori epoxidation system.[6] A Venturello catalyst in this regard is characterized by a phosphotungstate complex of the formula $Q_3PW_4O_{24}$, where Q represents a hydrophobic cation, typically a quaternary ammonium ion, while a Noyori catalyst is characterized by a system of Na_2WO_4-H_3PO_4-quaternary ammonium chloride.[7] The epoxidation of oils catalyzed by organometallic compounds is advantageous, for example being environmentally benign and efficient in both activity and selectivity.[8] However, concerns with tungsten-based systems include cost and product-impurities.[9]

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[1] US 2006/0020062 A1, paragraphs [0005-0006].

[2] US 2006/0020062 A1, paragraph [0005].

[3] Lane, Benjamin; Burgess, Kevin. Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide. *Chem. Rev.* **2003**, *103* (7), 2458.

[4] Lane, Benjamin; Burgess, Kevin. Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide. *Chem. Rev.* **2003**, *103* (7), 2459.

[5] Lane, Benjamin; Burgess, Kevin. Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide. *Chem. Rev.* **2003**, *103* (7), 2458-59.

[6] Lane, Benjamin; Burgess, Kevin. Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide. *Chem. Rev.* **2003**, *103* (7), 2459-60.

[7] WO 2009/082536 A1; Sato, Kazuhiko; Aoki, Masao; Ogawa, Masami; Hashimoto, Tadashi; Noyori, Ryoji. A Practical Method for Epoxidation of Terminal Olefins with 30% Hydrogen Peroxide under Halide-Free Conditions. J. Org. Chem. **1996**, *61*, 8310.

[8] Jiang, Pingping; Chen, Min; Dong, Yuming; Lu, Yun; Ye, Xia; Zhang, Weije. Novel Two-Phase Catalysis with Organometallic Compounds for Epoxidation of Vegetable Oils by Hydrogen Peroxide. J. Am. Oil Chem. Soc. **2010**, *87*, 90.

[9] Lane, Benjamin; Burgess, Kevin. Metal-Catalyzed Epoxidations of Alkenes with Hydrogen Peroxide. *Chem. Rev.* **2003**, *103* (7), 2460.

[0006] Overall, it would be especially advantageous to develop methods for recovering catalysts used in homogeneous systems for epoxidation.

SUMMARY OF THE INVENTION

[0007] The present invention relates in one aspect to a method of separating a catalyst from a product mixture comprising combining the product mixture with a complexing agent in the presence of a solvent, wherein the product mixture comprises the catalyst, and recovering a precipitate formed from combining the product mixture with the complexing agent, wherein the precipitate comprises a metal complex portion of the catalyst.

[0008] The present invention relates in another aspect to a method of reconstituting a catalyst comprising solubilizing a precipitate comprising a metal complex portion of the catalyst, thus forming a solution, and adding a phase transfer reagent to the solution, thus forming a reconstituted catalyst.

[0009] The present invention relates in yet another aspect to a method of recovering a catalyst from a product mixture comprising separating the catalyst from the product mixture, wherein the product mixture comprises the catalyst, and reconstituting the catalyst.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Figure 1 shows a scheme for catalyst separation by complexation followed by precipitation, as well as a scheme for catalyst recovery by reconstitution of the catalyst.

[0011] Figure 2 shows a scheme for catalyst separation by complexation followed by precipitation and subsequent further improved catalyst reconstitution.

[0012] Figure 3 shows catalyst complexing agents evaluated for precipitation of the Venturello catalyst.

[0013] Figure 4 shows the stepwise precipitation by a catalyst complexing agent in ethanol.

[0014] Figure 5 shows the conditions and results for the recovery and reconstitution of the Venturello catalyst using 1-ethyl-3-methyl imidazolium chloride as a complexing agent.

[0015] Figure 6 shows the comparative conversion and selectivity profiles for the epoxidation of methyl oleate using fresh catalyst and reconstituted catalyst.

[0016] Figure 7 shows the comparative conversion and selectivity profiles for the epoxidation of methyl oleate using fresh catalyst and reconstituted catalyst prepared by an improved method.

[0017] Figure 8 shows the comparative conversion and selectivity profiles for the epoxidation of methyl oleate using fresh catalyst and reconstituted catalyst prepared by a further improved method.

[0018] Figure 9 shows a scheme for catalyst separation by complexation followed by precipitation and a further improved catalyst reconstitution.

[0019] Figure 10 shows the structure of cetyl pyridinium chloride, a new complexing agent for the recovery of catalyst by complexation followed by precipitation.

[0020] Figure 11 shows a comparison of mono-dentate and bi-dentate complexing agents in the context of precipitation.

[0021] Figure 12 shows schema and ^{1}H NMR characterization for the formation of 1,6-diaminohexane dihydrochloride.

[0022] Figure 13 shows the structures of the bi-dentate ligands hexane-1,6-diamine dihydrochloride, N^1,N^1,N^1,N^8,N^8,N^8-hexaethyloctane-1,8-diaminium bromide, and 3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) bromide, along with a representative scheme for precipitation using a bi-dentate ligand

[0023] Figure 14 shows isolated, synthesized bi-dentate complexing agents (ligands).

[0024] Figure 15 shows a scheme for the synthesis of, as well as ^{1}H NMR characterization of, N^1, N^1, N^1, N^8, N^8, N^8-hexaethyloctane-1,8-diaminium bromide.

[0025] Figure 16 shows a scheme for the synthesis of, as well as ^{1}H NMR characterization of, 3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) bromide.

[0026] Figure 17 shows the structures of mono-dentate and bi-dentate complexing agents.

[0027] Figure 18 shows a large-scale separation (via precipitation) of Venturello catalyst using a catalyst complexing agent.

[0028] Figure 19 shows samples of recovered peroxophosphotungsten moiety from Venturello catalyst in epoxidized soybean oil.

[0029] Figure 20 shows structures of tungsten-containing precipitates and internal standards used for reconstitution of Venturello catalyst.

[0030] Figure 21 shows ^{1}H NMR characterization of fresh and reconstituted Venturello catalyst.

[0031] Figure 22 shows structures of sources of reconstituted Venturello catalyst.

[0032] Figure 23 shows structures of sources of reconstituted Venturello catalyst.

[0033] Figure 24 shows ^{1}H NMR characterization of fresh and improved, reconstituted Venturello catalyst.

[0034] Figure 25 shows comparative conversion and selectivity profiles of fresh Venturello catalyst and reconstituted Venturello catalyst for the scaled-up epoxidation of soybean oil.

[0035] Figure 26 shows a general scheme for complexing agents containing two functional groups.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS OF THE INVENTION

[0036] In an illustrative embodiment, a method of the present invention includes separating a catalyst from a product mixture comprising combining the product mixture with a complexing agent in the presence of a solvent, wherein the product mixture comprises the catalyst, and recovering a precipitate formed from combining the product mixture with the complexing agent, wherein the precipitate comprises a metal complex portion of the catalyst.

[0037] In another illustrative embodiment, a method of the present invention includes reconstituting a catalyst comprising solubilizing a precipitate comprising a metal complex portion of the catalyst, thus forming a solution, and adding a phase transfer reagent to the solution, thus forming a reconstituted catalyst.

[0038] In yet another illustrative embodiment, a method of the present invention includes recovering a catalyst from a product mixture comprising separating the catalyst from the product mixture, wherein the product mixture comprises the catalyst, and reconstituting the catalyst.

[0039] In a further embodiment, the separating the catalyst from the product mixture further comprises combining the product mixture with a complexing agent in the presence of a solvent, and recovering a precipitate formed from combining the product mixture with the complexing agent, wherein the precipitate comprises a metal complex portion of the catalyst.

[0040] In a further embodiment, the reconstituting the catalyst further comprises solubilizing the precipitate, thus forming a solution, and adding a phase transfer reagent to the solution, thus forming a reconstituted catalyst.

[0041] In a further embodiment, the product mixture further comprises an epoxidized vegetable oil. In yet a further embodiment, the epoxidized vegetable oil comprises epoxidized soybean oil. In one embodiment, the product mixture further comprises epoxidized soybean oil.

[0042] The present invention contemplates many catalysts, including a catalyst comprising an element selected from the group consisting of tungsten, phosphorous, and combinations of any thereof, as well as a catalyst comprising a Venturello catalyst characterized by a phosphotungstate complex of the formula $Q_3PW_4O_{24}$, where Q represents a hydrophobic cation. In one embodiment, the hydrophobic cation comprises a methyltrioctylammonium ion.

[0043] The present invention contemplates many solvents, including an alcohol, as well as a solvent selected from the group consisting of ethanol, methanol, isopropanol, and combinations of any thereof.

[0044] The present invention contemplates many complexing agents, including a complexing agent selected from the group consisting of quaternary amine salts, imidazolium salts, pyridinium salts, and combinations of any thereof. The present invention further contemplates many quaternary amine salts, including quaternary amine salts selected from the group consisting of tetra-butyl ammonium bromide, tris(hydroxymethyl)aminoethane hydrochloride, and combinations of any thereof. The present invention further contemplates many imidazolium salts, including imidazolium salts selected from the group consisting of methyl imidazolium chloride, imidazolium chloride, 1-ethyl-3-methyl imidazolium chloride, and combinations of any thereof. The method further contemplates a pyridinium salt comprising 2-chloropyridine hydrochloride.

[0045] In a further embodiment, the product mixture:solvent ratio is about 1:2 weight/weight.

[0046] In a further embodiment, the combining the product mixture with the complexing agent in the presence of the solvent is carried out while stirring for at least 30 minutes. In another embodiment, the combining the product mixture with the complexing agent in the presence of the solvent is carried out at room temperature.

[0047] In a further embodiment, the recovering the precipitate formed from combining the product mixture with the complexing agent is carried out by filtration, resulting in the precipitate and a filtrate. In another embodiment, the filtrate is allowed to stand for at least 8 hours, giving an additional amount of the precipitate.

[0048] In a further embodiment, the solubilizing the precipitate comprising the metal complex portion of the catalyst comprises stirring the precipitate in a hydrogen peroxide solution. In another embodiment, the solubilizing the precipitate comprising the metal complex portion of the catalyst comprises stirring the precipitate in the presence of an acid. In one embodiment, the acid is hydrochloric acid.

[0049] In a further embodiment, the adding the phase transfer reagent to the solution further comprises adding an organic solvent. The present invention contemplates many organic solvents, including dichloromethane, ethyl acetate, or combinations of any thereof.

[0050] In a further embodiment, the metal complex portion of the catalyst comprises a phosphotungstate complex.

[0051] In a further embodiment, the phase transfer reagent comprises a quaternary ammonium salt.

[0052] Referring now to the drawings, various schema are provided for performing a catalyst separation according to the present invention, and for recovering a catalyst according to another aspect. Thus, in Figure 1, a scheme for catalyst separation by complexation followed by precipitation, as well as a scheme for catalyst recovery by reconstitution of the catalyst, are shown. Epoxidized soybean oil containing Venturello catalyst (represented as MR_3, where M is a tri-negatively charged peroxophosphotungsten moiety $[PO_4\{WO(O_2)_2\}_4]^{3-}$ and R is the phase transfer cation is the methyltrioctylammonium cation $[\{(C_8H_{17})_3N(CH_3)\}^+]$) diluted with ethanol is reacted with 1-ethyl-3-methyl imidazolium chloride, giving a precipitate comprising the M group of the catalyst which may be separated by centrifugation. The precipitate is stirred for 30 minutes with H_2O_2, H_2O, and HCl to give a clear solution. The phase transfer reagent Aliquat® 336 along with dichloromethane and/or ethyl acetate are added to the clear solution, giving reconstituted Venturello catalyst.

[0053] In Figure 2, a scheme for catalyst separation by complexation followed by precipitation and subsequent further improved catalyst reconstitution is shown. Venturello catalyst (1 g) in 1 mL of toluene is stirred with 0.3 g of 1-ethyl-3-methyl imidazolium chloride in 2 mL of ethanol for about 2-3 minutes, giving 0.7 g of a precipitate, recovered by centrifugation. The precipitate is stirred in water for about 20 minutes to give a colloidal solution. The phase transfer reagent Aliquat® 336 along with dichloromethane are added to the colloidal solution, such that the aqueous layer gradually becomes clear, giving reconstituted Venturello catalyst.

[0054] In Figure 3, catalyst complexing agents evaluated for precipitation of the Venturello catalyst are shown. Quaternary amine salts are shown, including tetrabutyl ammonium bromide [compound 1a] and tris-(hydroxymethyl)aminomethane hydrochloride [compound 1b]. Imidazolium salts are shown, including methyl imidazolium chloride [compound 2a], imidazolium chloride [compound 2b], and 1-ethyl-3-methyl imidazolium chloride [compound 2c]. Pyridinium salts are shown, including 2-chloropyridine hydrochloride [compound 3a]. Compounds 1a, 1b, 2a, 2b, and 2c gave precipitation in ethanol. Compound 3a did not give precipitation in ethanol.

[0055] In Figure 4, stepwise precipitation by a catalyst complexing agent in ethanol is shown. In step 1, epoxidized soybean oil is diluted with ethanol. In step 2, the first precipitation is obtained after about 30 minutes of stirring with imidazolium chloride. In step 3, the result after centrifugation at 2400 rpm for 5 minutes is shown. In step 4, a second, light precipitation is obtained after the filtrate was left standing overnight.

[0056] In Figure 5, conditions and results for recovery and reconstitution of Venturello catalyst are shown. For catalyst recovery, 4 g of epoxidized soybean oil and 0.1 g of 1-ethyl-3-methyl imidazolium chloride were used, to give 52 mg of a first precipitate and 11 mg of a second precipitate for a total of 63 mg (88.7%). For catalyst reconstitution using the initial method, 31 mg of tungsten-imidazolium salt, 0.1 g of hydrogen peroxide, about 30 mg of hydrochloric acid, and 30 mg of the phase transfer reagent Aliquat® 336 were used, for an expected 51.8 mg of catalyst and an actual 52 mg (100.4%) of prepared catalyst. For catalyst reconstitution using the improved method, 31 mg of tungsten-imidazolium salt, 0.3 g of hydrogen peroxide, no hydrochloric acid, and 28 mg of the phase transfer reagent Aliquat® 336 were used, for an expected 49.8 mg of catalyst and an actual 40 mg (80.3%) of prepared catalyst.

[0057] In Figure 6, comparative conversion and selectivity profiles for epoxidation of methyl oleate using fresh catalyst and reconstituted catalyst are shown.

[0058] In Figure 7, comparative conversion and selectivity profiles for epoxidation of methyl oleate using fresh catalyst and reconstituted catalyst prepared by an improved method are shown.

[0059] In Figure 8, comparative conversion and selectivity profiles for epoxidation of methyl oleat using fresh catalyst and reconstituted catalyst prepared by a further improved method are shown.

[0060] In Figure 9, a scheme for catalyst separation by complexation followed by precipitation and a further improved catalyst reconstitution is shown. Epoxidized soybean oil (ESO) containing catalyst is diluted in ethanol to give a diluted product, which is reacted with a catalyst complexing agent to give precipitation (achieved through complexation). After centrifugation or filtration, the precipitate is separated from the product containing phase transfer reagent (in this case, Aliquat® 336, *N*-methyl-*N*,*N*,*N*-trioctylammonium chloride). The precipitate is stirred with water to give a clear solution which is reacted with the phase transfer reagent Aliquat® 336 to give reconstituted catalyst. The product containing PTRs is combined with cation exchange resin to give pure product and separated PTRs. The catalyst complexing agent may preferably be 1-ethyl-3-methyl imidazolium chloride or imidazolium chloride.

[0061] In Figure 10, the structure of a new complexing agent, the pyridinium salt cetyl pyridinium chloride [compound 3b] is shown.

[0062] In Figure 11, schemes for precipitation of Venturello catalyst via a mono-dentate ligand and via a bi-dentate ligand are shown.

[0063] In Figure 12, the schema and ^{1}H NMR results for the formation of 1,6-diaminohexane dihydrochloride are shown. In attempt 1, 3.5 g of 1,6-diamino hexane is reacted with concentrated hydrochloric acid (2 g) and acetone (60 mL) to give a pale yellow solution with 2 layers (the 1,6-diaminohexane dihydrochloride). In attempt 2, 2.2 g of 1,6-diamino hexane is reacted with concentrated hydrochloric acid (1.2 g) and acetone (120 mL) to give a white solid (the 1,6-diaminohexane dihydrochloride, 3.2 g, 89.4% yield).

[0064] In Figure 13, the structures of the bi-dentate ligands hexane-1,6-diamine dihydrochloride, N^1,N^1,N^1,N^8,N^8,N^8-hexaethyloctane-1,8-diaminium bromide, and 3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) bromide are shown, along with a representative scheme for precipitation using a bi-dentate ligand.

[0065] In Figure 14, isolated, synthesized bi-dentate complexing agents (ligands) are shown. These bidentate ligands are (from left to right) hexane-1,6-diamine dihydrochloride, N^1,N^1,N^1,N^8,N^8,N^8-hexaethyloctane-1,8-diaminium bromide, and 3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) bromide.

[0066] In Figure 15, the synthesis and characterization of N^1,N^1,N^1,N^8,N^8,N^8-hexaethyloctane-1,8-diaminium bromide is shown. For the synthesis, 5.44 g (20 mmol) of 1,6-dibromo hexane and 10.1 g (100 mmol) of triethyl amine are reacted in ethanol at 75°C under N_2 for 24 hours to give 2.9 g (31% yield) of N^1,N^1,N^1,N^8,N^8,N^8-hexaethyloctane-1,8-diaminium bromide.

[0067] In Figure 16, the synthesis and characterization of 3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) bromide is shown. For the synthesis, 5.44 g (20 mmol) of [dibromide compound] and 6.8 g (100 mmol) of [dinitrogen compound] are reacted in ethanol at 80°C under N_2 for 24 hours to give overall 4.1 g (50%) of 3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) bromide.

[0068] In Figure 17, the structures of monodentate and bi-dentate ligands which may be used as complexing agents are shown. Monodentate, imidazolium salts include methyl imidazolium chloride [compound 2a], imidazolium chloride [compound 2b], and 1-ethyl-3-methyl imidazolium chloride [compound 2c]. Monodentate, quaternary amine salts include tetrabutyl ammonium bromide [compound 1a]. Monodentate, pyridinium salts include cetyl pyridinium chloride [compound 3b]. Bi-dentate, quaternary amine salts include hexane-1,6-diamine dihydrochloride [compound 1b] and N^1,N^1,N^1,N^8,N^8,N^8-hexaethyloctane-1,8-diaminium bromide [compound 1c]. Bi-dentate, imidazolium salts include 3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) bromide.

[0069] In Figure 18, a sample large scale (440 g epoxidized soybean oil) separation (precipitation) of Venturello catalyst using a catalyst complexing agent is shown. On the left, 1320 g of a product mixture containing epoxidized soybean oil and 2-3% of a corresponding polyol (440 g total) solubilized in 880 g of ethanol is shown, wherein the maximum amount of precipitation achievable after standing overnight is settled on the bottom, and an overall cloudy appearance remains. On the right, 4 vials with precipitate settled and clear solution remaining are shown.

[0070] In Figure 19, 5 vials containing recovered peroxophosphotungsten moieties from Venturello catalyst (in epoxidized soybean oil) using different catalyst complexing agents is shown. The different catalyst complexing agents result in different R groups, wherein the different R groups are labeled by structure and number, with (1) = imidazolium group; (2) = 1-ethyl-3-methyl imidazolium group; (3) = cetyl pyridinium group; (4) = N^1, N^1, N^1, N^8, N^8, N^8-hexaethyloctane-1,8-diaminium group; and (5) = 3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) group. For the R groups (1), (2), and (3), the structure of the recovered peroxophosphotungsten moieties from Venturello catalyst have the structure $(PW_4O_{24})R_3$. For the R groups (4) and (5), the structure of the recovered peroxophosphotungsten moieties from Venturello catalyst have the structure $(PW_4O_{24})R_{3/2}$ or $(PW_4O_{24})_2R_3$.

[0071] In Figure 20, tungsten-containing precipitates and internal standards used for reconstitution of Venturello catalyst are shown. The formula for compound A is $(PW_4O_{24})R'_{3/2}$ wherein the the R' group of compound A = 3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) group. The formula for compound B is $(PW_4O_{24})R'_{3/2}$, wherein the R' group of compound B = N^1, N^1, N^1, N^8, N^8, N^8-hexaethyloctane-1,8-diaminium group. The formula for compound C is $(PW_4O_{24})R'_{3/2}$ wherein the R' group of compound C = imidazolium group. Compound X is N^1, N^1, N^1, N^8, N^8, N^8-hexaethyloctane-1,8-diaminium bromide. Compound Y is imidazolium chloride.

[0072] In Figure 21, the ^{1}H NMR spectra of fresh and reconstituted Venturello catalyst are shown.

[0073] In Figure 22, the structures of the compounds from which the Venturello catalyst was reconstituted are shown, where the R' group of A = 3,3'-

(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) group; and the R' group of B = N^1, N^1, N^1, N^8, N^8, N^8-hexaethyloctane-1,8-diaminium group. The formula for compound A and compound B is $(PW_4O_{24})R'_{3/2}$ In Figure 23, the structures of the compounds from which the Venturello catalyst was reconstituted are shown, where the R' group of A = hexane-1,6-diamine group; the R' group of B = N^1, N^1, N^1, N^8, N^8, N^8-hexaethyloctane-1,8-diaminium group; and the R' group of C = 3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) group. The formula for compounds A, B, and C is $(PW_4O_{24})R'_{3/2}$.

[0074] In Figure 24, the ^{1}H NMR spectra of fresh and improved, reconstituted Venturello catalyst are shown.

[0075] In Figure 25, comparative conversion and selectivity profiles for scaled-up epoxidation of soybean oil using fresh Venturello catalyst and reconstituted Venturello catalyst are shown.

[0076] In Figure 26, a general scheme for complexing agents containing two functional groups is shown. Similar complexing agents to hexane-1,6-diamine dihydrochloride, N^1,N^1,N^1,N^8,N^8,N^8-hexaethyloctane-1,8-diaminium bromide, and 3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) bromide may be used for precipitating catalysts such as Venturello catalyst. Complexing agents containing two quaternary ammonium groups may be used, of the formula $X^- \, {}^+N(R)_3—(CH_2)_n—N^+(R)_3 \, X^-$, wherein "n" may be 2, 3, 4, 5, 6, 7, 8, 9, or 10; "R" may be H, CH_3, C_2H_5, C_3H_7, or C_4H_9; and "X" may be Cl^-, Br^-, or I^-. Complexing agents containing two imidazolium groups may be used, of the formula $X^- C_3H_5N_2^+—(CH_2)_n—C_3H_5N_2^+ \, X^-$, wherein "n" may be 2, 3, 4, 5, 6, 7, 8, 9, or 10; and "X" may be Cl^-, Br^-, or I^-.

[0077] The present invention is more particularly illustrated by the following non-limiting examples:

[0078] Example 1: Selection of Solvents and Complexing Agents for Recovery of Catalyst by Complexation Followed by Precipitation. Common organic solvents were screened based on the solubility of epoxidized soybean oil (ESO) mixed with Venturello catalyst, the catalyst complexing agent, and the new complex formed by the reaction of the catalyst with the complexing agent in the organic solvents. Ethanol, methanol, and isopropanol were the organic solvents screened. Methanol was found to be immiscible with the new complex formed by the reaction of the catalyst with the complexing agent. Isopropanol gave no precipitation when imidazolium chloride was used as the catalyst complexing agent (Fig. 3). Therefore, ethanol was chosen as the organic solvent. Ethanol solubilized the catalyst, allowing for the catalyst complexing agent to easily react with the catalyst to form a new complex. This new complex formed a precipitate in ethanol (Fig. 4). After stirring for 30 minutes at room temperature the ESO/Venturello catalyst product with 1-ethyl-3-methyl imidazolium chloride in ethanol (product:ethanol ratio = 1:2, weight/weight), about 73% of the catalyst (52 mg) was precipitated as a white solid. The remaining filtrate, on further standing over night, yielded another 15.5% (11 mg) of the catalyst as a precipitate, giving a total yield of recovered catalyst of 88.7% (Fig. 5).

[0079] Imidazolium salts, quaternary amine salts, and pyridinium salts were evaluated for use as a catalyst complexing agent (Fig. 3). Notably, 2-chloropyridine hydrochloride did not yield any precipitation. The quaternary ammonium salt tris(hydroxylmethyl)aminomethane hydrochloride gave minimal precipitation, and tetrabutyl ammonium bromide gave only 19% precipitation. The imidazolium salts methyl imidazolium chloride, imidazolium chloride, and 1-ethyl-3-methyl imidazolium chloride gave 78.4% precipitation, 80.3% precipitation, and 98.7% precipitation, respectively. Using imidazolium chloride as the complexing agent for large scale separation (scaled up 10-fold) yielded 78.7% precipitation.

[0080] The details of the results obtained from Example 1 are summarized below in Table 1. The ratio of ethanol to epoxidized soybean oil (ESO) used for Table 1 was 2:1 (weight/weight).

[0081] Table 1: Quantitative Results for Catalyst Recovery by Complexation Followed by Precipitation

Entry	**Complexing agent (mg)**	**ESO (g)**	**Expected ppt. (mg)**	**1st ppt. (mg)**	**2nd ppt. (mg)**	**Total ppt. (mg)**	**Recovery %**
1	Tetrabutyl ammonium bromide (360)	4	80.7	12.2	3.1	15.3	19.0
2	Methyl imidazolium chloride (150)	4	60.2	42.0	5.2	47.2	78.4
3	Imidazolium chloride(100)	4	58.4	41.1	5.8	46.9	80.3

4	1-ethyl-3-methyl imidazolium chloride (100)	4	63.8	52.0	11.0	63.0	98.7
5	Imidazolium chloride (1006)	40 (scaled –up separation)	584	399.1	60.2	459.3	78.7

[0082] Example 2: Reconstitution of Recovered Catalyst. The catalyst recovered by Example 1 was reconstituted. The precipitate from Example 1 was solubilized by stirring in an aqueous hydrogen peroxide solution in the presence of a few drops of hydrochloric acid at room temperature. The precipitate became soluble within 12 hours. The addition of a stoichiometric amount (based on theoretical calculation) of the phase transfer reagent Aliquat® 336 (N-methyl-N,N,N-trioctyloctan-1-ammonium chloride, CAS 5137-55-3, Sigma-Aldrich) in either dichloromethane or ethyl acetate yielded reconstituted Venturello catalyst. However, this reconstituted catalyst showed reduced catalytic activity when used to epoxidize methyl oleate, as compared to fresh catalyst (Fig. 6). The reaction conditions for the epoxidation of methyl oleate were: 1 mmol of methyl oleate, 0.05 mmol of methyl palmitate (internal standard), 0.2 mL of 50% hydrogen peroxide, 2 mL of toluene, 52 mg of catalyst, and room temperature. The details of the results obtained from Example 2 are summarized below in Table 2. The overall scheme embodied by Example 2 is shown by Fig. 1.

[0083] Table 2: Comparative Conversion and Selectivity Profiles for Epoxidation of Methyl Oleate Using Fresh Catalyst and Reconstituted Catalyst

Entry	**Time (minutes)**	**Conversion**	**Selectivity**
Fresh catalyst (Fresh cat)	190	90.70%	97.10%
Reconstituted catalyst (RC cat)	190	54.70%	81.70%

[0084] Example 3: Improved Reconstitution of Recovered Catalyst. The catalyst recovered by Example 1 was reconstituted without the use of hydrochloric acid. The precipitate from Example 1 was stirred in a solution of hydrogen peroxide, in the presence of the phase transfer reagent (PTR) Aliquat® 336 in a suitable organic solvent (dichloromethane or ethyl acetate) for 30 minutes. This improved method of reconstitution of recovered catalyst took less time than the method of Example 2 and showed comparable catalytic activity when used to epoxidize methyl oleate, as compared to fresh catalyst (Fig. 7). The reaction conditions for the epoxidation of methyl oleate were: 1 mmol of methyl oleate, 0.05 mmol of methyl palmitate (internal standard), 0.2 mL of 50% hydrogen peroxide, 2 mL of toluene, 52 mg of catalyst, at room temperature. The details of the results obtained from Example 3 are summarized below in Table 3. The overall scheme embodied by Example 2 is shown by Fig. 1.

[0085] Table 3: Comparative Conversion and Selectivity Profiles for Epoxidation of Methyl Oleate Using Fresh Catalyst and Reconstituted Catalyst by Improved Method

Entry	**Time (minutes)**	**Conversion**	**Selectivity**
Fresh catalyst (Fresh cat)	180	76.90%	110.00%
Reconstituted catalyst (RC cat)	180	78.50%	111.00%

[0086] Example 4: Further Improved Reconstitution of Catalyst. Venturello catalyst was reconstituted without the use of hydrochloric acid or hydrogen peroxide. Fresh Venturello catalyst (1g) was dissolved in 1 mL of toluene and diluted with 2 mL of ethanol, followed by the addition of 0.3g of 1-ethyl-3-methyl imidazolium chloride. The solution was stirred for about 2-3 minutes and formed about 0.7g of the tungsten-imidazolium complex. This complex was separated by centrifugation as a white precipitate. This precipitate formed a colloidal solution in water. When the phase transfer reagent (PTR) Aliquat® 336 was added in a methylene chloride solution to the colloidal solution, the colloidal solution became transparent over time. The overall scheme embodied by Example 4 is show by Fig. 2. The isolated yield of this reconstituted Venturello catalyst was about 94.5%. This reconstituted catalyst showed almost comparable catalytic activity when used to epoxidize methyl oleate, as compared to fresh catalyst (Fig. 8). The reaction conditions for the epoxidation of methyl oleate were: 1 mmol of methyl oleate, 0.05 mmol of methyl palmitate (internal standard), 2 mL of toluene, 52 mg of catalyst, at room temperature. The details of the results obtained from Example 4 are summarized below in Table 4. The overall scheme embodied by Example 4 is shown by Fig. 9.

[0087] Table 4: Comparative Conversion and Selectivity Profiles for Epoxidation of Methyl Oleate Using Fresh Catalyst and Reconstituted Catalyst by Further Improved Method

Entry	Time (hours)	Conversion	Selectivity
Fresh catalyst (FC)	3	91.20%	100.70%
Reconstituted catalyst (RC)	3	89.1%	100.10%

[0088] Example 5: Additional Complexing Agent for Recovery of Catalyst by Complexation Followed by Precipitation. Cetyl pyridinium chloride (CPC) (Fig. 10) was tested as a catalyst complexing agent to precipitate the phosphotungsten moiety from the Venturello catalyst (neat or mixed with product). CPC gave 86% isolated precipitation when 4 g of epoxidized soybean oil (reaction product) mixed was used. The detailed results are shown below in Table 5. The reaction conditions were: reaction time = 30 minutes; reaction product = 4 g epoxidized soybean oil containing 0.1 g Venturello catalyst; ethanol:ESO ratio = 2:1 (weight percent); precipitate separated by centrifugation for 5 minutes at 2500 rpm. Upon scaling up to use 40 g of epoxidized soybean oil (reaction product), CPC gave about 83% isolated precipitation. The reaction conditions were: reaction time = 30 minutes; reaction product = 40 epoxidized soybean oil containing 1 g Venturello catalyst; ethanol:ESO ratio = 2:1 or 1:1 (weight percent); precipitate separated by centrifugation for 10 minutes at 2500 rpm. When both the amount of complexing agent (CPC) and the amount of solvent (ethanol) were reduced by 2 fold, the extent of recovery of catalyst through precipitation was reduced to about 76%. (Entry 3, Table 6). The filtrate upon prolonged standing gave a small amount of precipitate, slightly increasing the total recovery of catalyst.

[0089] Table 5: Quantitative Results for Catalyst Recovery by Complexation Followed by Precipitation.

Entry	Complexing agent (mg)	ESO (g)	Expected ppt. (mg)	1st ppt. (mg)	2nd ppt. (mg)	Total ppt. (mg)	Recovery %
1	Cetyl pyridinium chloride (340 mg)	4	93	72	8	80	86

[0090] Table 6: Quantitative Results for Catalyst Recovery by Complexation Followed by Precipitation, Scaled-Up

Entry	**Complexing agent (g; equivalents)**	**ESO (g)**	**Ethanol added (g)**	**Expected ppt. (mg) (considering 100%)**	**1st ppt. (mg)**	**2nd ppt. (mg)**	**Total ppt. (mg)**	**Recovery %**
1	Imidazolium chloride (1 g; 4.6)	40	80	584	399.1	60.2	459.3	78.6
2	Cetyl pyridinium chloride (3.4 g; 5.2)	40	80	930	692	78	770	82.8
3	Cetyl pyridinium chloride (1.7 g; 2.6)	40	40	930	641	70	711	76.45

[0091] Example 6: Design and Synthesis of a New Catalyst Complexing Agent for Recovery of Catalyst by Complexation Followed by Precipitation. The monodentate quaternary salts imidazolium, cetylpyridinium, and tetrabutyl ammonium can act as complexing agents to precipitate Venturello catalyst as a discrete molecule, in this case as the peroxophosphotungsten moiety surrounded by three complexing agents. The extent of precipitation is dependent on many factors, including molecular weight of the complex formed and the chemical nature of the complexing agent (i.e. the nature of the functional groups and the chemical environment). Therefore, quantitative precipitation using the majority of monodentate complexing agents is not possible, and the time of the reaction must be increased to several hours up to several days. In order to achieve almost quantitative precipitation within a very short amount of time, for example within 30 minutes, a simple molecule was designed to have bi-functional groups (i.e. a quaternary amine group) to serve as a model complexing agent. Any molecule containing two quaternary amine groups can either coordinate with one peroxophosphotungsten moiety (PM) (by satisfying 2 of the negative charges on the 1 PM) or coordinate with two PM’s (by satisfying 1 negative charge on each of the PM’s). In the former case, the remaining third negative charge on the PM will be satisfied by the quaternary group of another complexing agent whose second quaternary group can then satisfy the negative charge of another PM, thus allowing precipitation of two PM's.

[0092] In this example, the molecule 1,6-diaminohexane was chosen as a starting point for designing a new complexing agent, in part because its longer chain length would not allow its two quaternary groups to bind with the same PM. Therefore, use of 1,6-diaminohexane allowed for one quaternary group to bind to one PM and the other quaternary group to bind to a second PM, thus helping form a coordination polymer with a high effective molecular weight having many cross-linkages. Upon formation of this kind of coordination polymer, the PM was precipitated out of solution quickly and quantitatively.

[0093] A new complexing agent (Fig. 11) was prepared in a simple manner and characterized by ^{1}H NMR (Fig. 12). A total of 3.2 g of 1,6-diaminohexane dihydrochloride (DAH, HCl) was prepared (89.4% yield) as a white solid from 1,6-diaminohexane (2.2 g, about 19 mmol) dissolved in acetone (120 mL) with HCl (1.2 g concentration) at room temperature. Appearance of ^{1}H proton (-CH_2 group) peaks of the synthesized compound in the lower field region as compared to the spectra for 1,6-diaminohexane confirmed yield of the desired compound (Fig. 12). This simple bi-functional complexing agent gave almost quantitative precipitation (98%) of Venturello catalyst from epoxidized soybean oil (ESO) in ethanol (Table 7). The reaction conditions were: reaction time = 30 minutes; reaction product = 4 g epoxidized soybean oil containing 0.1 g Venturello catalyst; ethanol:ESO ratio = 2:1 (weight percent); 98 mg of 1,6-diammonium dihydrochloride (3 equivalents compared to tungsten present and 4 equivalents compared to PTR required); precipitate separated by centrifugation for 5 minutes at 2500 rpm. When Venturello catalyst was reconstituted from the hexanediammonium salt of PM, 95% yield was obtained, as confirmed by ^{1}H NMR (Table 8). After reconstitution of the Venturello catalyst, the extent of DAH, HCl in the aqueous solution was found to be 90.1% based on ^{1}H NMR using imidazolium chloride as an external standard.

[0094] Table 7: Quantitative Results for Catalyst Recovery by Complexation Followed by Precipitation.

Entry	Complexing agent (mg)	ESO (g)	Expected ppt. (mg)	1st ppt. (mg)	2nd ppt. (mg)	Total ppt. (mg)	Recovery %
1	Hexane 1,6-diamine dihydrochloride (98 mg)	4	65.4	64	-	64	98

[0095] Table 8: Quantitative Results for Catalyst Reconstitution from Precipitation Using CPC and DAH, HCl

Entry ID of ppt.	Catalyst Precipitating Agent used	Ppt. taken (mg)	D_2O (g)	Aliquat® 336 used (mg)	Solvent (1 g)	Internal Standard (imidazolium chloride) (mg)	Amt. of Product (mg)	Yield %	Extent of complexing agent in aqueous solution (based on ^{1}H NMR)	ID of new Venturello catalyst
E-74	CPC	100	1	58	toluene	32.5	111	99.5	-	E-86
E-85	DAH, HCl	64	1	54	DCM	37.2	98	95.0	90.1	E-87

[0096] The effectiveness of DAH, HCl was compared to CPC and imidazolium chloride (Im-Cl). Greater than 99% yield of reconstituted catalyst was achieved when cetylpyridinium chloride (CPC) was used as the complexing agent. The reconstituted catalysts prepared either from the tungsten-CPC complex or from the tungsten-DAH, HCl complex were not as active as the reconstituted catalyst prepared by using Im-Cl as the complexing agent. Under similar conditions, comparing catalytic efficiency, the catalysts reconstituted from tungsten complexes of CPC; DAH, HCl; and Im-Cl showed conversion of 55%, 29%, and 89% respectively at 3 hours (Table 9). The reaction conditions were: catalyst = 52 mg; methyl oleate (5% MP) = 1 mmol; toluene = 2 g; H_2O_2 (50% aqueous) = 0.2 g; room temperature; batch mode. Although the reconstituted catalysts using CPC and DAH, HCl were not as active as the reconstituted catalyst using imidazolium chloride as a complexing agent, DAH, HCl can be used for gravimetric estimation of trace amounts of tungsten present in the epoxide after removal of the catalyst.

[0097] Table 9: Comparative Conversion and Selectivity Profiles for Epoxidation of Methyl Oleate Using Reconstituted Catalysts

Entry	Reaction ID	Catalyst	Complexing Agent	Time of reaction (hours)	Conversion (%)	Selectivity (%)
1a	BR27	Reconstituted Venturello catalyst, E-86	CPC	2	49.3	82.7
1b	BR27	Reconstituted Venturello catalyst, E-86	CPC	3	55.2	87.6
2a	BR28	Reconstituted Venturello catalyst, E-87	DAH, HCl	2	27.1	68.1
2b	BR28	Reconstituted Venturello catalyst, E-87	DAH, HCl	3	29.2	74.0
3	BR8c	Reconstituted Venturello catalyst, E40d	Imidazolium chloride	3	89.1	100.1
4a.1	BR29	Venturello catalyst	-	2	84.0	87.2
4a.2	BR29	Venturello catalyst	-	3	95.9	83.8
4b	BR8a	Venturello catalyst	-	3	91.0	100.7

[0098] Examples 7 and 8: Design and Synthesis of 2 Additional New Catalyst Complexing Agents for Recovery of Catalyst by Complexation Followed by Precipitation. Two bidentate ligands, one containing the quaternary ammonium group and the other containing the imidazolium group, were prepared with 31% and 50% isolated yield respectively. These bi-dentate ligands were designed to provide maximum quantitative precipitation of Venturello catalyst present in a reaction mixture by forming coordination polymers (Fig. 13). Fig. 14 shows the isolated yield of these synthesized bi-dentate ligands as well as the synthesized DAH, HCl. ^{1}H NMR confirmed the exclusive formation of quaternary ammonium group containing two bi-dentate ligands

(Fig. 12 and Fig. 15). ^{1}H NMR suggested the formation of the imidazolium group containing bi-dentate desired ligand (majority) admixture with minor amounts of two side products, which, in principle, can precipitate Venturello catalyst similarly as the desired counterpart (Fig. 16).

[0099] Example 9: Performance of Newly Designed and Synthesized Catalyst Complexing Agents for Recovery of Catalyst by Complexation Followed by Precipitation. Each of the three newly synthesized bi-dentate ligands, hexane-1,6-diamine dihydrochloride, *N*^{1},*N*^{1},*N*^{1},*N*^{8},*N*^{8},*N*^{8}-hexaethyloctane-1,8-diaminium bromide, and 3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) bromide (1b, 1c, and 2d of Fig. 17) can precipitate Venturello catalyst almost quantitatively within a short amount of time (10 minutes), with the exception that *N*^{1},*N*^{1},*N*^{1},*N*^{8},*N*^{8},*N*^{8}-hexaethyloctane-1,8-diaminium bromide provided a 2nd precipitation upon standing for 3-4 hours after the first precipitation, as shown by the results in Table 10 below. Overall, the imidazolium-based complexing agent was determined to be the most promising, as it quantitatively precipitated Venturello catalyst from a reaction mixture within 10 minutes at room temperature with only 1.25 equivalents (with respect to the phase transfer reagent) of complexing agent. The reaction conditions were: 0.1 g Venturello catalyst in 4 g of epoxidized soybean oil; reaction time = 10 minutes; ethanol:epoxidized soybean oil ration = 2:1 (weight %); centrifugation for 5-10 minutes at 2500 rpm to separate the precipitate.

[00100] Table 10: Performance Testing of New Bi-dentate Ligands

Entry	**Complexing agent (mg)**	**ESO (g)**	**Expected# ppt. (mg)**	**1st ppt. (mg)**	**2nd ppt. (mg)**	**Total ppt. (mg)**	**Recovery %**
1	Hexane-1,6-diamine dihydrochloride (98), 4 equiv.	4	65.4	64.0	-	64.0	98.0
2	*N*^{1},*N*^{1},*N*^{1},*N*^{8},*N*^{8},*N*^{8}-hexaethyloctane-1,8-diaminium bromide (109), 4 equiv.	4	69.2	55	12	67.0	96.8
3	3,3'-(octane-1,8-diyl)bis(1*H*-	4	72.6	74.3	-	74.3	102.0

	imidazol-3-ium) bromide (126), 4 equiv.						
4	3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) bromide (64), 2 equiv.	4	72.6	72.0	-	72.0	99.2
5	3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) bromide (40), 1.25 equiv.	4	72.6	71.2	-	71.2	98.1

[00101] Example 10: Effect of Concentration of Catalyst Complexing Agent for Recovery of Catalyst by Complexation Followed by Precipitation. Commercially available, inexpensive imidazolium salt was tested to determine the effect of concentration on catalyst precipitation. Based on the results of Table 11 below, use of 4-5 equivalents of ligand with respect to stoichiometric amount yields optimum precipitation. The reaction conditions were: epoxidized soybean oil reaction mixture containing Venturello catalyst = 4g; ethanol = 8g; stirring for 30 minutes followed by overnight precipitate settlement; centrifugation for 10 minutes at 2600 rpm.

[00102] Table 11: Effect of Concentration of Catalyst Complexing Agent

Entry	**Complexing Agent (mg)**	**Equivalency (with respect to required amount)**	**Expected Precipitation (mg)**	**Precipitation obtained (mg)**	**Recovery of Catalyst (isolated %)**
1	150	6	58.4	47	80.5
2	125	5	58.4	46	78.8
3	100	4	58.4	42	72.0
4	75	3	58.4	34	58.2
5	50	2	58.4	31	53.0

[00103] Example 11: Large-Scale Recovery and Reconstitution of Venturello Catalyst using Imidazolium Chloride as Catalyst Complexing Agent. Imidazolium chloride was chosen as the catalyst complexing agent for this experiment due to its commercial availability and inexpensiveness. About 80% isolated precipitation of

Venturello catalyst was obtained from 440 g of reaction mixture, as shown in Figure 18 and Table 12. This was comparable to results from small scale experiments. Figure 19 shows precipitated tungsten-complexes using various catalyst complexing agents. In Figure 19, the different R groups are labeled by structure and number, with (1) = imidazolium group; (2) = 1-ethyl-3-methyl imidazolium group; (3) = cetyl pyridinium group; (4) = N^1, N^1, N^1, N^8, N^8, N^8-hexaethyloctane-1,8-diaminium group; and (5) = 3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) group. Large scale reconstitution of Venturello catalyst was possible with 96.4% isolated yield, which was greater than the yield obtained by preparing fresh Venturello catalyst using improved literature methods (typically 82-86%, with 89.5% maximum yield achieved). When 4.1 g of phase transfer reagent (Aliquat® 336) was dissolved in 150 g of DCM and mixed with 5.1 g of precipitate suspended in 110 g of water and stirred for 30 minutes, 8.12 g of isolated catalyst was obtained.

[00104] Table 12: Large-Scale Recovery of Venturello Catalyst using Imidazolium Chloride

Epoxidized Soybean Oil (g)	**Ethanol (g)**	**Complexing Agent (imidazolium chloride)**	**Length of Stirring**	**Expected Precipitate (100%)**	**Precipitate Obtained**	**Recovered Catalyst**
440	880	7.65 g (4 equivalents with respect to required phase transfer reagent)	30 minutes	6.39 g	5.12 g	80.1%

[00105] Example 12: Reconstitution of Venturello Catalyst from Precipitated Tungsten-Complex. Venturello catalyst was reconstituted on both a milligram and gram scale from precipitated tungsten-complexes obtained using two synthesized bi-dentate ligands and one commercially available mono-dentate ligand. In all cases, reconstituted catalyst was isolated with ≥96% yield. The extent of recovered complexing agent (quaternary ammonium group containing bi-dentate ligand) in the aqueous layer was 96.4% based on ^{1}H NMR using imidazolium chloride as an external standard. Using imidazolium chloride as the complexing agent, a scaled-up (gram scale) reconstitution of Venturello catalyst (Entry 3, Table 13) showed similar results as compared to the small scale reconstitution in terms of isolated yield. In the case of imidazolium-based bi-dentate ligand, ethyl acetate was used as opposed to dichloromethane (DCM) because DCM resulted in an emulsion from which catalyst recovery was difficult. The results of these experiments are summarized in Table 13. The structures of the precipitates and internal standards referenced in Table 13 are shown in Figure 20. In Figure 20, the R' group of compound A = 3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) group; the R' group of compound B = N^1, N^1, N^1, N^8, N^8, N^8-hexaethyloctane-1,8-diaminium group; the R' group of compound C = imidazolium group; compound X = N^1, N^1, N^1, N^8, N^8, N^8-hexaethyloctane-1,8-diaminium bromide; and compound Y = imidazolium chloride. Based on ^{1}H NMR results, the reconstituted Venturello catalyst synthesized from precipitated tungsten-complexes with two bi-dentate ligands contained few impurities, likely from the catalyst complexing agent, as shown in Figure 21. Therefore, thorough washing of the organic layer with distilled water several times could be beneficial to remove impurities from the final reconstituted catalyst, as all complexing agents tested are highly water soluble.

[00106] Table 13: Reconstitution of Venturello Catalyst

Entry	**ID**	**Precipitate**	**Amount of Tungsten-containing Precipitate (mg)**	**Aliquat® 336 (mg)**	**Solvent (g)**	**D_2O (g)**	**Internal Standard (g)**	**Expected Catalyst (mg)**	**Obtained Catalyst (mg)**	**Yield of Catalyst (%)**	**Recovered Complexing Agent (%) in Aqueous Layer**
1	E-99	A	110	75	Ethyl acetate (3)	3	X	151.5	146.6	96.8	-
2	E-100	B	68.2	49	Dichloromethane (3)	2	Y	100	96	96.0	96.4
3	E-101	C	5.1	4.1	Dichloromethane (150 mL)	H_2O (110)	-	8.42	8.12	96.4	-

[00107] Example 13: Performance Testing of Reconstituted Venturello Catalyst Using Bi-dentate Ligands. When bi-dentate ligands were used for tungsten precipitation, reconstituted Venturello catalyst showed slightly lower conversion (80-82% vs. 96-98%) but higher selectivity (95.5% vs. 84-87%) compared to fresh Venturello catalyst when epoxidizing soybean oil in batch mode at room temperature, as shown in Table 14 below. Figure 22 shows the structures of the compounds from which the Venturello catalyst was reconstituted, where the R' group of A = 3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) group; and the R' group of B = *N*^{1}, *N*^{1}, *N*^{1}, *N*^{8}, *N*^{8}, *N*^{8}-hexaethyloctane-1,8-diaminium group. Adjustment of the phase transfer reagent (PTR) amount based on the recovered complexing agent in aqueous solution (based on ^{1}H NMR) and thorough washing of the reconstituted catalyst with water (to remove residual impurities) could improve performance of the reconstituted catalyst. Using the stoichiometric ratio of PTR with respect to the theoretical content of tungsten in the precipitated tungsten-complex by the bi-dentate ligands and after thorough washing of the reconstituted catalyst several times with deionized water, conversion increased from 80-82% to 93-94%, with the exception of the precipitation using a tertiary amine containing ligand, when epoxidizing soybean oil in batch mode at room temperature, as shown in Table 15 below. Figure 23 shows the structures of the compounds from which the Venturello catalyst was reconstituted, where the R' group of A = hexane-1,6-diamine group; the R' group of B = *N*^{1}, *N*^{1}, *N*^{1}, *N*^{8}, *N*^{8}, *N*^{8}-hexaethyloctane-1,8-diaminium group; and the R' group of C = 3,3'-(octane-1,8-diyl)bis(1*H*-imidazol-3-ium) group. The ^{1}H NMR spectra of the reconstituted catalyst (after washing) were seen to contain small or no amounts of impurities, as shown in Figure 24.

[00108] Table 14: Performance Testing of Reconstituted Venturello Catalyst

Entry	**ID**	**Catalyst (prepared from)**	**Amount of Catalyst (mg)**	**H_2O_2 (50% aqueous) (mg)**	**Soybean oil (mg)**	**Toluene (g)**	**Reaction Time (hours)**	**Conversion (%)**	**Selectivity (%)**
1	E-101	A	128	775	775	1.8	3	82.5	95.1
2	E-	Fresh	128	775	775	1.8	3	98.6	86.7

	101a	catalyst						
3	E-102	B	70	424	424	1.0	3	80.5	95.2
4	E-102a	Fresh catalyst	70	424	424	1.0	3	96.4	84.2

[00109] Table 15: Performance Testing of Improved, Reconstituted Venturello Catalyst

Entry	**ID**	**Catalyst (prepared from)**	**Amount of Catalyst (mg)**	**H2O2 (50% aqueous) (mg)**	**Soybean oil (mg)**	**Toluene (g)**	**Reaction Time (hours)**	**Conversion (%)**	**Selectivity (%)**
1	E-105	A	42	254	254	0.6	3	94.3	94.5
2	E-106	B	42	254	254	0.6	3	85.3	95.5
3	E-107	C	42	254	254	0.6	3	93.2	95.1
4	E-108	Fresh catalyst	42	254	254	0.6	3	99.3	84.7

[00110] Example 14: Performance Testing of Reconstituted Venturello Catalyst Using Imidazolium Chloride. When imidazolium chloride was used for tungsten precipitation, and reconstituted Venturello catalyst (large scale) was used for scaled-up epoxidation of soybean oil (518 g) under optimized reaction conditions, conversion and selectivity were seen to be similar to that of the epoxidation reaction using fresh Venturello catalyst. The conditions for this scaled-up epoxidation of soybean oil are shown below in Table 16. At 2 hours, conversion was 95.0% and 94.1% respectively, whereas selectivity was 97.9% and 97.8% respectively for fresh and reconstituted Venturello catalyst, as shown in Figure 25. Therefore, Venturello catalyst can be reconstituted on a large-scale basis and can be used for a scaled-up epoxidation of soybean oil successfully, as reconstituted catalyst showed similar reactivity compared to fresh catalyst in terms of conversion and selectivity.

[00111] Table 16: Reaction Conditions for Scaled-up Soybean Oil Epoxidation Using Reconstituted Venturello Catalyst

Entry	**Description**
Reactor	3L glass jacketed
Amount of soybean oil	581 g (2.68 mol)
Weight of H_2O_2 (50% aqueous)	205.3 g (1.1 equivalents with respect to the double bonds)
Amount of catalyst (Venturello catalyst)	7.6 g
Rate of H_2O_2 addition	2 mL/minute
Catalyst:substrate ratio	1:792 (0.5 weight % of tungsten)
Ramp of JKEM pump (for H_2O_2 addition) (representative case)	57°C (set) 66°C (after H_2O_2 addition decreases) 69°C (H_2O_2 addition stops)
Set Temperature	57°C
Agitation speed	600-700 rpm
Flow rate of recirculating heating unit	~20 L/minute
N_2 Flow rate	~15 L/minute
Toluene (to dissolve catalyst) added	20 g
Reaction Time	150-165 minutes

[00112] Example 15: Reusability Testing of Reconstituted Venturello Catalyst Using Imidazolium Chloride. Reconstituted Venturello catalyst was recycled from three consecutive batches of soybean oil epoxidation reactions conducted at room temperature in batch mode. The average precipitation of the phosphotungsten moiety ($PW_4O_{24}^{3-}$) by imidazolium chloride (as a representative complexing agent due to its commercial availability) was about 83% after 30 minutes of stirring using an epoxidized soybean oil (ESO) to ethanol ratio of 1:2 (weigh percent) and complexing agent greater than 10 equivalents with respect to the stoichiometric amount (with respect to the charge of the phosphotungsten moiety). The average yield of reconstituted catalyst from the precipitated tungsten moiety by imidazolium chloride was about 82%. The recycled catalyst showed slightly lower conversion (about 82-89% vs. 97%, after 3 hours) but higher selectivity (95-98% vs. 90%) compared to fresh Venturello catalyst. The recycled catalyst showed comparable activity in the case of all three consecutive batches. The reaction conditions are shown below in Table 17 and Table 18. In Table 18, FC stands for fresh catalyst and RC stands for reconstituted catalyst using imidazolium chloride as the complexing agent and Aliquat® 336 as the phase transfer reagent.

[00113] Table 17: General Conditions for Soybean Oil Epoxidation Using Fresh and Reconstituted Venturello Catalyst, Batch Mode

Entry	**Value**
Venturello catalyst (fresh or reconstituted)	35 mg (0.0152 mmol)
Soybean oil	0.18 g (0.92 mmol)
H_2O_2 (50 % aq.)	0.18 g (2.65 mmol)
Toluene	0.8 g
Temperature	Room temperature (~22°C)
Time of reaction	3 hours

[00114] Table 18: Results for Soybean Oil Epoxidation Using Fresh and Reconstituted Venturello Catalyst

Entry	**Cycle**	**ID**	**Conversion %**	**Selectivity %**	**Yield%**
1	0 (FC)	E 108-1	97.28	90.0	87.55
2	1 (RC)	E108-2	83.22	95.1	79.14
3	2 (RC)	E108-3	89.34	97.2	86.84
4	3 (RC)	E108-4	81.40	97.5	79.36

[00115] The present invention has been described with reference to certain examples. However, it will be recognized by those of ordinary skill in the art that various substitutions, modifications, or combinations of any of the examples may be made without departing from the spirit and scope of the invention. Thus, the invention is not limited by the description of the examples, but rather by the appended claims as originally filed.

CLAIMS

What is claimed is:

1. A method of separating a catalyst from a product mixture comprising:

combining the product mixture with a complexing agent in the presence of a solvent;

wherein the product mixture comprises the catalyst; and

recovering a precipitate formed from combining the product mixture with the complexing agent,

wherein the precipitate comprises a metal complex portion of the catalyst.

2. The method of claim 1, wherein the product mixture further comprises an epoxidized vegetable oil.

3. The method of claim 1 or claim 2, wherein the product mixture further comprises epoxidized soybean oil.

4. The method of claim 1 or claim 2, wherein the catalyst comprises an element selected from the group consisting of tungsten, phosphorous, and combinations of any thereof.

5. The method of claim 1 or claim 2, wherein the catalyst comprises a Venturello catalyst characterized by a phosphotungstate complex of the formula $Q_3PW_4O_{24}$, where Q represents a hydrophobic cation.

6. The method of claim 1 or claim 2, wherein the solvent is an alcohol.

7. The method of claim 1 or claim 2, wherein the solvent is selected from the group consisting of ethanol, methanol, isopropanol, and combinations of any thereof.

8. The method of claim 1 or claim 2, wherein the solvent is ethanol.

9. The method of claim 1 or claim 2, wherein the complexing agent is selected from the group consisting of quaternary amine salts, imidazolium salts, pyridinium salts, and combinations of any thereof.

10. The method of claim 9, wherein the quaternary amine salts are selected from the group consisting of tetra-butyl ammonium bromide, tris(hydroxymethyl)aminoethane hydrochloride, and combinations of any thereof.

11. The method of claim 9, wherein the imidazolium salts are selected from the group consisting of methyl imidazolium chloride, imidazolium chloride, 1-ethyl-3-methyl imidazolium chloride, and combinations of any thereof.

12. The method of claim 9, wherein the pyridinium salt comprises 2-chloropyridine hydrochloride.

13. The method of claim 1 or claim 2, wherein the complexing agent is selected from the group consisting of 1-ethyl-3-methyl imidazolium chloride, imidazolium chloride, and combinations of any thereof.

14. The method of claim 1 or claim 2, wherein the product mixture:solvent ratio is about 1:2 weight/weight.

15. The method of claim 1 or claim 2, wherein the combining the product mixture with the complexing agent in the presence of the solvent is carried out while stirring for at least 30 minutes.

16. The method of claim 1 or claim 2, wherein the combining the product mixture with the complexing agent in the presence of the solvent is carried out at room temperature.

17. The method of claim 1 or claim 2, wherein the recovering the precipitate formed from combining the product mixture with the complexing agent is carried out by filtration, resulting in the precipitate and a filtrate.

18. The method of claim 17, further comprising allowing the filtrate to stand for at least 8 hours, giving an additional amount of the precipitate.

19. A method of reconstituting a catalyst comprising:

solubilizing a precipitate comprising a metal complex portion of the catalyst, thus forming a solution; and

adding a phase transfer reagent to the solution;

thus forming a reconstituted catalyst.

20. The method of claim 19, wherein the solubilizing the precipitate comprising the metal complex portion of the catalyst comprises stirring the precipitate in a hydrogen peroxide solution.

21. The method of claim 20, wherein the solubilizing the precipitate comprising the metal complex portion of the catalyst further comprises stirring the precipitate in the presence of an acid.

22. The method of claim 21, wherein the acid is hydrochloric acid.

23. The method of claim 19 or claim 20, wherein the adding the phase transfer reagent to the solution further comprises adding an organic solvent.

24. The method of claim 23, wherein the organic solvent is selected from the group consisting of dichloromethane, ethyl acetate, or combinations of any thereof.

25. The method of claim 19 or claim 20, wherein the metal complex portion of the catalyst comprises a phosphotungstate complex.

26. The method of claim 19 or claim 20, wherein the phase transfer reagent comprises a quaternary ammonium salt.

27. A method of recovering a catalyst from a product mixture comprising:

separating the catalyst from the product mixture;

wherein the product mixture comprises the catalyst; and

reconstituting the catalyst.

28. The method of claim 27, wherein the product mixture further comprises an epoxidized vegetable oil

29. The method of claim 28, wherein the expoxidized vegetable oil comprises epoxidized soybean oil.

30. The method of claim 27 or claim 28, wherein the catalyst comprises an element selected from the group consisting of tungsten, phosphorous, and combinations of any thereof.

31. The method of claim 27 or claim 28, wherein the catalyst comprises a Venturello catalyst characterized by a phosphotungstate complex of the formula $Q_3PW_4O_{24}$, where Q represents a hydrophobic cation.

32. The method of claim 31, wherein the hydrophobic cation comprises a methyltrioctylammonium ion.

33. The method of claim 27 or claim 28, wherein the separating the catalyst from the product mixture further comprises:

combining the product mixture with a complexing agent in the presence of a solvent; and

recovering a precipitate formed from combining the product mixture with the complexing agent;

wherein the precipitate comprises a metal complex portion of the catalyst.

34. The method of claim 33, wherein the solvent is an alcohol.

35. The method of claim 33, wherein the solvent is selected from the group consisting of ethanol, methanol, isopropanol, and combinations of any thereof.

36. The method of claim 33, wherein the complexing agent is selected from the group consisting of quaternary amine salts, imidazolium salts, pyridinium salts, and combinations of any thereof.

37. The method of claim 33, wherein the complexing agent is selected from the group consisting of tetra-butyl ammonium bromide, tris(hydroxymethyl)aminoethane hydrochloride, methyl imidazolium chloride, imidazolium chloride, 1-ethyl-3-methyl imidazolium chloride, 2-chloropyridine hydrochloride, and combinations of any thereof.

38. The method of claim 33, wherein the product mixture to solvent ratio is about 1:2 weight/weight.

39. The method of claim 33, wherein the reconstituting the catalyst further comprises:

solubilizing the precipitate, thus forming a solution; and

adding a phase transfer reagent to the solution, thus forming a reconstituted catalyst.

40. The method of claim 39, wherein the solubilizing the precipitate further comprises stirring the precipitate in the presence of an acid.

41. The method of claim 40, wherein the acid is hydrochloric acid.

42. The method of claim 39, wherein the adding the phase transfer reagent to the solution further comprises adding an organic solvent.

43. The method of claim 42, wherein the organic solvent is selected from the group consisting of dichloromethane, ethyl acetate, or combinations of any thereof.

44. The method of claim 39, wherein the phase transfer reagent comprises a quaternary ammonium salt.

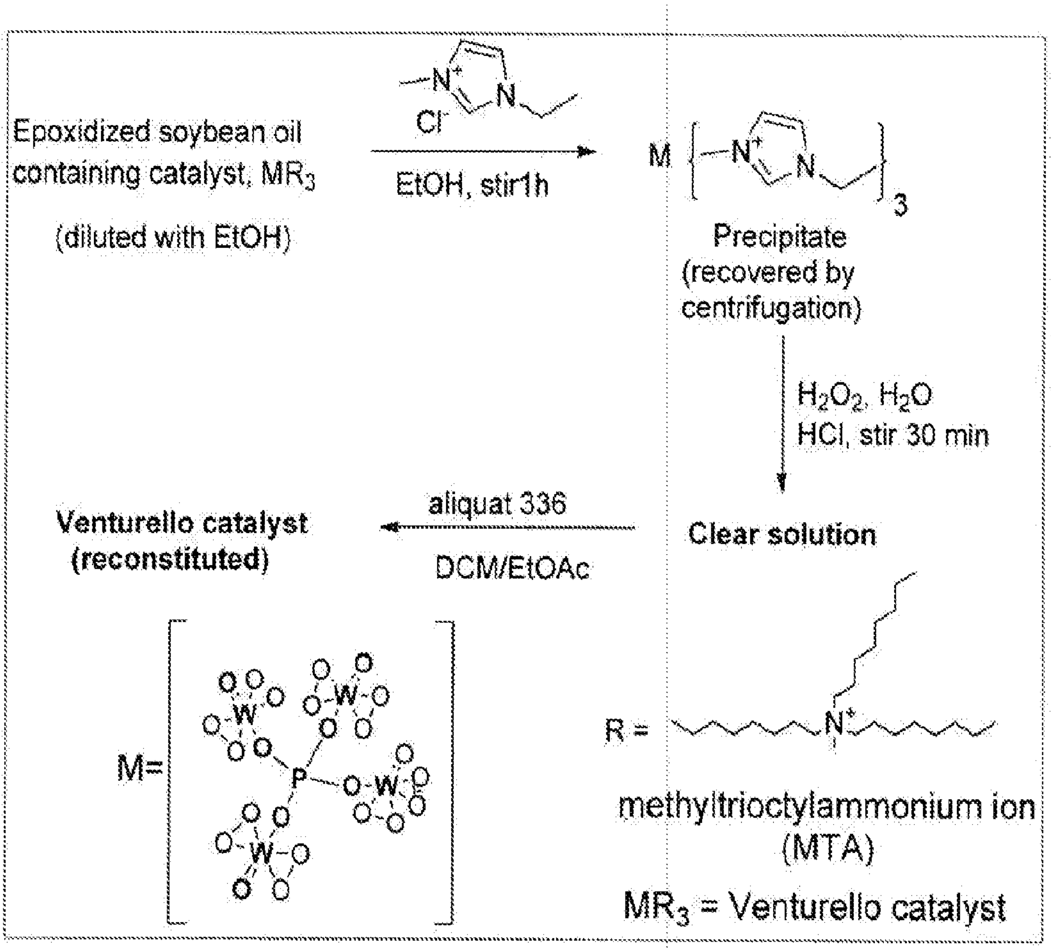


Fig. 1: Catalyst Separation by Complexation Followed by Precipitation and Catalyst Reconstitution

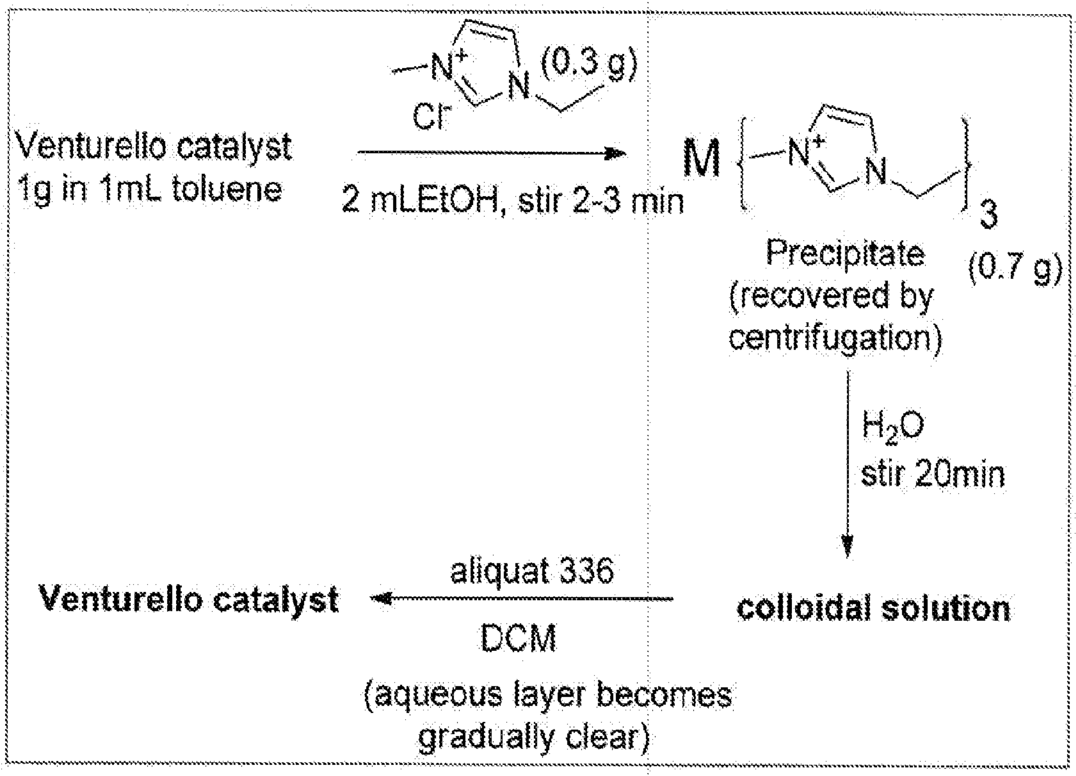
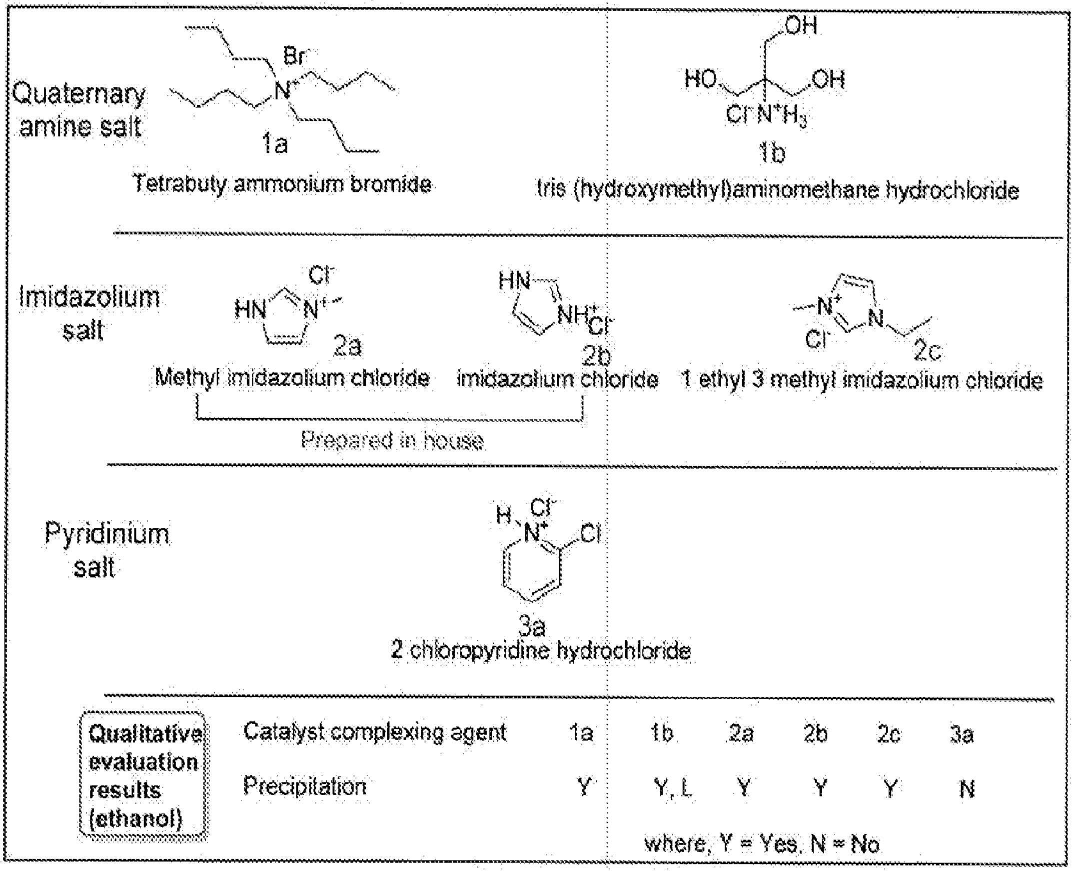


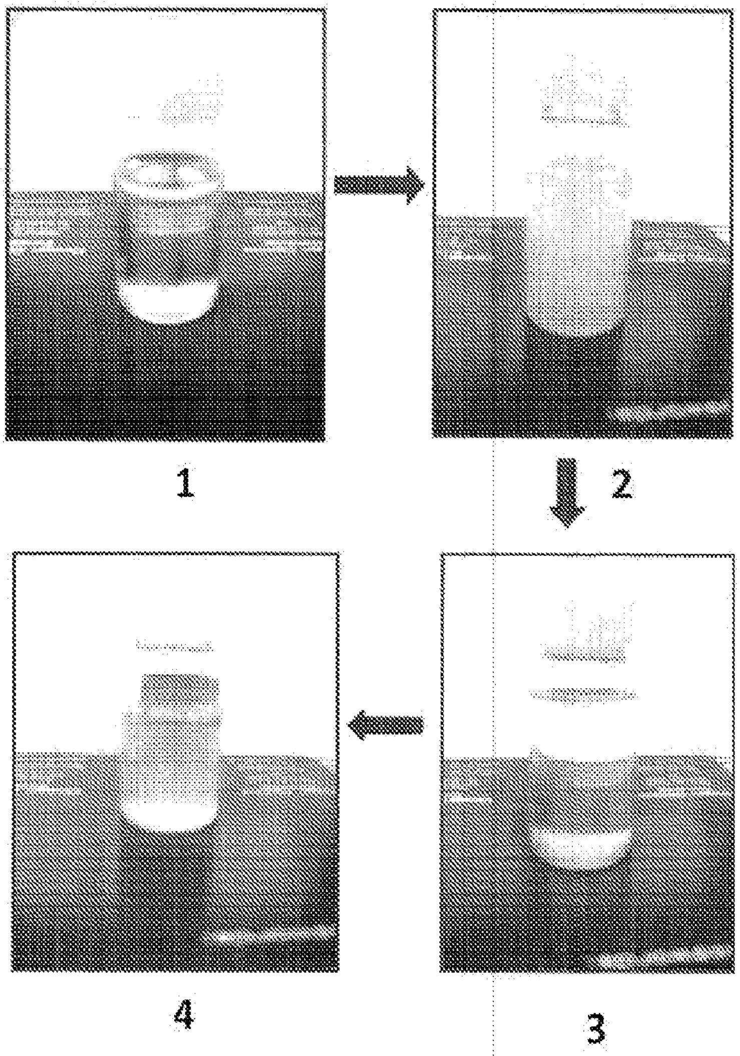
Fig. 2: Catalyst Separation by Complexation Followed by Precipitation and Further Improved Catalyst Reconstitution



Catalyst complexing agent	1a	1b	2a	2b	2c	3a
Precipitation	Y	Y, L	Y	Y	Y	N

where, Y = Yes, N = No

Fig. 3: Catalyst Complexing Agents Evaluated for Precipitation of Venturello Catalyst



1. Epoxidized soybean oil diluted with EtOH
2. Precipitation (1st) after ~ 30 min stirring with imidazolium chloride
3. After centrifugation; 2400 rpm, 5 min.
4. Light precipitation (2nd) on standing the filtrate for over night

Fig. 4: Stepwise Precipitation Formed by Catalyst Complexing Agent in Ethanol

Catalyst recovery: Salt used 1ethyl3methylimidazolium chloride

ESO used	Imidazolium salt used (2C)	1st precipiation % (mg)	2nd precipitation % (mg)	Total precipitation % (mg)
4g	0.1g	73.2 (52)	15.5 (11)	88.7 (63)

Catalyst reconstitution: Salt used 1ethyl3methylimidazolium chloride

W-imidazolium salt	H_2O_2	HCl (conc.)	Aliquat 336	Amount of expected catalyst	Amount of prepared catalyst
Initial method: 31 mg	0.1g	~30 mg	30 mg	51.8 mg	52 mg (100.4%)
Improved method: 31 mg	0.3g	No	28 mg	49.8 mg	40 mg (80.3 %)

Fig. 5: Conditions and Results for Recovery and Reconstitution of Venturello Catalyst

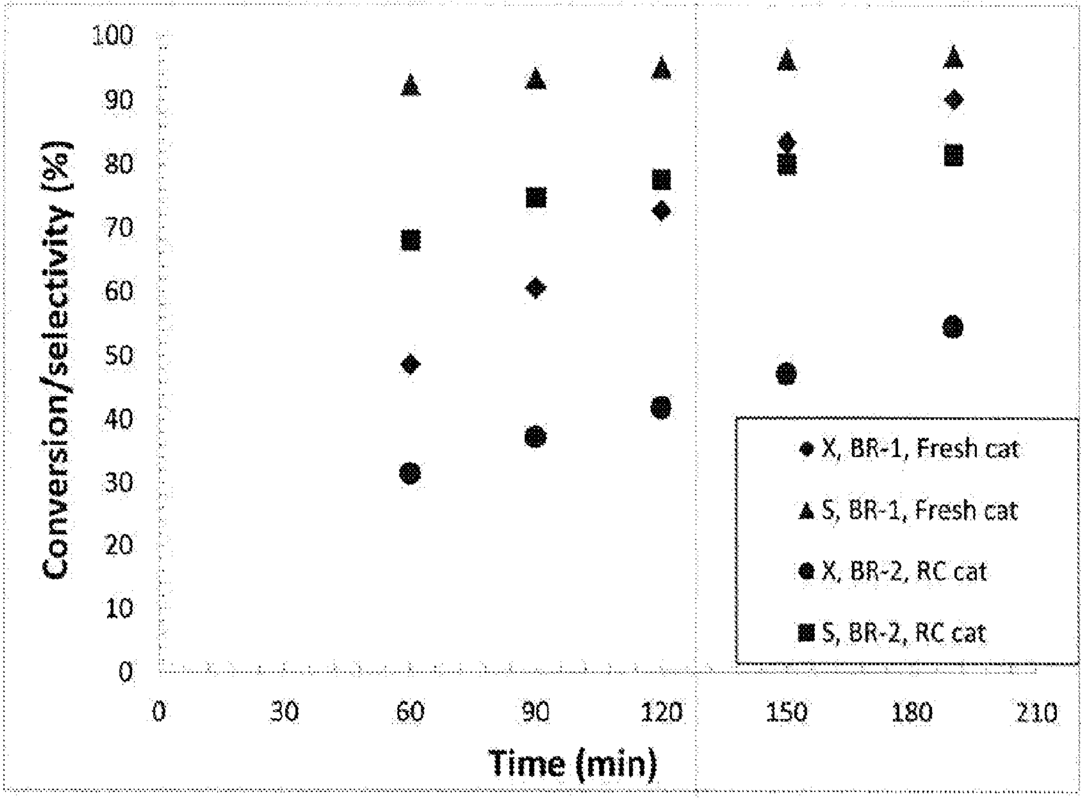


Fig. 6: Comparative Conversion and Selectivity Profiles for Epoxidation of Methyl Oleate Using Fresh Catalyst (Fresh Cat) and Reconstituted Catalyst (RC Cat)

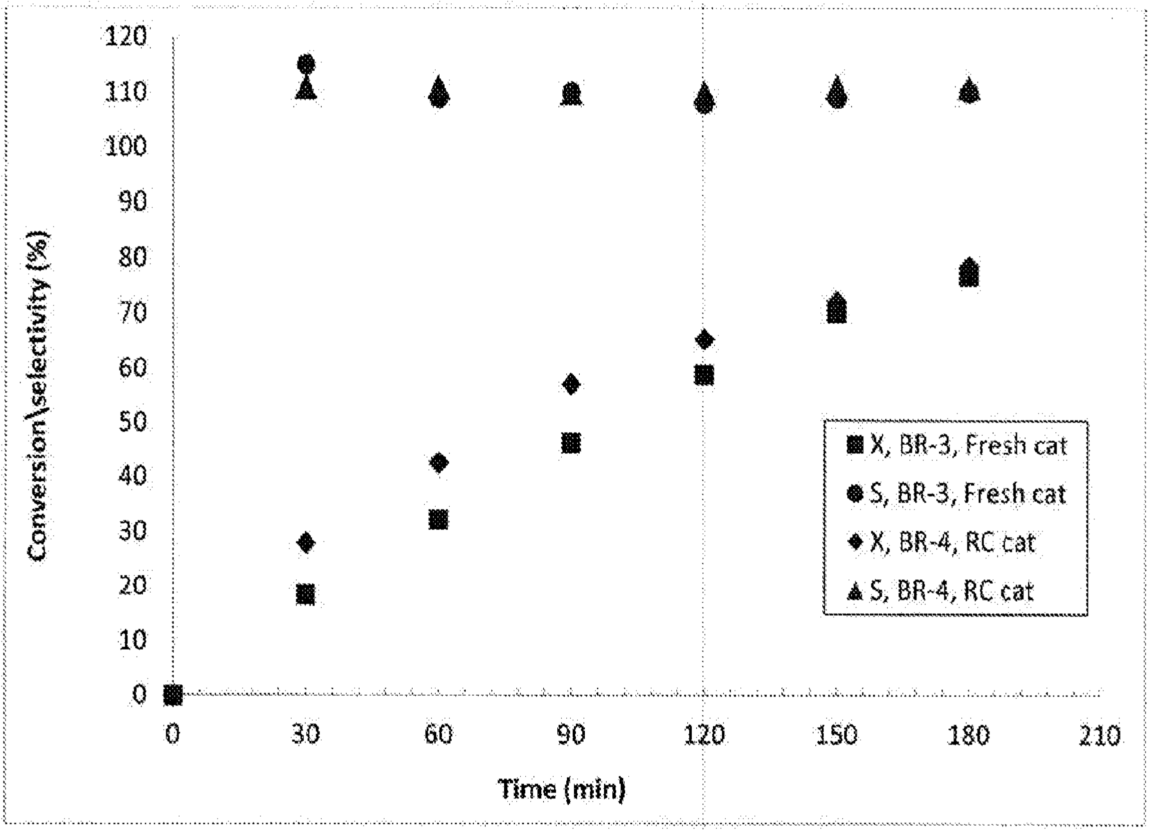


Fig. 7: Comparative Conversion and Selectivity Profiles for Expoxidation of Methyl Oleate Using Fresh Catalyst (Fresh Cat) and Reconstituted Catalyst (RC Cat) Prepared by Improved Method

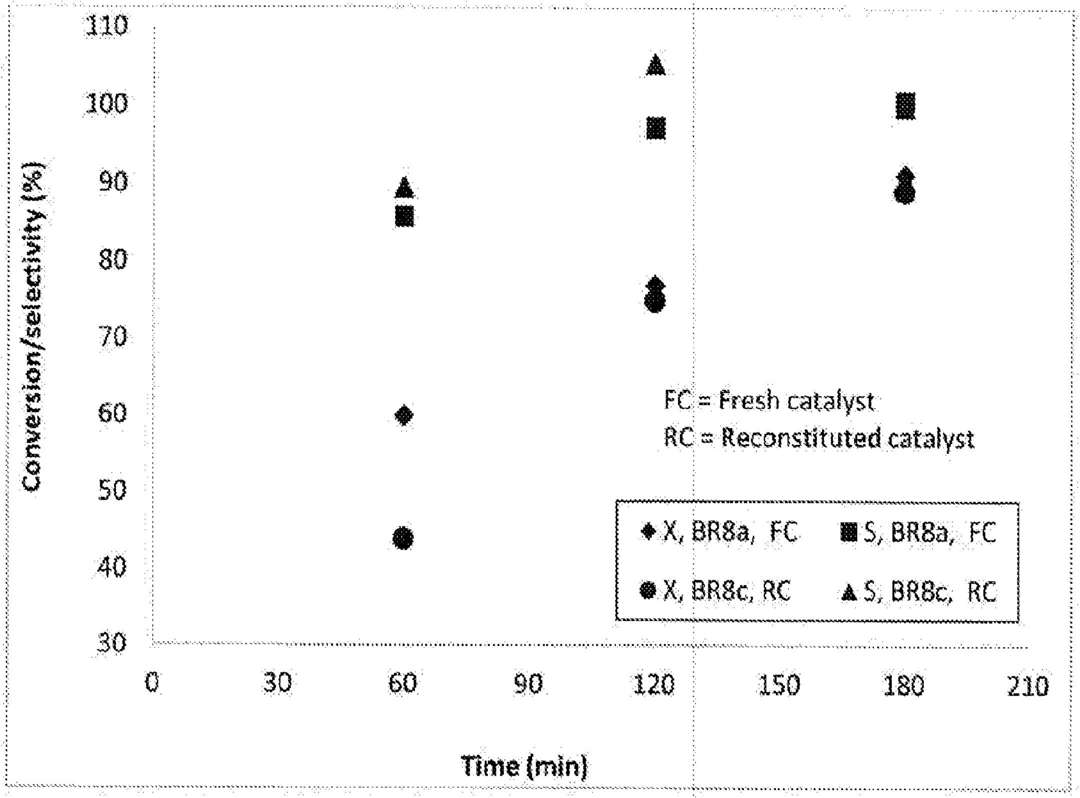


Fig. 8: Comparative Conversion and Selectivity Profiles for Epoxidation of Methyl Oleate Using Fresh Catalyst (Fresh Cat) and Reconstituted Catalyst (RC Cat) Prepared by Further Improved Method

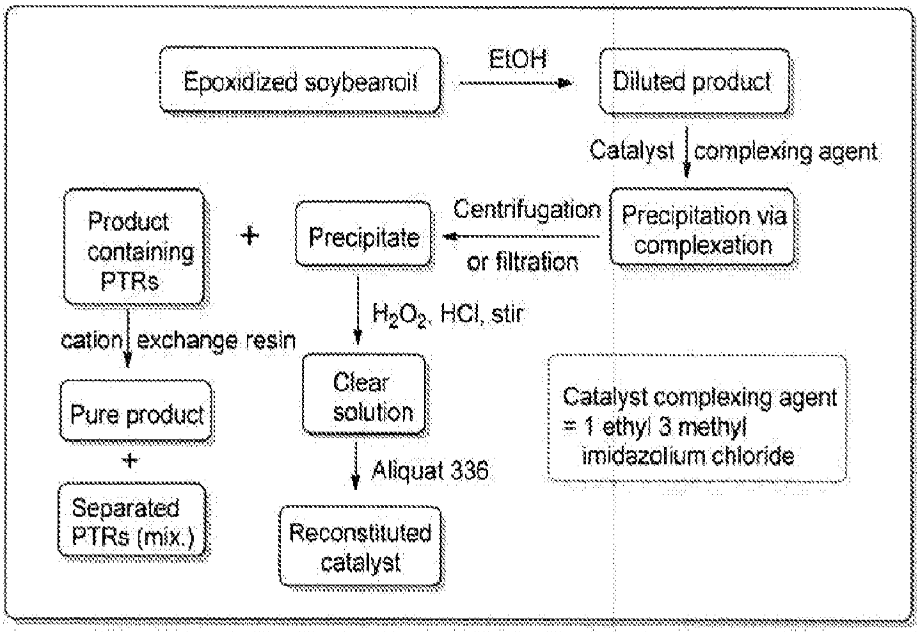


Fig. 9: Catalyst Separation by Complexation Followed by Precipitation and Further Improved Catalyst Reconstitution

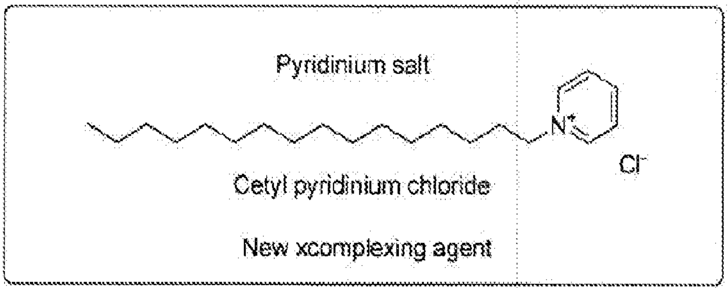


Fig. 10: Cetyl Pyridinium Chloride as Complexing Agent for Recovery of Catalyst by Complexation Followed by Precipitation.

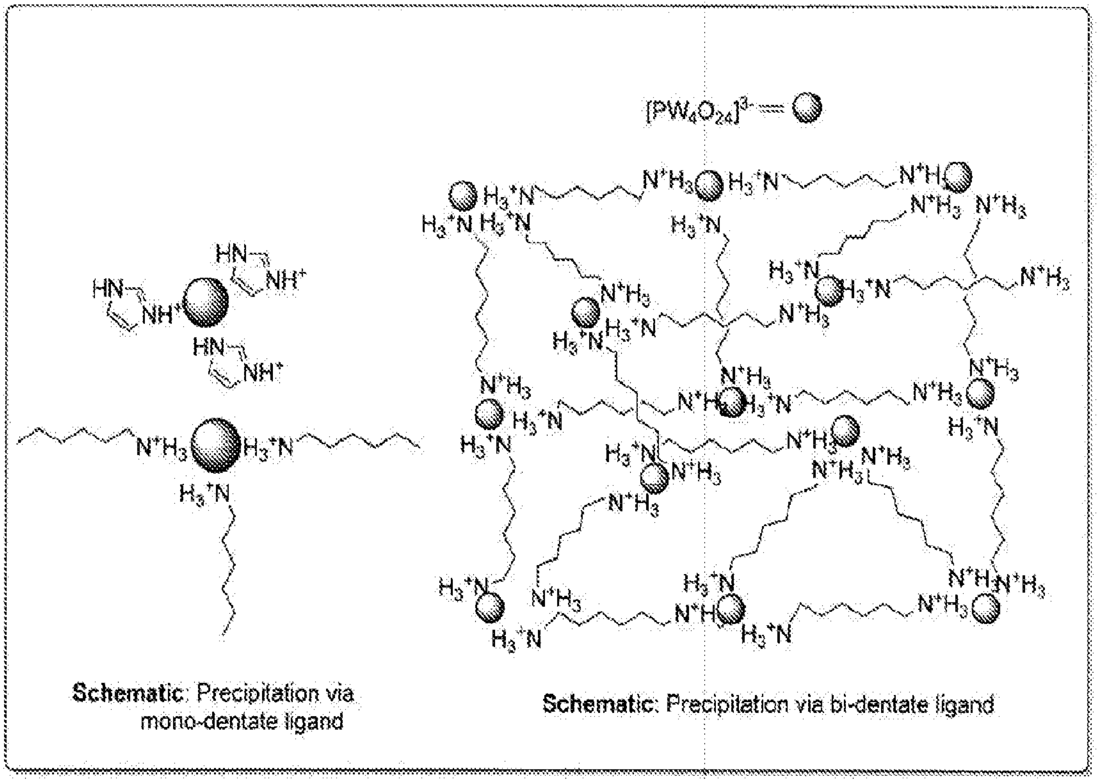


Fig. 11: Comparison of Mono-dentate and Bi-dentate Complexing Agents

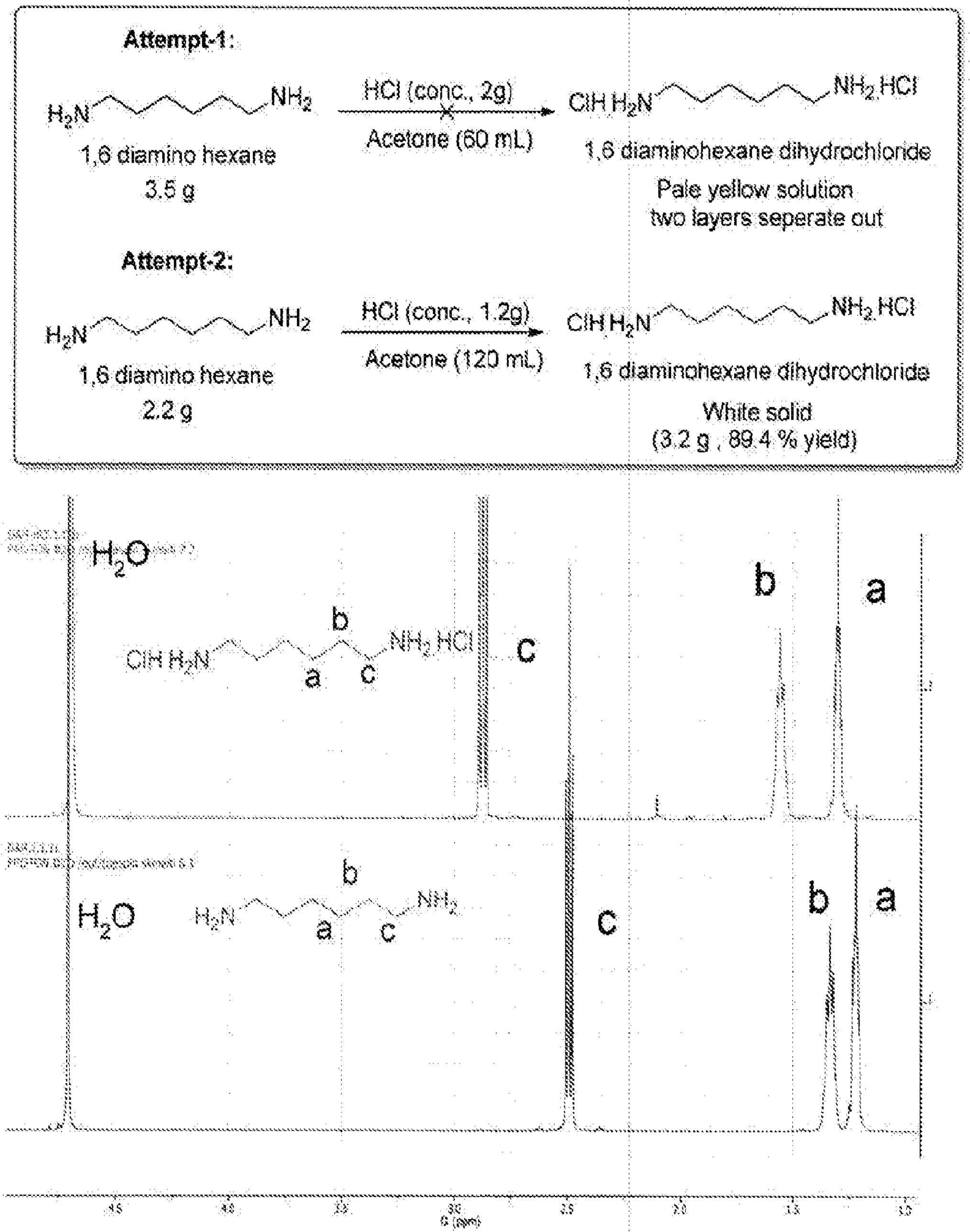


Fig. 12: Preparation of 1, 6-Diaminohexane Dihydrochloride and its 1H NMR spectra

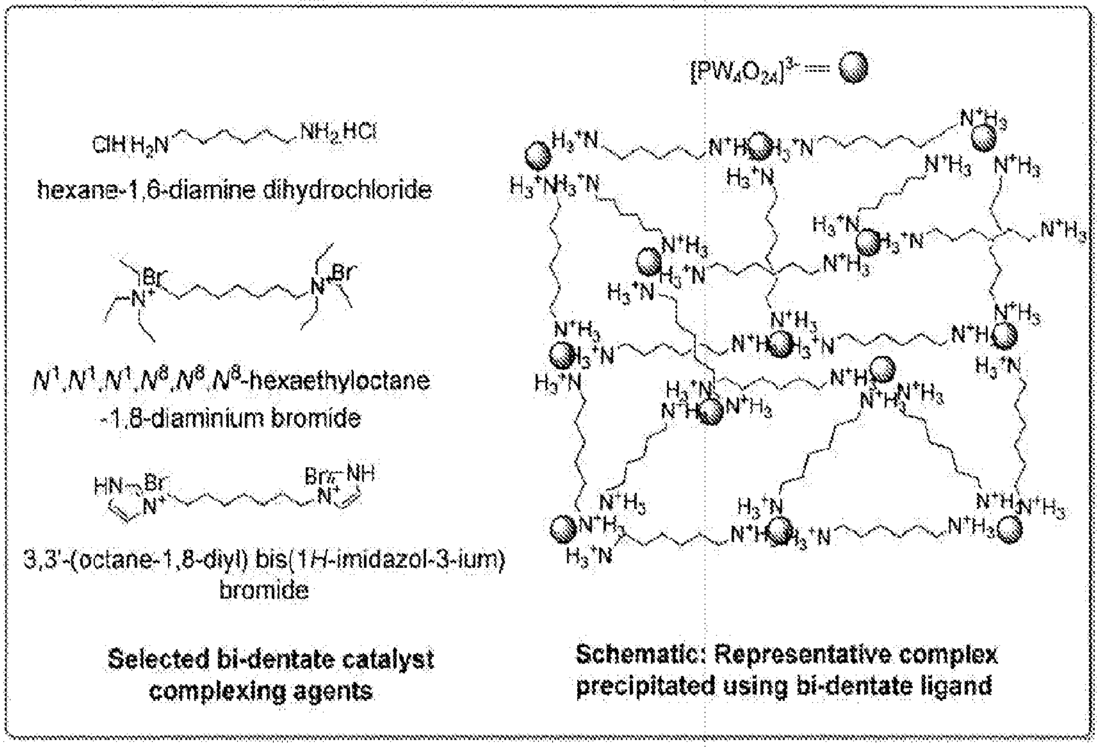


Fig. 13: Additional Bi-dentate Complexing Agents (Ligands)

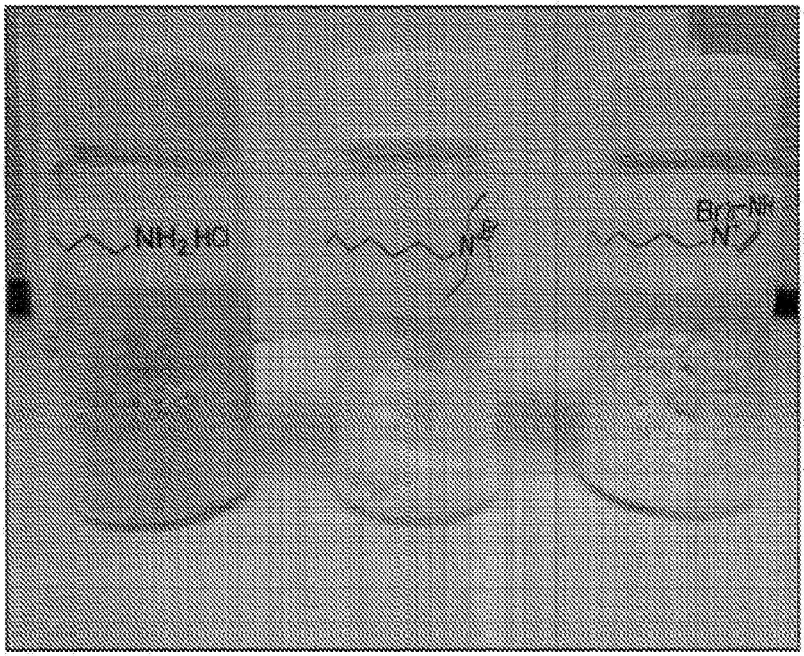


Fig. 14: Isolated Synthesized Bi-Dentate Complexing Agents (Ligands)

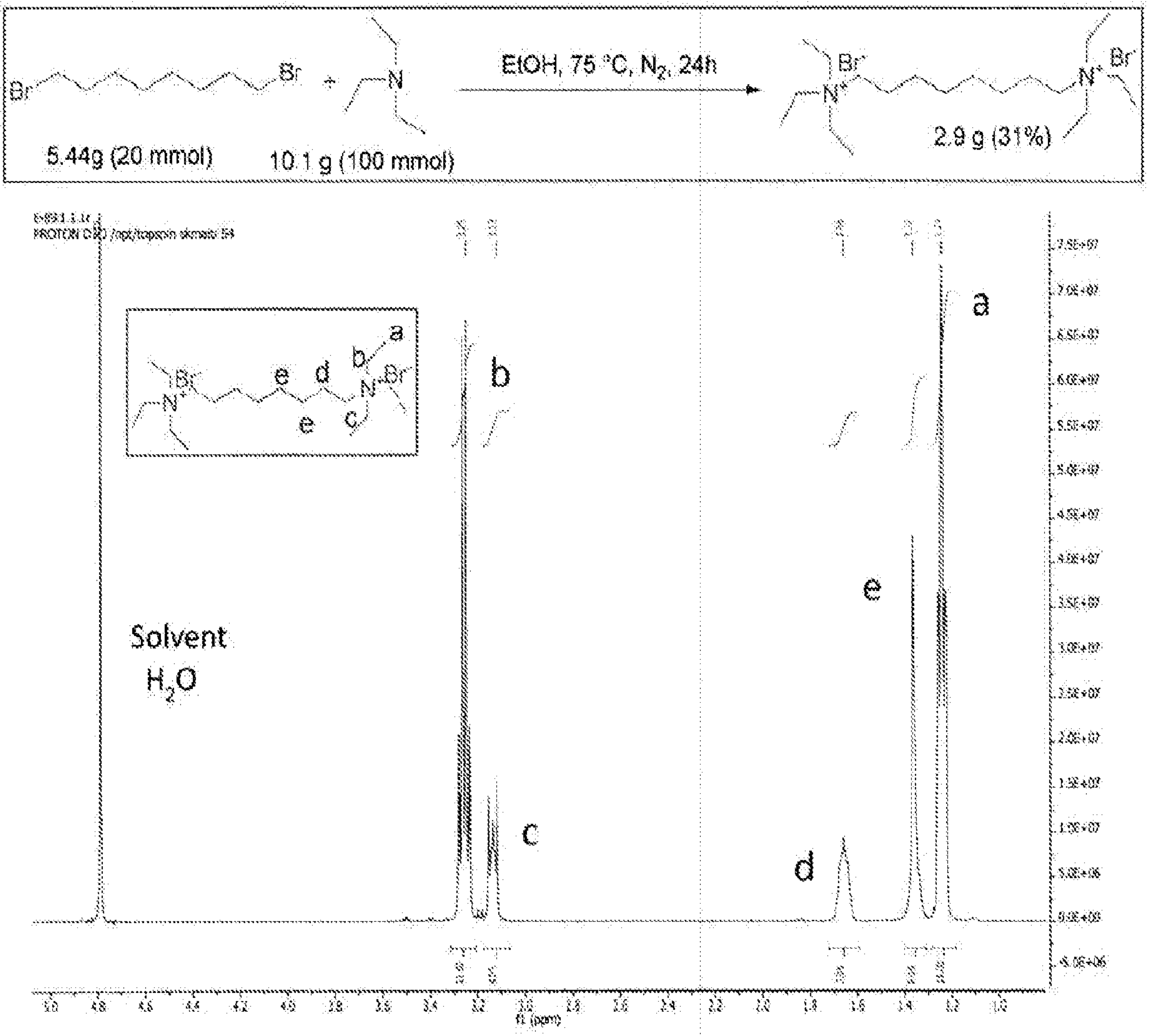


Fig. 15: Synthesis and Characterization of N^1, N^1, N^1, N^8, N^8, N^8-hexaethyloctane-1,8-diaminium bromide by 1H NMR spectroscopy

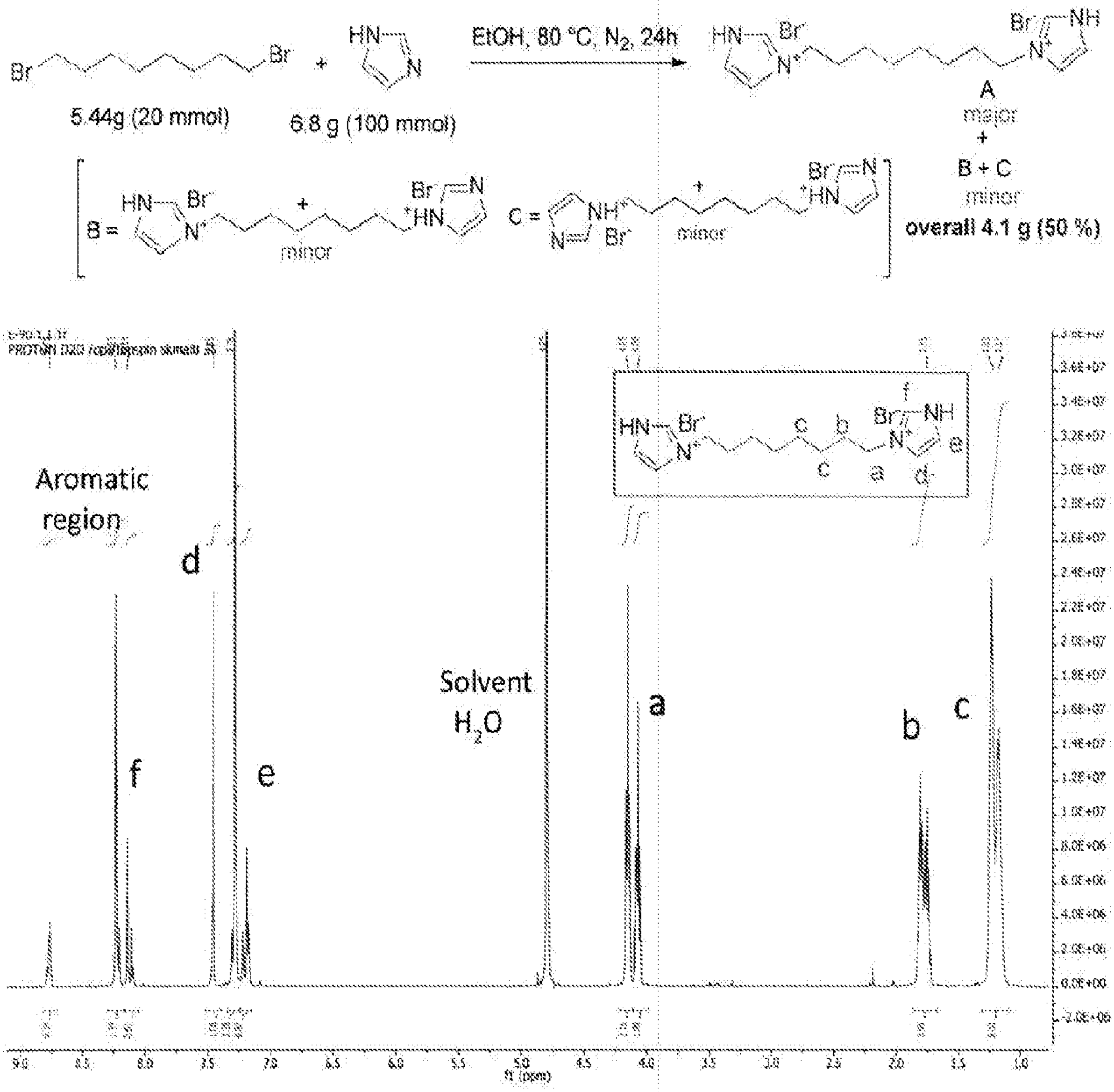


Fig. 16: Synthesis and Characterization of 3,3'-(octane-1,8-diyl) bis (1*H*-imidazol-3-ium) bromide

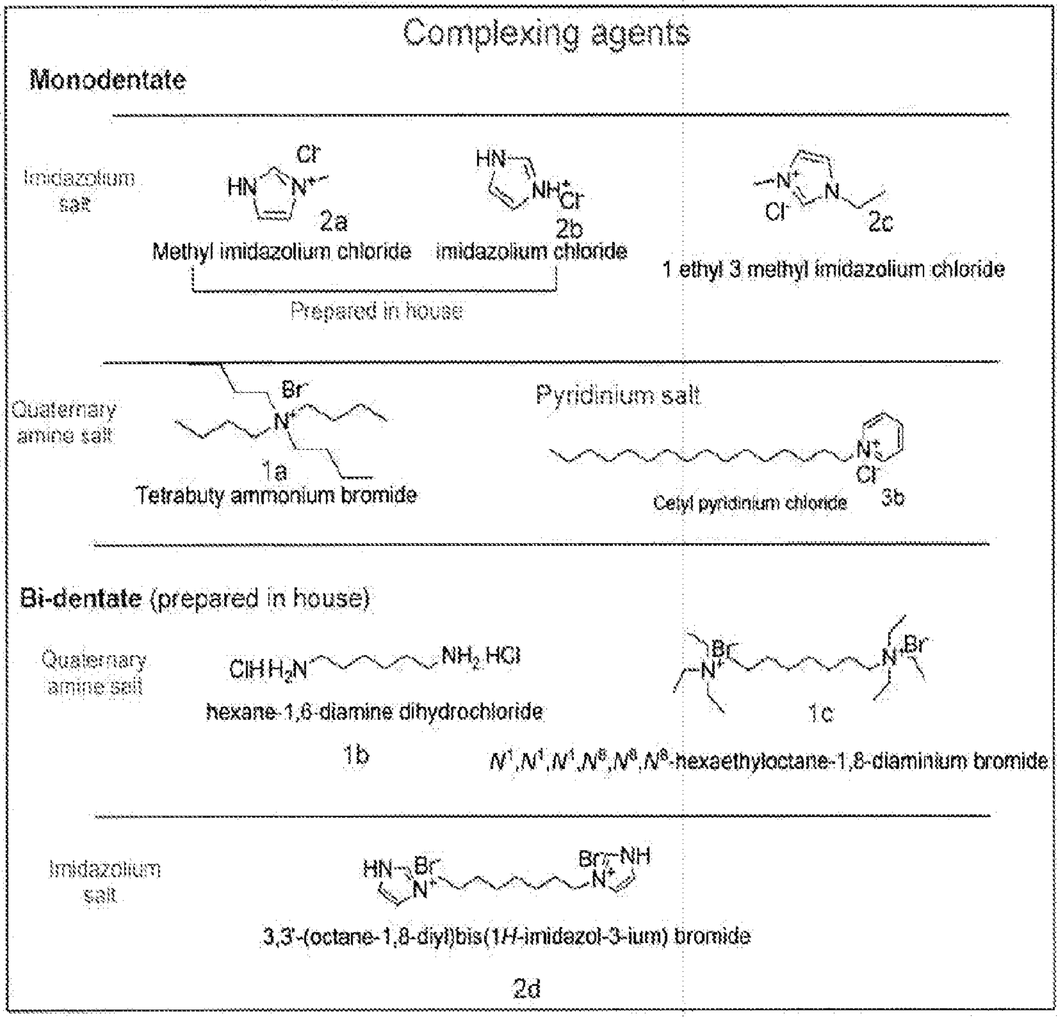
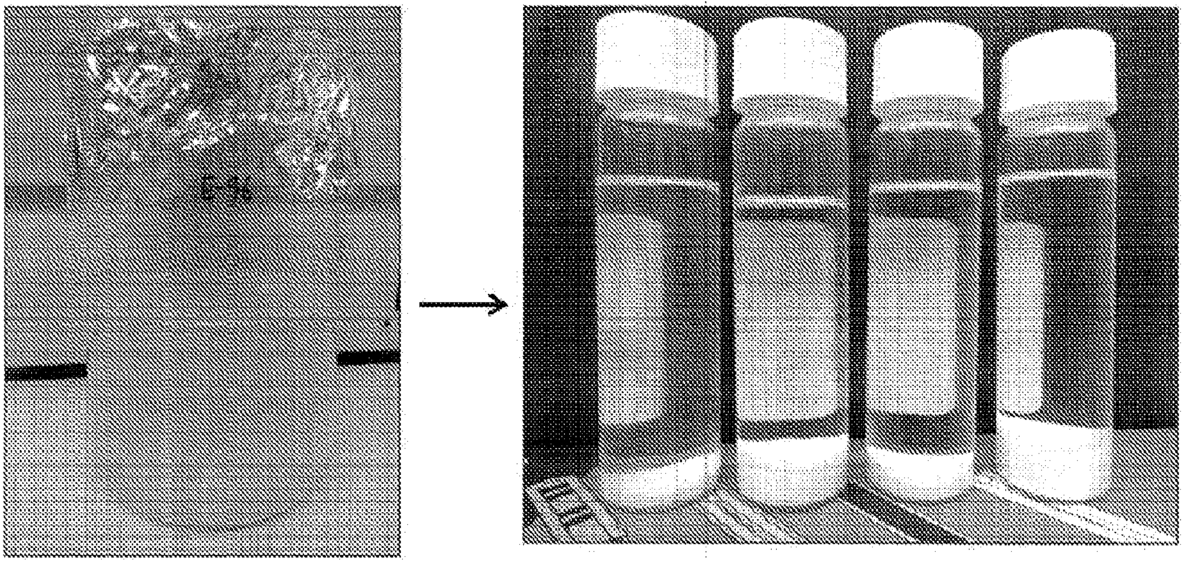


Fig. 17: Mono-dentate and Bi-dentate Complexing Agents



1320g
Maximum precipitate settle at the bottom (overnight standing)

After centrifugation
(cumulative precipitation)

Fig. 18: Large-Scale Separation (from 440 g ESO) of Venturello Catalyst

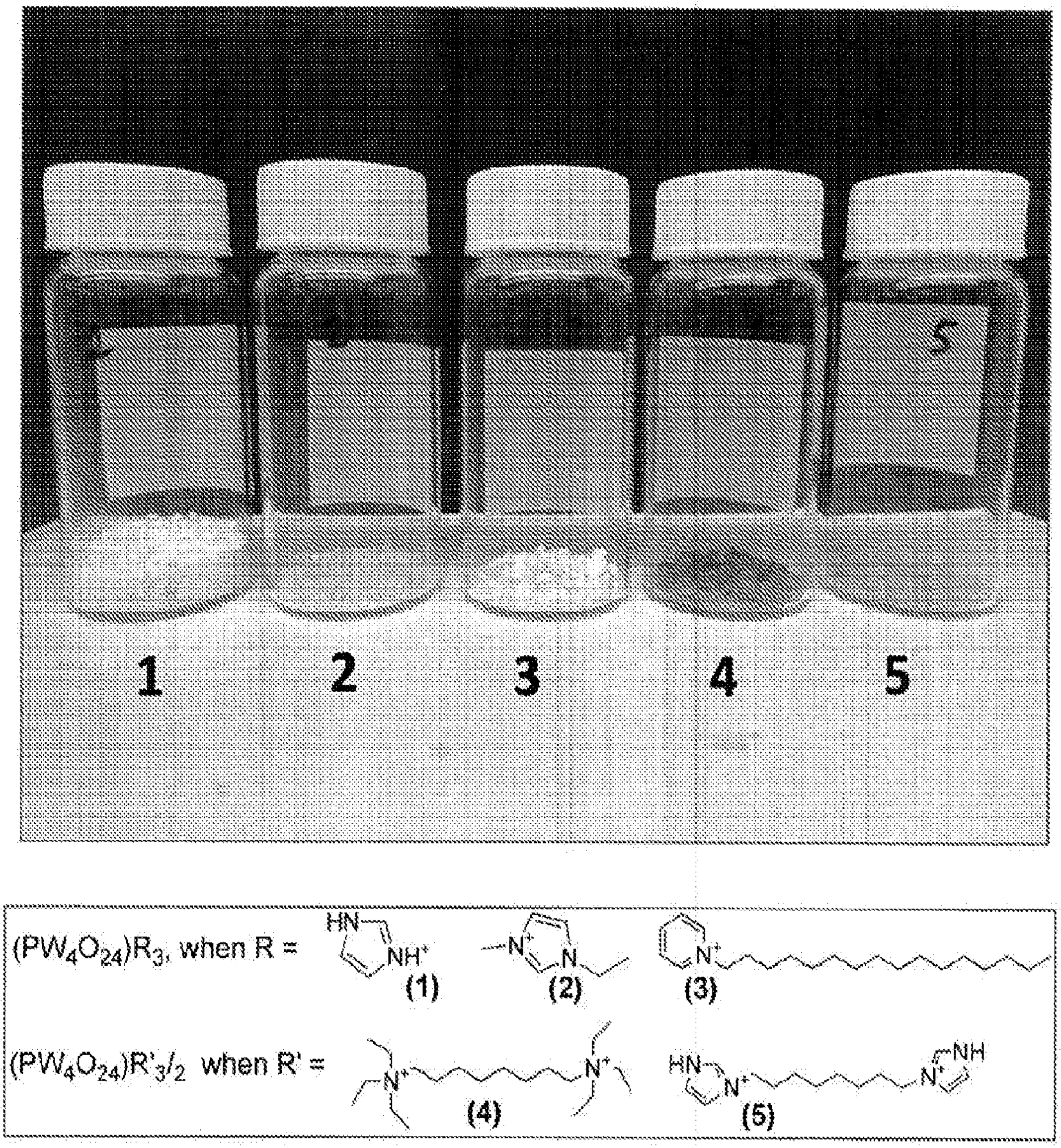


Fig. 19: Recovered Peroxophosphotungsten Moiety from Venturello Catalyst in Epoxidized Soybean Oil

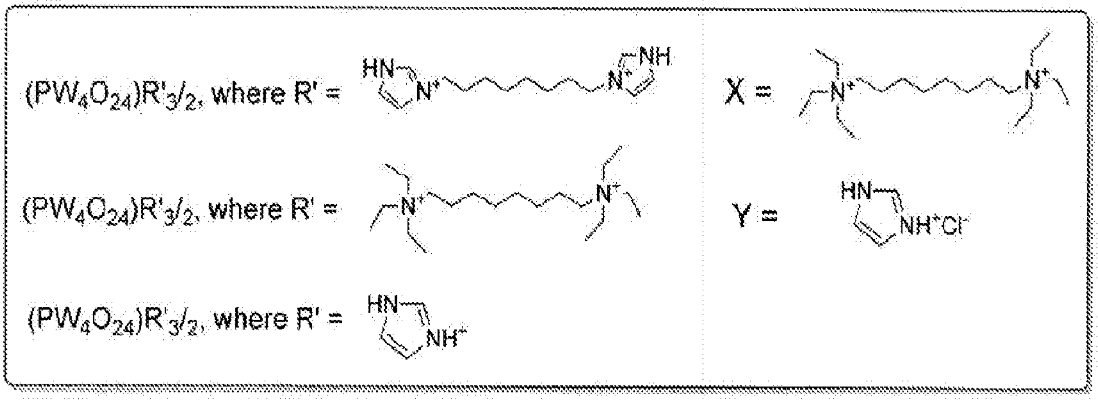


Fig. 20: Tungsten-containing Precipitates and Internal Standards (X, Y) Used for Reconstitution of Venturello Catalyst

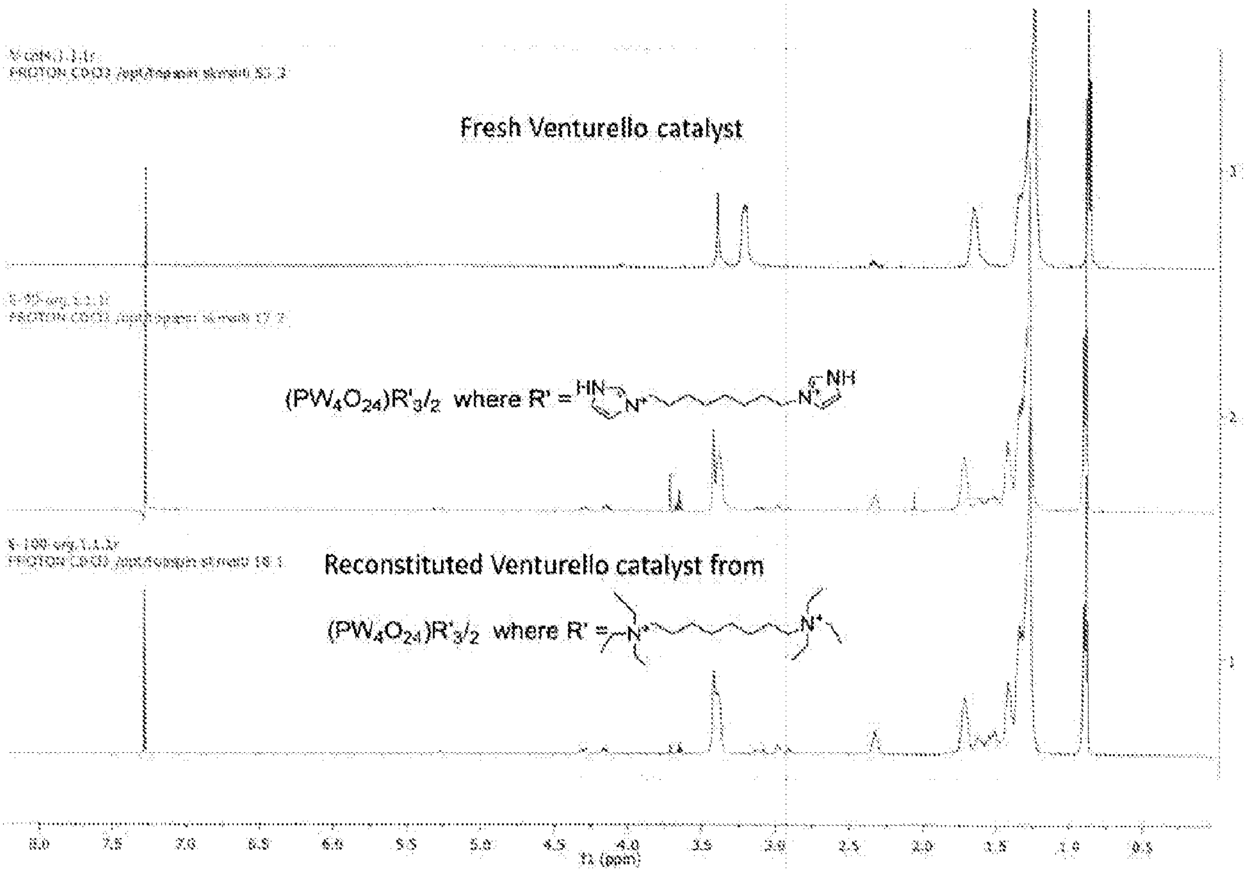


Fig. 21: ^{1}H NMR of Fresh and Reconstituted Venturello Catalyst

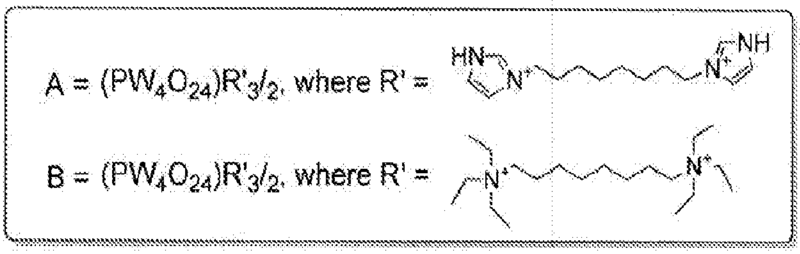


Figure 22: Sources of Reconstituted Venturello Catalyst

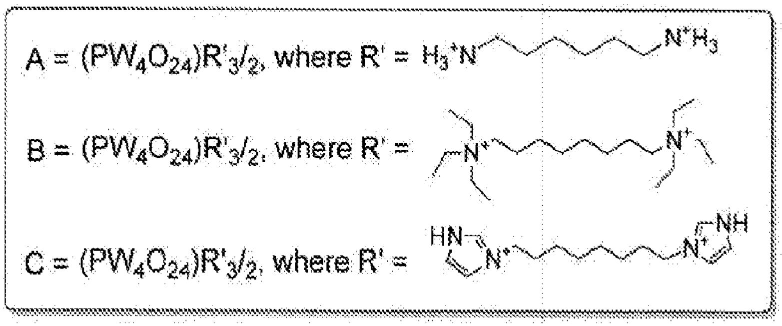


Fig. 23: Sources of Reconstituted Venturello Catalyst

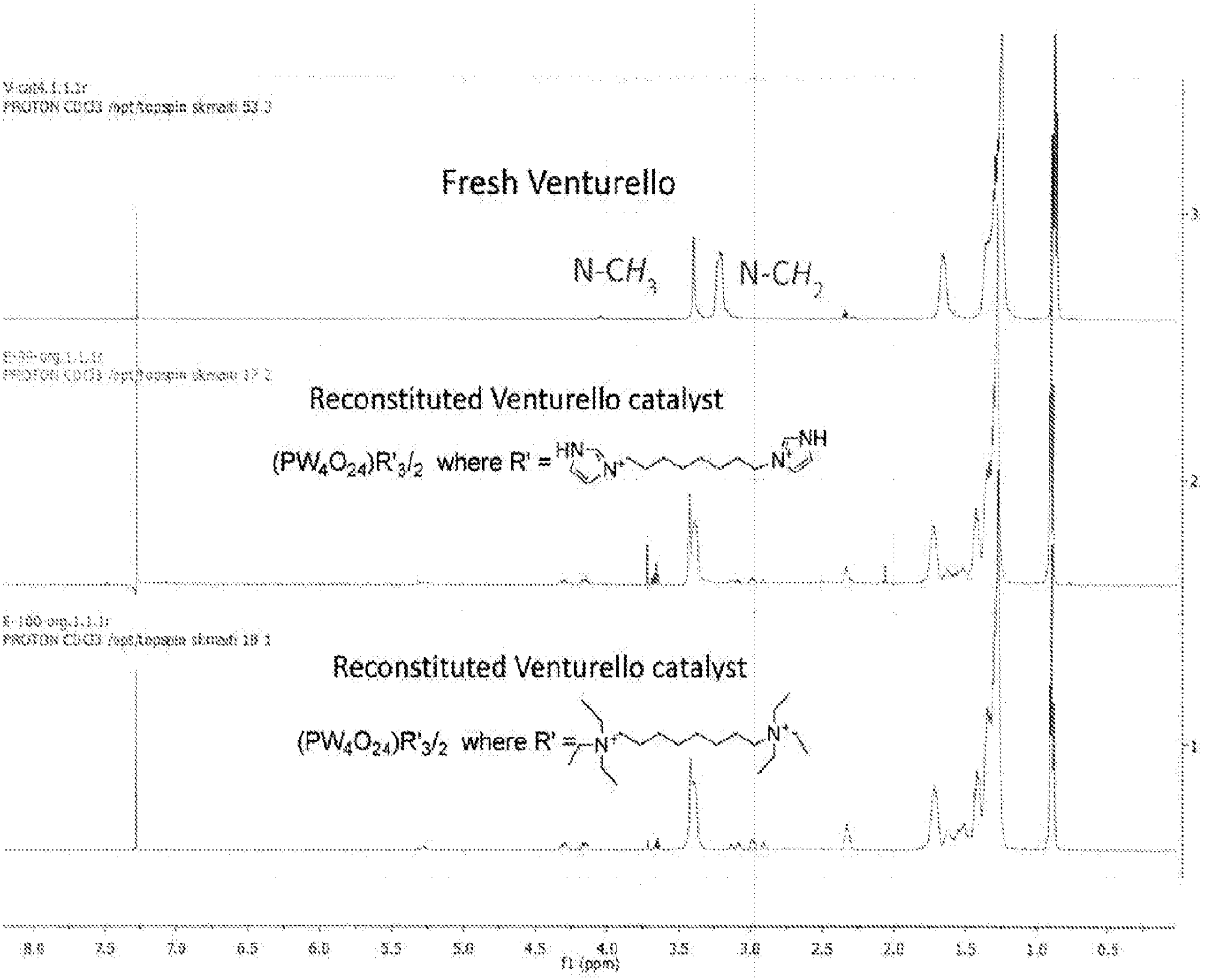


Fig. 24: ^{1}H NMR of Fresh and Improved, Reconstituted Venturello Catalyst

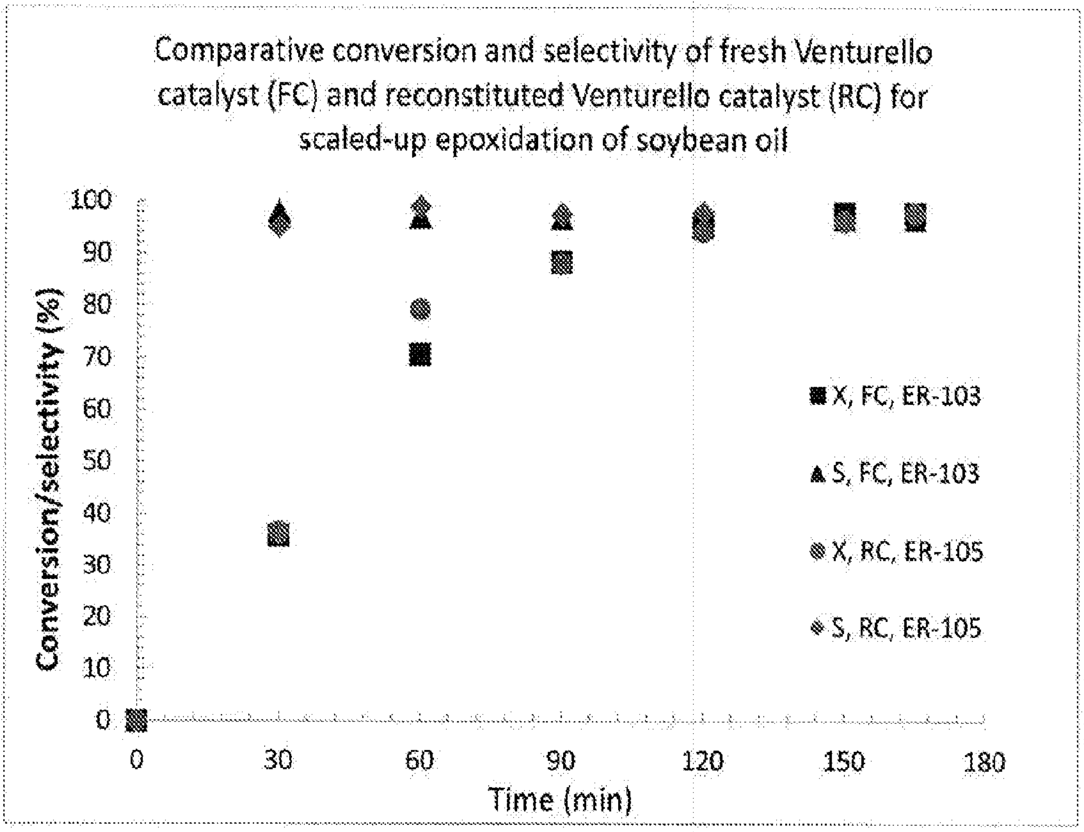


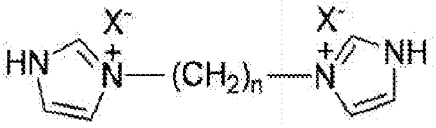
Fig. 25: Conversion and Selectivity of Fresh Venturello Catalyst (FC) and Reconstituted Venturello Catalyst (RC) for Scaled-up Epoxidation of Soybean Oil

A. Complexing agents containing two quaternary ammonium groups

$$X^- \;{}^+N(R)_3 — (CH_2)_n — N^+(R)_3 \; X^-$$

Where 'n' may be 2-10; 'R' may be H, $-CH_3$, $-C_2H_5$, $-C_3H_7$, $-C_4H_9$ and 'X' may be Cl^-, Br^- or I^-

B. Complexing agents containing two imidazolium groups



Where 'n' may be 2-10 and 'X' may be Cl^-, Br^- or I^-

Fig. 26: General Scheme for Complexing Agents Containing Two Functional Groups

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US17/14296

A. CLASSIFICATION OF SUBJECT MATTER
IPC - B01J 31/02, 31/22, 31/24, 38/68; C08F 4/22; C08G 65/30 (2017.01)
CPC - B01J 31/02, 31/0239, 31/22, 31/24, 38/68; C08F 4/22; C08G 65/30, 65/46

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
See Search History document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3,857,895 A (BOOTH, FB) 31 December 1974; abstract; column 2, lines 1-30; column 3, lines 30-40; column 6, lines 20-25; column 8, lines 25-45; column 11, lines 35-55; column 13, lines 30-55; claims 1, 5	1, 4/1, 6/1, 7/1, 14/1, 16/1, 17/1, 19, 23/19, 27, 30/27, 33/27, 34/33/27, 35/33/27, 38/33/27, 39/33/27, 40/39/33/27, 41/40/39/33/27, 42/39/33/27
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Y		2, 3/1-2, 4/2, 5/1-2, 6/2, 7/2, 8/1-2, 9/1-2,10/9/1-2, 11/9/1-2, 12/9/1-2,13/1-2, 14/1-2, 15/1-2, 16/2, 17/2, 18, 20-22, 23/20, 24/23/19-20, 25/19-20, 26/19-20, 28-29, 30/28, 31/27-28, 32/31/27-28, 33/28, 34/33/28, 35/33/28, 36/33/27-28, 37/33/27-28, 38/33/28, 39/33/28, 40/39/33/28, 41/40/39/33/28, 42/39/33/28, 43/42/39/33/27-28, 44/39/33/27-28

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search
28 February 2017 (28.02.2017)

Date of mailing of the international search report
07 APR 2017

Name and mailing address of the ISA/
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-8300

Authorized officer
Shane Thomas
PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US17/14296

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	(MILCHERT, E et al.) Technological aspects of chemoenzymatic epoxidation of fatty acids, fatty acid esters and vegetable oils: a review. Molecules. Vol. 20. No. 12. 2 December 2015. 21481-21493; page 21481, paragraph 2; page 21483, paragraphs 4-5; page 21486, paragraphs 2-3; page 21487, paragraphs 1, 3; page 21488, paragraph 3; table 1	2, 3/1-2, 4/2, 5/2, 6/2, 7/2, 8/1-2, 9/2, 10/9/2, 11/9/2, 12/9/2, 13/2, 14/2, 15/2, 16/2, 17/2, 18/17/2, 20-22, 23/19-20, 24/23/19-20, 25/20, 26/20, 28-29, 30/28, 31/28, 33/28, 34/33/28, 35/33/28, 36/33/28, 37/33/28, 38/33/28, 39/33/28, 40/39/33/28, 41/40/39/33/28, 42/39/33/28, 43/42/39/33/27-28, 44/39/33/28
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