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(71) Applicant (*for all designated States except US*): **SHELL OIL COMPANY** [US/US]; One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US).

(72) Inventor; and
(75) Inventor/Applicant (*for US only*): **EDWARDS, Charles, Lee** [US/US]; 12526 Piping Rock, Houston, TX 77077 (US).

(74) Agent: **HAAS, Donald, F.**; SHELL OIL COMPANY, One Shell Plaza, P.O. Box 2463, Houston, TX 77252-2463 (US).

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(54) Title: PREPARATION OF EARTH PHOSPHATE CATALYSTS FROM CARBONATE SALTS AND THEIR USE IN ALKOXYLATION REACTIONS

(57) Abstract: A method is provided for ensuring production of efficient rare earth metal phosphate catalysts for alkoxylation of organic compounds. The method comprises: selecting as a reactant one or more carbonate salts of the one or more rare earth metals; reacting the one or more carbonate salts with a source of phosphate under conditions effective to produce the efficient rare earth metal phosphate catalysts; wherein the efficient rare earth metal phosphate catalysts provide an increased activity for the alkoxylation compared to the activity of substantially the same catalyst produced when one or more salts other than carbonate salts of the rare earth metals are selected as the reactant.

PREPARATION OF RARE EARTH PHOSPHATE CATALYSTS FROM CARBONATE SALTS AND THEIR USE IN ALKOXYLATION REACTIONS

Field of the Invention

The application relates to a method of ensuring the production of efficient lanthanum phosphate catalysts (LAPO's) and rare earth phosphate catalysts (REPO's).

Background

Methods are always needed to ensure the production of catalysts with high activity toward catalyzing a particular reaction.

Summary

A method is provided for ensuring production of efficient rare earth metal phosphate catalysts for alkoxylation of organic compounds. The method comprises: selecting as a reactant one or more carbonate salts of the one or more rare earth metals; reacting the one or more carbonate salts with a source of phosphate under conditions effective to produce the efficient rare earth metal phosphate catalysts; wherein the efficient rare earth metal phosphate catalysts provide an increased activity for the alkoxylation compared to the activity of substantially the same catalyst produced when one or more salts other than carbonate salts of the rare earth metals are selected as the reactant. Suitably, the increased activity for the alkoxylation is at least 1.5 times, preferably 2 times, more preferably 3 times, and most preferably 4 times the activity of substantially the same catalyst produced when one or more salts other than carbonate salts of the rare earth metals are selected as the reactant.

In one aspect, the phosphate catalyst comprises a lanthanum phosphate catalyst (LAPO). In another aspect, the phosphate catalyst comprises a rare earth metal selected from the group consisting of those having atomic

numbers 39 and 57 through 71. As used herein, the "rare earth metals" are those of atomic numbers 39 and 57 through 71. In another aspect, the phosphate catalyst comprises a catalytically effective amount of one of the following groups: one or more of the phosphate salts of elements selected from the group consisting of cerium, lanthanum, praseodymium, neodymium, yttrium, samarium, gadolinium, dysprosium, erbium, and ytterbium; one or more of the phosphate salts of the cerium earth group elements; one or more of the phosphate salts of elements selected from the group consisting of cerium and lanthanum; one or more of the phosphate salts of the lanthanum elements (atomic numbers 57-71); one or more of the phosphate salts of the lanthanide series elements (atomic numbers 58-71); yttrium phosphate; one or more phosphate salts of metals derived from natural mineral ores; one or more phosphate salts of rare earth elements derived from natural mineral ores selected from the group consisting of bastnasite, monazite, xenotime, didymium, gadolinite and euxenite.

The conditions comprise mixing the one or more carbonate salts of the one or more rare earth metals with a volume of water to form a slurry. In one embodiment, the one or more carbonate salts comprise the carbonates of the following metals in the following quantities: from 8% to 15% Ce, from 44% to 65% La, from 20% to 25% Nd, and from 2% to 10% Pr. In another embodiment, the one or more carbonate salts are the carbonates of the following metals in the following quantities: 12.5%w Ce, 59.3%w La, 22.4%w Nd and 5.8% Pr.

The conditions further comprise preparing an aqueous solution of from 5% to 15% phosphoric acid with agitation at a temperature of from 25 °C. to 80 °C., preferably 25 °C. The conditions further comprise either (a) adding the carbonate slurry to the aqueous solution of phosphoric acid to produce a reaction mixture, or, preferably (b) adding the aqueous phosphoric acid to the carbonate slurry under slurrying conditions effective to produce a reaction mixture.

The slurrying conditions preferably comprise agitation at a temperature of from 25 °C. to 100 °C and over a slurrying period of time sufficient to consume the carbonate. The slurrying period of time is from 10 minutes to 60 minutes, preferably 30 minutes. The method preferably further comprises cooling the reaction mixture to a slurrying temperature effective to produce first solids; and subjecting the first solids to second slurrying conditions effective to separate the first solids from the reaction mixture and to form an aqueous second slurry comprising the first solids. The second slurrying conditions preferably comprise stirring at a temperature of from 25 °C. to 80 °C., preferably 50 °C., for from 10 minutes to 60 minutes, preferably 30 minutes, to produce a heated second slurry.

The method preferably further comprises cooling the heated second slurry, preferably to 25 °C, producing a cooled second slurry comprising second solids; and, subjecting the second solids to neutralizing conditions effective to neutralize the mixture, producing a neutralized second slurry comprising neutralized solids. The neutralizing conditions preferably comprise adding aqueous NH4OH. The method preferably further comprises cooling the neutralized second slurry, preferably to 25°C, and collecting the neutralized solids. The method preferably further comprises drying the neutralized solids to produce a cake comprising the one or more phosphate salts. The method also preferably further comprises grinding the cake to produce a free flowing powder.

The application also provides a method comprising reacting alkylene oxides and organic compounds comprising active hydrogen in the presence of a catalytically effective amount of a carbonate salt derived catalyst made according to the foregoing methods. The alkylene oxides preferably comprise one or more vicinal alkylene oxides. The catalytically effective amount of carbonate salt derived catalyst typically is 0.006 %w or more, more typically 0.013 to 3.33 % w or more, even more typically from 0.067 to 1.33 %w or more. In another aspect, the catalytically effective amount of a carbonate salt derived catalyst is 0.0025 %w or more, more typically from 0.005 to 1.25 % w or more, even more typically from 0.025 to 0.5 % w or more.

Stated another way, if a quantity (x) of a carbonate derived catalyst of a given rare earth or lanthanum series metal or mixture is used, and the same quantity(x) of the same catalyst which is not carbonate derived is used to catalyze a reaction under the same conditions, then the reaction time for the reaction catalyzed by the carbonate-derived catalyst will be 2/3 or less, preferably ½ or less, more preferably ¼ or less the reaction time required to achieve the same level of catalysis by the non-carbonate salt derived catalyst.

The organic compound comprises active hydrogen. In a preferred embodiment, the active hydrogen comprises a primary active hydrogen. Suitably, the organic compound is one or more compound selected from the group consisting of alkanols, phenols, thiols, amines, polyols, and carboxylic acids.

In one aspect, the carboxylic acids are selected from the group consisting of mono- and dicarboxylic acids, both aliphatic (saturated and unsaturated) and aromatic. In another aspect, the carboxylic acid is selected from the group consisting of acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, rosin acids, tall oil acids, terephthalic acid, benzoic acid, phenylacetic acid, toluic acid, acrylic acid, methacrylic acid, crotonic acid, and maleic acid;

In another aspect, the amines preferably are selected from the group consisting of primary, secondary, and tertiary alkylamines, and alkylamines containing both amino and hydroxyl groups, such as N'N-di(n-butyl)-ethanol amine and tripropanolamine.

In another aspect, the thiols are selected from the group consisting of primary, secondary, and tertiary alkane thiols having from 1 to 30 carbon atoms, particularly those having from 8 to 20 carbon atoms. Where the thiol is a tertiary thiol, the tertiary thiol suitably comprises a branched carbon chain derived via hydrosulfurization of the products of the oligomerization of lower olefins, particularly the dimers, trimers, and tetramers and pentamers of propylene and the butylenes. Where the thiol is a secondary thiol, suitable secondary thiols are selected from the group consisting of lower alkane thiols, such as 2-propanethiol, 2-butanethiol, and 3-pentanethiols, and the products of the hydrosulfurization of the substantially linear oligomers of ethylene as are produced by the Oxo process. Where the thiol is a primary thiol, suitable thiols are selected from the group consisting of 2-decanethiol, 3-decanethiol, 4-decanethiol, 5-decanethiol, 3-dodecanethiol, 5-dodecanethiol, 2-hexadecanethiol, 5-hexadecanethiol, and 8-octadencanethiol, 2-methyl-4-tridecanethiol, 1-butanethiol, 1-hexanethiol, 1-dodecanethiol, 1-tetradecanethiol and 2-methyl-1-tridecanethiol.

In another aspect, the polyols have from 2 to 30 carbon atoms and from 2 to 6 hydroxyl groups. In one aspect, the polyol is selected from the group consisting of alkylene glycols and polyalkylene glycol ethers. In another aspect, the polyol is selected from the group consisting of ethylene glycol, propylene glycol, hexylene glycol, and decylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, glycerine, and sorbitol.

In yet another aspect, the phenols are selected from the group consisting of phenol and of alkyl-substituted phenols comprising alkyl substituents having from one to 30 (preferably from one to 20) carbon atoms. In another aspect, suitable phenols are selected from the group consisting of p-methylphenol, p-ethylphenol, p-hexylphenol, nonylphenol, p-decylphenol, and didecyl phenol.

In even another aspect, the organic compound is one or more acyclic aliphatic mono-hydric alkanols having from 1 to 30 carbon atoms, preferably from 6 to 24 carbon atoms, more preferably from 8 to 20 carbon atoms. In another aspect, the alkanols comprise greater than 50 percent, more preferably greater than 60 percent and most preferably greater than 70 percent molecules having a linear (straight-chain) carbon structure.

In yet another aspect, the organic compound is the alkoxylate product of a previous alkoxylation of an active hydrogen containing compound.

In a preferred embodiment, the alkylene oxide is selected from the group consisting of ethylene oxide, propylene oxide, and mixtures thereof.

In another preferred embodiment, the alkylene oxide is ethylene oxide and the organic compound is a C_1 to C_{30} primary alkanol. In this aspect, the catalyst preferably consists essentially of salts having the formula LPO_4.

Detailed Description

The present application provides a method to ensure the production of lanthanum phosphate catalysts (LAPO's) and rare earth phosphate catalysts (REPO's) which are highly efficient at catalyzing alkoxylation processes. Specifically, the method involves selecting a particular salt of the lanthanum or rare earth metal--namely, the carbonate salt--as the reactant to be treated with a phosphate.

The catalyst comprises the phosphate salt(s) of either one or a mixture of the rare earth elements. As used herein, the "rare earth metals" are those of atomic numbers 39 and 57 through 71, metals of the "lanthanum series" are those of atomic numbers 57 through 71; the "lanthanide" metals are those of atomic numbers 58 through 71. Traditionally, the lanthanum metals have further been divided into the "cerium earth" group of atomic numbers 57 through 62, the "terbium earth" group of atomic numbers 63 through 66, and the "yttrium earth" group of atomic numbers 67 through 71 (so named not because yttrium is a member of the group, but because yttrium is found with these elements in nature).

In one respect, preference can be expressed for catalysts comprising in catalytically effective amount one or more of the phosphate salts of elements selected from the group comprising cerium, lanthanum, praseodymium, neodymium, yttrium, samarium, gadolinium, dysprosium, erbium, and ytterbium. In another respect, catalysts comprising a catalytically effective amount of one or more of the phosphate salts of the cerium earth group elements are particularly preferred, while catalysts comprising a catalytically effective amount of one or more of the phosphate salts of elements selected from the group consisting of cerium and lanthanum are considered most preferred. In a further respect, preferred catalysts comprise a catalytically effective amount of one or more of the phosphate salts of the lanthanum elements (atomic numbers 57-71). Still further, a preferred class of catalysts comprise a catalytically effective amount of one or more of the phosphate salts of the lanthanide series elements (atomic numbers 58-71). In still another respect, preference can be expressed for catalysts comprising yttrium phosphate in catalytically effective amounts.

Natural mineral ores which serve as the commercial sources of the rare earth elements generally contain several of the elements. These ores are often refined without separating this mixture into distinct elements. For this reason, the use of mixtures of the phosphate salts of several rare earth elements may be preferred from the standpoint of availability and cost. Specific examples of suitable mixtures of rare earth elements include those derived from natural mineral ores known as bastnasite, monazite, xenotime, didymium, gadolinite and euxenite.

In addition to a catalytically effective amount of the rare earth element compounds, the catalyst also may suitably contain other substances, including both those which may be introduced into the process as impurities in the phosphate salt catalyst as well as those which may be added to promote or modify catalyst activity.

The phosphate salt catalyst compounds are suitably characterized by the formula $Lp(PO_4)q$, wherein L is a rare earth element. The phosphate salts of the rare earth elements principally comprise rare earth elements in the trivalent state and have the formula LPO4. However, the process encompasses divalent metal salts and tetravalent metal salts, in which case the subscripts p and q satisfy the relevant valency relationships, that is, when L is divalent p is 3 and q is 2, and when L is tetravalent p is 3 and q is 4.

Phosphate salt compounds of the rare earth elements are effective catalysts for the addition reactions of alkylene oxides with organic compounds having active hydrogen atoms. Basically, an alkylene oxide reactant comprising one or more vicinal alkylene oxides is contacted with an active hydrogen reactant comprising one or more organic compounds (e.g., alcohols, phenols, thiols, amines, polyols, carboxylic acids, etc.) having one or more active hydrogen atoms, in the presence of a catalyst comprising one or more of the phosphate salts of the rare earth elements.

In a preferred embodiment, the rare earth phosphate catalyst is prepared as follows. A quantity of a rare earth carbonate mixture is added to a volume of water to form a slurry. The water preferably is distilled, more preferably distilled and degassed. A suitable rare earth carbonate mixture comprises at least La carbonate and preferably comprises one or more of Ce carbonate, Nd carbonate, and Pr carbonate. A most preferred carbonate mixture comprises the carbonates of the following metals in the following quantities: from 8% to 15% Ce, from 44% to 65% La, from 20% to 25% Nd, and from 2% to 10% Pr. A preferred commercially available carbonate mixture is Unical 76 (lot# R-1220), which comprises metallic composition of 12.5%w Ce, 59.3%w La, 22.4%w Nd and 5.8% Pr.

An aqueous solution of phosphoric acid is prepared at a concentration of from 5% to 15%. The water used in the solution also is preferably distilled, most preferably distilled and degassed. The solution is stirred rapidly at a temperature of from 25 °C. to 80 °C., preferably 25 °C.

It is possible to either add the carbonate slurry to the phosphoric acid or to add the phosphoric acid to the slurry. Preferably, the phosphoric acid is added to the slurry with agitation at a temperature of from 25 °C. to 100 °C and over a period of time sufficient to consume the carbonate. The period of time typically is from 10 minutes to 60 minutes, preferably 30 minutes. The reaction mixture is then heated to reflux (~ 100°C) while stirring rapidly for a period of time effective to consume all carbonate, typically from 1 to 3 hours, preferably 2.5 hours. The heat is removed, the stirring is stopped, and the reaction mixture is allowed to cool, preferably to room temperature, for example 25 °C. The solids are filtered and then transferred again to the reaction vessel wherein they are diluted with an excess of water, preferably degassed distilled water, to form a slurry. The slurry is stirred while maintained at a temperature of from 25 °C. to 80 °C., preferably 50 °C., for from 10 minutes to 60 minutes, preferably 30 minutes. The heat is removed and the mixture is allowed to cool to room temperature, for example 25 °C. The solids are filtered and treated with a solution of aqueous base in an amount and at a concentration effective to neutralize the mixture. A preferred aqueous base is NH4OH, most preferably 10 N NH_4OH.

The resulting slurry is stirred with heating for a time and at a temperature effective to neutralize all acid. Suitable temperatures are from 25 °C. to 80 °C., preferably 50 °C. A suitable time is from 10 minutes to 60 minutes, preferably 30 minutes. The heat is removed and the mixture is allowed to cool to room temperature, for example 25 °C. The solids are filtered and dried using any suitable drying technique. In a preferred embodiment, the solids are dried overnight at room temperature under vacuum, and then dried further by heating under full vacuum for an effective drying period. Suitable temperatures for this heating are from 25

°C. to 80 °C., preferably 50 °C. The drying period will vary depending upon the conditions, but suitably is from 4 to 10 hours, preferably 8 hours. The resulting product is collected as a cake, ground using any suitable technique, such as a mortar and pestle, to produce a free flowing off white powder comprising one or more of the phosphate salts of the rare earth elements.

A catalytically effective amount of the powder is used in an alkoxylation reaction. A catalytically effective amount is an amount sufficient to cause the H-containing compound to react with ethylene or propylene oxide. The catalyst made according to the present method are 1.5 or more times as active, typically 2 or more times as active, preferably from 2 to 4 times as active as the same catalyst prepared using non-carbonate salts of rare earth metals. The more active catalyst made using carbonate salts may be used to achieve a savings in time and/or cost.

A catalytically effective amount of a non-carbonate derived salt typically is 0.01 percent or more by weight (% w), more typically from 0.02 to 5% w, even more typically from 0.1 to 2% w. These percentages are in terms of the weight of rare earth metal ions in the process mixture relative to the weight of active hydrogen containing compounds in that mixture. Substantially greater quantities of catalyst, e.g., up to 10% w or more, are also suitable.

In contrast, under the same conditions of reaction, a catalytically effective amount of a carbonate salt derived catalyst typically is 0.006 %w or more, more typically 0.013 to 3.33 % w or more, even more typically from 0.067 to 1.33 %w or more. In a preferred embodiment, under the same conditions of reaction, a catalytically effective amount of a carbonate salt derived catalyst is 0.005 %w or more, more typically from 0.01 to 2.5 %w or more, and even more typically from 0.5 to 1 % w or more. In a most preferred embodiment, under the same conditions of reaction, a catalytically effective amount of a carbonate salt derived catalyst is 0.0025 %w or more, more typically from 0.005 to 1.25 % w or more, even more typically from 0.025 to 0.5 % w or more.

Alternately, if a quantity (x) of a carbonate derived catalyst of a given rare earth or lanthanum series metal or mixture is used, and the same quantity (x) of the same catalyst which is not carbonate derived is used to catalyze a reaction under the same conditions, then the reaction catalyst by the carbonate-derived catalyst will take 2/3 or less, preferably ½ or less, more preferably ¼ or less of the reaction time required to achieve the same level of catalysis by the non-carbonate salt derived catalyst.

In the alkoxylation processes catalyzed, alkylene oxides are reacted with compounds having active hydrogen atoms in the presence of catalysts comprising one or more carbonate derived phosphate salts of lanthanum or the rare earth elements. The preparation of an alkanol ethoxylate (represented by formula III below) by addition of a number (n) of ethylene oxide molecules (formula II) to a single alkanol molecule (formula I) is represented by the equation

I II III

A large variety of products useful, for instance, as nonionic surfactants, wetting and emulsifying agents, solvents, and chemical intermediates, are prepared by the addition reaction (alkoxylation reaction) of alkylene oxides (epoxides) with organic compounds having one or more active hydrogen atoms. Examples include, but are not necessarily limited to alkanol ethoxylates and alkyl-substituted phenol ethoxylates prepared by reacting ethylene oxide with aliphatic alcohols or substituted phenols having from 6 to 30 carbon atoms. Ethoxylates, and to a lesser extent corresponding propoxylates and compounds containing mixed oxyethylene and oxypropylene groups, are widely employed as nonionic detergent components of commercial cleaning formulas used in industry and in the home. The addition reaction of propylene oxide with polyols provides intermediates for the preparation of polyurethane products. In preferred embodiments, the alkoxylate products are useful as nonionic surfactants.

Preferably, the alkoxylation process minimizes the quantity of unreacted (or residual) active hydrogen reactant remaining in the final product. A high level of residual reactant either represents a loss of valuable reactant, or requires that further processing of the product be carried out to recover the reactant. Moreover, the presence of the unreacted material is often a disadvantage from the standpoint of product quality and environmental concerns. For instance, residual alkanol in a detergent alcohol ethoxylate product contributes to volatile organic emissions during spray drying of detergent formulations.

The rare earth phosphate salts are present in the alkoxylation mixture in catalytically effective amount in either (or both) homogeneous or heterogeneous form(s). The catalyst has been found to be heterogeneous, or at least essentially heterogeneous, in preferred embodiments. The process, as a general rule, suitably is conducted using such reactants and practicing under such processing procedures and reaction conditions as are well known in the art for alkoxylation reactions. Certain preferences may, however, be expressed for particular reactants, procedures and conditions.

Thus, for instance, the invention is preferably applied to processes utilizing an alkylene oxide (epoxide) reactant which comprises one or more vicinal alkylene oxides, particularly the lower alkylene oxides and more particularly those in the C_2 to C_4 range. Likewise, the active hydrogen reactants suitably utilized in the process of the invention include those known in the art for reaction with alkylene oxides and conversion to alkoxylate products. Suitable classes of active hydrogen reactants include (but are not necessarily limited to) alcohols, phenols, thiols (mercaptans), amines, polyols, carboxylic acids, and mixtures thereof. Generally, but not necessarily, the active hydrogen moiety of the reactant is of the form --XH wherein X represents either an oxygen, sulfur or (substituted, e.g., amino) nitrogen atom. Preference generally exists for use of hydroxyl-containing reactants. More preferably, the active hydrogen-containing reactant consists essentially of one or more active hydrogen containing compounds selected from the group consisting of alkanols, alkyl polyols and phenols (including alkyl-substituted phenols).

Preference can also be expressed for the application of this invention to the alkoxylation of primary active hydrogen containing compounds, that is, compounds wherein the active hydrogen moiety is attached to a primary carbon atom. As is often the case for alkoxylation reactions, such primary compounds are more reactive, and in some cases substantially more reactive, in the process of this invention than are the corresponding secondary and tertiary compounds. Moreover, the invention has been found to produce relatively broad-range alkylene oxide adduct distribution products when applied to secondary and tertiary active hydrogen containing reactants.

Among the suitable carboxylic acids, particular mention may be made of the mono- and dicarboxylic acids, both aliphatic (saturated and unsaturated) and aromatic. Specific examples include acetic acid, propionic acid, butyric acid, valeric acid, caproic acid, lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, rosin acids, tall oil acids, terephthalic acid, benzoic acid, phenylacetic acid, toluic acid, acrylic acid, methacrylic acid, crotonic acid, or maleic acid. It has been observed that, as a rule, carboxylic acids undergo alkoxylation in the process of this invention at a relatively slow rate.

Among the suitable amines, particular mention may be made of primary, secondary and tertiary alkylamines and of alkylamines containing both amino and hydroxyl groups, e.g., N'N-di(n-butyl)-ethanol amine and tripropanolamine.

Among the suitable thiols, particular mention may be made of primary, secondary and tertiary alkane thiols having from 1 to 30 carbon atoms, particularly those having from 8 to 20 carbon atoms. Specific examples of suitable tertiary thiols are those having a highly branched carbon chain which are derived via hydrosulfurization of the products of the oligomerization of lower olefins, particularly the dimers, trimers, and tetramers and pentamers of propylene and the butylenes. Secondary thiols are exemplified by the lower alkane thiols, such as 2-propanethiol, 2-butanethiol, and 3-pentanethiols, as well as by the products of the hydrosulfurization of the substantially linear oligomers of ethylene as are produced by the Oxo process. Representative, but by no means limiting, examples of thiols derived from ethylene oligomers include the linear carbon chain products, such as 2-decanethiol, 3-decanethiol, 4-decanethiol, 5-decanethiol, 3-dodecanethiol, 5-dodecanethiol, 2-hexadecanethiol, 5-hexadecanethiol, and 8-octadencanethiol, and the branched carbon chain products, such as 2-methyl-4-tridecanethiol.Primary thiols are typically prepared from terminal olefins by hydrosulfurization under free-radical conditions and include, for example, 1-butanethiol, 1-hexanethiol, 1-dodecanethiol, 1-tetradecanethiol and 2-methyl-1-tridecanethiol.

Among the polyols, particular mention may be made of those having from 2 to 6 hydroxyl groups. Specific examples include the alkylene glycols such as ethylene glycol, propylene glycol, hexylene glycol, and decylene glycol, the polyalkylene glycol ethers, such as diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, glycerine, or sorbitol.

The alcohols (both mono- and poly-hydroxy) and the phenols (including alkyl-substituted phenols) are preferred classes of active hydrogen reactants for purposes of the invention. Among the phenols, particular mention may be made of phenol and of alkyl-substituted phenols wherein each alkyl substituent has from one to 30 (preferably from one to 20) carbon atoms, for example, p-methylphenol, p-ethylphenol, p-hexylphenol, nonylphenol, p-decylphenol, or didecyl phenol.

Acyclic aliphatic mono-hydric alcohols (alkanols) form a most preferred class of reactants, particularly the primary alkanols, although secondary and tertiary alkanols are also very suitably utilized in the process of the invention. Preference can also be expressed, for reason of both process performance and commercial value of the product, for alkanols having from 1 to 30 carbon atoms, with C_6 to C_{24} alkanols considered more preferred and C_8 to C_{20} alkanols considered most preferred. As a general rule, the alkanols may be of branched or straight chain structure, although preference further exists for alkanol reactants in which greater than 50 percent, more preferably greater than 60 percent and most preferably greater than 70 percent of the molecules are of linear (straight-chain) carbon structure.

The general suitability of such alkanols as reactants in alkoxylation reactions is well recognized in the art. Commercially available mixtures of primary mono-hydric alkanols prepared via the oligomerization of ethylene and the hydroformylation or oxidation and hydrolysis of the resulting higher olefins are particularly preferred. Examples of commercially available alkanol mixtures include the NEODOL Alcohols, trademark of and sold by Shell Chemical Company, including mixtures of C_9, C_{10} and C_{11} alkanols (NEODOL 91 Alcohol), mixtures of C_{12} and C_{13} alkanols (NEODOL 23 Alcohol), mixtures of C_{12}, C_{13}, C_{14}, and C_{15} alkanols (NEODOL 25 Alcohol), and mixtures of C_{14} and C_{15} alkanols (NEODOL 45 Alcohol); the ALFOL Alcohols, trademark of and sold by Vista Chemical Company, including mixtures of C_{10} and C_{12} alkanols (ALFOL 1012), mixtures of C_{12} and C_{14} alkanols (ALFOL 1214), mixtures of C_{16} and C_{18} alkanols (ALFOL 1618), and mixtures of C_{16}, C_{18} and C_{20} alkanols (ALFOL 1620); the EPAL Alcohols, trademark of and sold by Ethyl Chemical Company, including mixtures of C_{10} and C_{12} alkanols (EPAL 1012), mixtures of C_{12} and C_{14} alkanols (EPAL 1214), and mixtures of C_{14}, C_{16}, and C_{18} alkanols (EPAL 1418); and the TERGITOL-L Alcohols, trademark of and sold by Union Carbide Corporation, including mixtures of C_{12}, C_{13}, C_{14}, and C_{15} alkanols (TERGITOL-L 125). Also very suitable are the commercially available alkanols prepared by the reduction of naturally occurring fatty esters, for example, the CO and TA products of Proctor and Gamble Company and the TA alcohols of Ashland Oil Company.

Among the polyols, particular mention may be made of those having from 2 to 6 hydroxyl groups and 2 or more, preferably 2 to 30 carbon atoms. Specific examples include the alkylene glycols such as ethylene glycol, propylene glycol, hexylene glycol, and decylene glycol, the polyalkylene glycol ethers, such as diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, glycerine, or sorbitol. Higher oligomers and polymers of the polyols are also very suitable.

The active hydrogen containing reactant is also very suitably the alkoxylate product of a previous alkoxylation of an active hydrogen containing compound.

Persons of ordinary skill in the art will be familiar with additional examples of both specific alkylene oxide reactants and specific active hydrogen containing reactants suitable for use in the present process.

In preferred embodiments, the alkylene oxide reactant is ethylene oxide or propylene oxide or a mixture of ethylene oxide and propylene oxide and the active hydrogen containing reactant is an alcohol, a polyol or another hydroxyl containing compound in the presence of a catalytically effective amount of the rare earth phosphate salt catalyst. In a particularly preferred embodiment, ethylene oxide is contacted and reacted with a C_1 to C_{30} primary alkanol in the presence of a catalytically effective amount of a catalyst wherein the rare earth phosphate compounds consist essentially of salts having the formula LPO_4.

In terms of processing procedures, the alkoxylation reaction in the invention may be conducted in a generally conventional manner. For example, the catalyst may initially be mixed with liquid active hydrogen reactant. The mixture of catalyst and liquid reactant is contacted, preferably under agitation, with alkylene oxide reactant, which is typically introduced in gaseous form, at least for the lower alkylene oxides. The order in which the reactants and catalyst are contacted has not been found to be critical to the invention.

While these procedures describe a batch mode of operation, the invention is equally applicable to a continuous process.

The catalyst is either soluble (either partially or completely) or insoluble in this liquid reactant as well as in liquid mixtures of the reactant and the product formed as the process is carried out. The catalyst is insoluble, or at least essentially insoluble, in the preferred active hydrogen containing reactants, particularly in primary alcohols and the products of their alkoxylation. While it is not intended to limit the scope of the invention to one theory or mechanism of operation, it is believed that the presence of phosphate salts in a hexagonal crystal structure in the alkoxylation mixture, particularly in alkanol alkoxylation mixtures, may have a beneficial influence on reaction rate and adduct distribution. Salts in the monoclinic form have been observed in some cases to be less active than the salts in the hexagonal form. Preference has also been observed for use of phosphate salts having a certain water content associated with their crystal structure, particularly a water content of greater than 5% w (e.g., 5-20% w), although the amount of water contained in the phosphate salt is not considered critical to the alkoxylation.

Overall, the two reactants are utilized in quantities which are predetermined to yield an alkoxylate product of the desired mean or average adduct number. The average adduct number of the product is not critical to this process. Such products commonly have an average adduct number in the range from less than one to 30 or greater.

In general terms, suitable and preferred process temperatures and pressures for purposes of this invention are the same as in conventional alkoxylation reactions between the same reactants, employing conventional catalysts. A temperature of at least 90 °C., particularly at least 120 °C. and most particularly at least 130 °C., is typically preferred from the standpoint of the rate of reaction, while a temperature of 250 °C. or less, particularly 210 °C. or less, and most particularly 190 °C. or less, typically is desirable to minimize degradation of the product. As is known in the art, the process temperature can be optimized for given reactants, taking such factors into account.

Superatmospheric pressures, e.g., pressures between 10 and 150 psig (0.07 and 1 MPa gauge), are preferred, with pressure being sufficient to maintain the active hydrogen reactant substantially in the liquid state.

When the active hydrogen reactant is a liquid and the alkylene oxide reactant is a vapor, alkoxylation is then suitably conducted by introducing alkylene oxide into a pressure reactor containing the liquid active hydrogen reactant and the catalyst. For considerations of process safety, the partial pressure of a lower alkylene oxide reactant is preferably limited, for instance, to less than 60 psia (0.4 MPa), and/or the reactant is preferably diluted with an inert gas such as nitrogen, for instance, to a vapor phase concentration of 50 percent or less. The reaction can, however, be safely accomplished at greater alkylene oxide concentration, greater total pressure and greater partial pressure of alkylene oxide if suitable precautions, known in the art, are taken to manage the risks of explosion. A total pressure of from 40 to 110 psig (0.3 to 0.8 MPa gauge), with an alkylene oxide partial pressure of from 15 to 60 psig (0.1 to 0.4 MPa gauge), is particularly preferred, while a total pressure of from 50 to 90 psig (0.34 to 0.6 MPa gauge), with an alkylene oxide partial pressure of from 20 to 50 psig (0.14 to 0.34 MPa gauge), is considered more preferred.

The time required to complete a process according to the invention is dependent both upon the degree of alkoxylation desired (i.e., upon the average alkylene oxide adduct number of the product) as well as upon the rate of the alkoxylation reaction (which is, in turn, dependent upon temperature, catalyst quantity and nature of the reactants). A typical reaction time for preferred embodiments is from 1 to 24 hours.

After the ethoxylation reaction has been completed, the product preferably is cooled. If desired, catalyst can be removed from the final product, although catalyst removal is not necessary to the process of the invention. Catalyst residues may be removed, for example, by filtration, precipitation, or extraction. A number of specific chemical and physical treatment methods have been found to facilitate removal of catalyst residues from a liquid product. Such treatments include contact of the alkoxylation product with strong acids such as phosphoric and/or oxalic acids or with solid organic acids such as NAFION H+ or AMBERLITE IR 120H; contact with alkali metal carbonates and bicarbonates; contact with zeolites such as Type Y zeolite or mordenite; or contact with certain clays. Typically, such treatments are followed by filtration or precipitation of the solids from the product. In many cases filtration, precipitation, or centrifugation is most efficient at elevated temperature.

Alkoxylation product mixtures prepared under the present invention are of high quality and have greater stability, relative to the product mixtures of acid or base catalyzed alkoxylation reactions. In this regard, the invention is particularly useful for the preparation of colorless or less colored product relative to those of conventional practice, because the neutral salts do not promote degradation reactions which lead to color forming impurities.

The following Examples are provided to further illustrate certain specific aspects of the invention but are not intended to limit its broader scope.

Example 1

Lanthanum and rare earth metal phosphate catalysts (LAPO's and REPO's, respectively) were made using a variety of lanthanum and rare earth metal salts as precursors. The following were the salts from which the catalysts were derived:

Sample:	Salt:
A:	nitrate
B:	carbonate
C:	carbonate
D:	carbonate
E:	carbonate
F:	carbonate
G:	carbonate

The following table reflects the time required to add approximately 200 grams of ethylene oxide to a reaction mixture containing an alcohol and the specified catalyst. The entries in the table indicate the grams of ethylene oxide that were successfully added to the reaction mixture at various times.

Time	A	B	C	D	E	F	G
0	0	0	0	0	0	0	0
1				22		13	18
2	4	23				34	33
3				51	47	39	56
4		32	38	67		49	
5		49	49				72
6	25	70	54	84	61	61	
7	35	88	62			71	85
8	50		73	105	82	76	93
9			94		92		105
10					100	85	
11	61	116	106	115	109	95	
12		123				102	117
13	73		116	122	120		
14			127				131
15	80	140			128		138
16				141		124	
17			150		144	132	
18				148			151
19			158		155	137	
20			166				157
21				159	167	147	161
22							
23	105	158	178		175	152	174
24			183	173	181		179
25		172	193	178	189	156	
26			196			166	186

Time	A	B	C	D	E	F	G
27			201				191
28	112	196		189	198	174	197
29					200		
30				197			200
31						183	
32							
33				201		191	
34		200					
35							
36						200	
48	133						
55	138						
58	145						
61	153						
64	170						
75	183						
78	191						
85	200						

The catalysts derived from carbonate salts were 2-3 times more active than the catalysts derived from other salts.

Example 2

A number of lanthanum and rare earth phosphate catalysts were prepared for comparison of their catalytic activity in alkoxylation reactions. The procedures used to prepare the catalysts were as follows:

A. Lanthanum Phosphate Catalyst Prepared from Lanthanum Nitrate (LAPO 1)

A supplier was instructed to prepare lanthanum phosphate catalyst from lanthanum nitrate using the following procedures:

Dissolve 20 grams (0.046 moles) of lanthanum nitrate hexahydrate in 100 ml of N_2 purged distilled H_2O. Prepare an aqueous phosphoric acid solution by dissolving 5.3 g of 85% phosphoric acid (0.046 moles) in 50 grams of distilled H_2O. Add the lanthanum nitrate solution to the phosphoric acid solution at 25 °C. in a 500 ml round bottom flask equipped with overhead stirrer, reflux condenser, N_2 sparge inlet and thermocouple. Heat the white precipitate to 100 °C. for 3 hours. Remove the heat, stop the stirring, and allow the reaction mixture to cool to 25 °C. Again filter and transfer the solids to the reaction vessel. Add 100 ml of N_2 degassed distilled H2O to the wet white powder, and stir the slurry at 50 °C. for 30 minutes. Remove the heat and allow the mixture to cool to 25 °C. Filter and treat the solids with a solution containing 5 ml of 10N NH_4OH dissolved in 100 ml of water. Stir this slurry at 50 °C. for 30 minutes. Remove the heat and allow the mixture to cool to 25 °C. Filter the solids and allow the filtered solids to dry overnight at 25 °C. under vacuum. Dry the solids further by heating under full vacuum at 50 °C. for 8 hours. Collect the product as a cake, grind with a mortar and pestle, producing 13.9 grams of a free flowing off white powder.

B. Rare Earth Phosphate Catalyst 1 (REPO 1)

A mixed rare earth phosphate catalyst (REPO 1) was prepared according to the following procedures: 312.6 g (0.68 moles) of a rare earth carbonate mixture obtained from Unocal 76 (lot# R-1220), consisting of a metallic composition of 12.5%w Ce, 59.3%w La, 22.4%w Nd and 5.8% Pr was added to 2000 ml N_2 degassed distilled H_2O. A solution of aqueous phosphoric acid was prepared by dissolving 165 g of 85% H_3PO_4 (1.43 moles) in 2000 ml of N_2 degassed distilled H_2O contained in a 12 liter reaction flask equipped with overhead stirrer, reflux condenser, N_2 sparge inlet and thermocouple. The reaction solution was stirred rapidly at 25 °C. at which time the aqueous rare earth carbonate slurry was added over a 30 minute period. The reaction mixture was then heated to reflux (~ 100 °C.) while stirring rapidly for a period of 2.5 hours. Heat was removed and stirring stopped. The reaction was allowed to cool to 25 °C. The solids were filtered and then transferred again to the reaction vessel. 5000 ml of N_2 degassed distilled H2O was added to the wet white powder, and the slurry was allowed to stir at 50 °C. for 30 minutes. The heat was removed and the mixture was allowed to cool to 25 °C. The solids were filtered and treated again with a solution containing 100 ml of 10N NH_4OH dissolved. This slurry was allowed to stir at 50 °C. for 30 minutes. The heat was removed and the mixture was allowed to cool to 25 °C. The solids were filtered and allowed to dry overnight at 25 °C. under vacuum. The solids were dried further by heating under full vacuum at 50 °C. for 8 hours. The product was collected as a cake, ground with a mortar and pestle producing 286 grams of a free flowing off white powder.

C. Rare Earth Phosphate Catalyst 2 (REPO 2)

A mixed rare earth phosphate catalyst was prepared in the same manner as REPO 1 except on 1/10th the scale, and the rare earth carbonate mixture was prepared in the laboratory using pure single metal carbonates: a mixture of rare earth carbonates was prepared by mixing 3.9 g of cerium carbonate hydrate, 18.5 g of lanthanum carbonate hydrate, 7.0 g of neodymium carbonate hydrate and 1.8 g of praseodymium carbonate hydrate. This mixture (31.2 g, 0.068 moles) was added to 200 ml. of N_2 degassed distilled H_2O. A solution of aqueous phosphoric acid was prepared by dissolving 16.5 g of 85% H_3PO_4 (0.143 moles) in 200 ml of N_2 degassed distilled H_2O contained in a 1000 ml round bottom flask equipped with overhead stirrer, reflux condenser, N_2 sparge inlet and thermocouple. The reaction solution was stirred rapidly at 25 °C. at which time the aqueous rare earth carbonate slurry was added over a 15 minute period. The reaction mixture was then heated to reflux (~ 100 °C.) while stirring rapidly for a period of 3 hours. Heat was removed and stirring stopped. The reaction was allowed to cool to 25 °C. The solids were filtered and then transferred again to the reaction vessel. 500 ml of N_2 degassed distilled H_2O was added to the wet white powder, and the slurry was allowed to stir at 50 °C. for 30 minutes. The heat was removed and the mixture was allowed to cool to 25 °C. The solids were filtered and treated again with a solution containing 10 ml of 10N NH_4OH dissolved in 500 ml of water. This slurry was allowed to stir at 50 °C. for 30 minutes. The heat was removed and the mixture was allowed to cool to 25 °C. The solids were filtered and allowed to dry overnight at 25 °C. under vacuum. The solids were dried further by heating under full vacuum at 50 °C. for 8 hours. The product was collected as a cake, ground with a mortar and pestle producing 32 grams of a free flowing off white powder. This catalyst was evaluated as REPO 2.

D. Rare Earth Phosphate Catalyst 3 (REPO 3)

The procedures in paragraph C were repeated exactly producing another mixed rare earth phosphate catalyst with the same composition of rare earth metals as REPO 1. This catalyst was evaluated as REPO 3.

E. Lanthanum Phosphate Catalyst (LAPO 2)

A lanthanum phosphate catalyst was prepared according to the procedures used in paragraph C except that 31.2 grams (0.068 moles) of lanthanum carbonate hydrate was used instead of the rare earth phosphate mixture. This catalyst was evaluated as LAPO 2.

F. Lanthanum Phosphate Catalyst (LAPO 3)

The procedure in paragraph C was repeated exactly producing another lanthanum phosphate catalyst. This catalyst evaluated as LAPO 3.

G. Rare Earth Phosphate Catalyst (REPO 4)

The procedure in paragraph C was repeated exactly producing another mixed rare earth phosphate catalyst with the same composition of rare earth metals as in paragraph C. This catalyst evaluated as REPO 4.

The foregoing catalysts were used to catalyze alkoxylation according to the following protocol:

General Protocol For the Evaluation of Lanthanum or Rare Earth Phosphate Ethoxylation Catalysts

In the following Examples, the ethoxylations were conducted under the following procedures. The alkylene oxide reactant for this process embodiment consisted of ethylene oxide and the active hydrogen containing reactant consisted of NEODOL 23 Alcohol (NEODOL is a trademark of Shell Chemical Company) characterized as a mixture of primary, 80% linear (20% branched), alkanols having twelve and thirteen carbon atoms (about 40% by mol C_{12} and 60% by mol C_{13}).

Initially, 0.5 grams of the powder prepared as described above was added to 125 grams (0.644 moles) of NEODOL 23 Alcohol which had been predried under a N_2 sparge for 2 hours at 125 °C. to drive off water. The resulting slurry was transferred to a 500 ml autoclave reactor maintained under nitrogen atmosphere. The temperature of the reactor and contents was raised to 160 °C. A mixture of nitrogen and ethylene oxide was then introduced into the reactor to a total pressure of 75 psia (0.52 MPa) (45 psia nitrogen and 30 psia ethylene oxide) (0.31 MPa nitrogen and 0.21 MPa ethylene oxide). Alkoxylation (ethoxylation) commenced immediately. Additional ethylene oxide was supplied on demand to maintain an essentially constant 75 psia (0.52 MPa) pressure. Temperature was maintained at 160 °C. A total of 200 grams of ethylene oxide was charged to the reactor. The reactor was maintained for an additional 1 hour to consume unreacted ethylene oxide in the system. Catalyst activity was measured according to the amount of time it took to consume 200 grams of ethylene oxide at the constant EO gas pressures. The results are shown in the following Table:

Results of Catalyst Activity for the Ethoxylation of NEODOL 23

Metal Source	Catalyst Type	wt. Cat. (g) EO	Time of EO addition (min)
Nitrate Salt	LAPO 1	0.5	85
Carbonate	REPO 1	0.5	34
Carbonate	REPO 2	0.5	27
Carbonate	REPO 3	0.5	33
Carbonate	LAPO 2	0.5	29
Carbonate	LAPO 3	0.5	36
Carbonate	REPO 4	0.5	30

The carbonate derived LAPO and REPO catalysts consistently demonstrated at least 1.5 times the catalytic activity of the nitrate derived LAPO's, typically from about 2 to about 4 times the catalytic activity of the nitrate derived LAPO's.

Example 3

LAPO catalysts were prepared varying certain parameters. The catalytic activity of the resulting catalysts was then evaluated to determine the impact of those parameters on catalytic activity.

A. Standard LAPO Catalyst (LAPO 1A)

A slurry of lanthanum carbonate hydrate in distilled H_2O was prepared by addition of 31.2 g (0.068 moles) of carbonate to 200 ml of N_2 degassed distilled H_2O. A phosphoric acid solution was prepared by dissolving 16.5 g of 85% H_3PO_4 (0.143 moles) in 200 ml of N_2 degassed distilled H_2O. The acid solution was placed in a 1000 ml glass reactor equipped with reflux condenser, N_2 inlet, overhead stirrer and thermowell. The carbonate slurry was added to the acid solution at 25 °C. over 15 minutes. The reaction was heated to 100 °C. for 3 hours. The reaction mixture was cooled and the product filtered. The white solids were transferred to the reaction vessel and treated with 500 ml of N2 degassed distilled H_2O at 50 °C for 30 minutes with rapid stirring. The product was cooled and the solids filtered. The white solids were transferred to the reaction vessel and treated with a solution of 10 ml of 10N NH_4OH dissolved in 500 ml of distilled H_2O. The mixture was stirred rapidly at 50 °C. for 30 minutes. The reaction mixture was cooled to 25°C, and the product was isolated by vacuum filtration. The white solids were dried overnight at 50 °C. using full vacuum. The white filter cake was ground using a mortar and pestle producing 29.2 grams of product.

B. Reverse addition (LAPO 1B)

A catalyst was prepared according to the procedures described in paragraph A in all respects except that the phosphoric acid solution was added to the lanthanum carbonate slurry, the latter being contained in the reaction vessel.

C. Lower Temperature of Digestion Step (LAPO 1C)

A catalyst was prepared according to paragraph A in all respects except that the product was stirred at 25 °C. instead of 100 °C. for the 3 hour period.

D. Fast Addition of Carbonate Slurry to Acid (LAPO 1D)

A catalyst was prepared according to paragraph A in all respects except that the carbonate slurry was added in 15-20 seconds instead of 15 minutes.

E. High Temperature Addition of Slurry to Acid (LAPO 1E)

A catalyst was prepared according to paragraph A in all respects except that the carbonate slurry was added to the acid at 95 °C. over 15 minutes.

F. Elimination of NH4OH treatment (LAPO 1F)

A catalyst was prepared according to Example 1 in all respects except that the NH4OH treatment step was eliminated. Instead, after the first water wash, the catalyst was filtered and dried as described.

The foregoing catalysts were used to catalyze alkoxylation according to the general protocol outlined in paragraph A, with the following results:

Catalyst type	Temp. of Add'n (°C.)	Time of Add'n (min)	Source/ Temperature of Digestion (°C.)	Method of Add'n/ NH_4OH Treatment	Rate of EO Add'n (min)
Supplier	---	--	nitrate/ ---	---/---	69
LAPO 1A	20	20	carbonate/ 100	slurry to acid/ yes	35
LAPO 1B	25	20	carbonate/ 100	acid to slurry/ yes	18

LAPO 1C	25	20	carbonate/ 25	slurry to acid/ yes	37
LAPO 1D	25	5	carbonate/ 100	slurry to acid/ yes	24
LAPO 1E	100	20	carbonate/ 100	slurry to acid/ yes	42
LAPO 1F	25	20	carbonate/ 100	slurry to acid/ no	24

The batch times for each carbonate derived LAPO was approximately 2-4 times faster than the nitrate derived material. Surprisingly, the addition of aqueous phosphoric acid to the carbonate slurry produced the mostactive catalyst.The batch times for each carbonate derived LAPO was approximately 2-4 times faster that the nitrate derived material. Surprisingly, the addition of aqueous phosphoric acid to the darbonate slurry produced t he most active catalyst. This is a positive finding as it is much easier to pump acid to a slurry system than the reverse. The lack of NH_4OH treatment produced a very active catalyst; however, PEG and other side products tend to be higher when this neutralization step is eliminated.

Example 4

While all lanthanide phosphates will act as ethoxylation catalysts, that activity generally decreases as the atomic weight increases. The following experiment evaluates various salts of cerium, praseodymium and neodymium, since these lanthanides show greater overall activity for ethoxylation than do the rest of the series. Thirteeen lanthanide salts were prepared using the same catalyst synthesis protocol and were evaluated each under the same ethoxylation protocol.

The order of catalyst synthesis was randomized, as was the order of ethoxylation experiments. The data in the following table is organized according to the lanthanide precursor used, and general order of activity. A standard lanthanum phosphate catalyst, prepared from lanthanum nitrate by a toll contractor, was used at the beginning, in the middle and at the end of the series to verify repeatability. This was done to ensure there was no bias in the data from a historical (order of evaluation) perspective.

A solution or slurry of the lanthanide salt was prepared in 200 ml of N_2 sparged DI water in a 1000 ml flask equipped with an overhead stirrer, 250 ml pressure equalized dropping funnel, reflux condenser, N_2 sparger and thermo well. For each experiment, 0.68 moles of the salt was used. For the first experiment, this amounted to 31.2 g of lanthanum carbonate (assumed m.w. = 458). The amount of acid was adjusted depending upon whether the salt had the following formulas (i.e. whether there are two atoms of Ln per molecule or one atom of Ln per molecule):

Lanthanide Salt Formula	Amount H3PO4 Used (20m % excess)	Moles Lanthanide Salt
Ln2(X)3	0.143	0.068
LnY3	0.071	0.068

In the foregoing formulas, X = CO_3, SO_4 and Y= Cl-, NO_3-, acetate-.

A phosphoric acid solution was prepared by dissolving 16.5 g of 85% H_3PO_4 0.143 moles) in 200 ml of N_2 sparged DI H_2O. The phosphoric acid solution was transferred to the addition funnel. If the salt had the formula LnY_3, only 8.25 g of 85%

H_3PO_4 (0.071 moles) in 200 ml of N_2 sparged DI H_2O was used. The phosphoric acid solution was added to the well stirred lanthanide salt/H2O mixture in equal portions over 15 minutes at 25 °C. The reaction mixture was heated to reflux (100 °C.) for 3 hours. The product was cooled and filtered. The product was then taken up into 500 ml of H_2O, added to reactor, and and mixed well for 30 minutes at 50 °C., after which the product was cooled and filtered product. The product was then taken up into 500 ml of H_2O and added to the reactor. 10 ml of 10N NH_4OH was added and mixed well for 30 minutes at 50 °C. The resulting product was cooled, the pH measured, and the product filtered. The product was air dryed by letting air flow through filtered powder overnight. Thereafter, the product was dried further at 50 °C. at full vacuum in a vacuum oven. The resulting catalyst was weighed and sent in for thermographic analysis (TGA).

The lanthanide salts were tested in the following order:

1. Lanthanum Carbonate (as a standard)
2. Cerium acetate
3. Praseodymium chloride
4. Neodymium carbonate
5. Neodymium chloride
6. Cerium chloride
7. Lanthanum chloride
8. Lanthanum sulfate
9. Praseodymium acetate
10. Praseodymium carbonate
11. Cerium carbonate
12. Neodymium acetate
13. Lanthanum acetate

The ethoxylation protocol was the same as in Example 2.

The results are given in the following Table:

Activity of Various Lanthanide Phosphate Catalysts for Ethoxylation of NEODOL 23 Alcohol

Precursor Salt	Product	Activity (min)
lanthanum nitrate	lanthanum phosphate	88
lanthanum carbonate	lanthanum phosphate	26
lanthanum sulfate	lanthanum phosphate	121
lanthanum acetate	lanthanum phosphate	45
lanthanum chloride	lanthanum phosphate	32
praseodymium carbonate	praseodymium phosphate	29
praseodymium chloride	praseodymium phosphate	45
praseodymium acetate	praseodymium phosphate	46
lanthanum nitrate	lanthanum phosphate	75
neodymium carbonate	neodymium phosphate	23
neodymium chloride	neodymium phosphate	49
neodymium acetate	neodymium phosphate	45
cerium carbonate	cerium phosphate	39
cerium chloride	cerium phosphate	50
cerium acetate	cerium phosphate	39
lanthanum nitrate	lanthanum phosphate	90

One lanthanide salt (cerium acetate) produced a catalyst with similar activity as the comparable carbonate precursor. However, none of the lanthanide salts produced a more active lanthanide phosphate than lanthanide carbonate.

Persons of ordinary skill in the art will recognize that many modifications may be made to the foregoing without departing from the spirit and scope thereof. The embodiment described herein is meant to be illustrative only and should not be taken as limiting the invention, which is defined in the following claims.

CLAIMS

1. A method for ensuring production of efficient rare earth metal phosphate catalysts for alkoxylation of organic compounds, said method comprising:
selecting as a reactant one or more carbonate salts of said one or more rare earth metals;
reacting said one or more carbonate salts with a source of phosphate under conditions effective to produce said efficient rare earth metal phosphate catalysts;
wherein said efficient rare earth metal phosphate catalysts provide an increased activity for said alkoxylation compared to activity of substantially the same catalyst produced when one or more salts other than carbonate salts of said rare earth metals are selected as said reactant.

2. The method of claim 1 wherein said rare earth metal phosphate catalyst comprises a lanthanum series metal phosphate catalyst (LAPO); or
wherein the rare earth metal comprises a metal selected from the group consisting of those having atomic numbers 39 and 57 through 71.

3. The method of claims 1 or 2 wherein said catalyst comprises a catalytically effective amount of:

one or more of the phosphate salts of elements selected from the group consisting of cerium, lanthanum, praseodymium, neodymium, yttrium, samarium, gadolinium, dysprosium, erbium, and ytterbium; or

one or more of the phosphate salts of the cerium earth group elements; or one or more of the phosphate salts of elements selected from the group consisting of cerium and lanthanum; or

one or more of the phosphate salts of the lanthanum elements (atomic numbers 57-71); or

one or more of the phosphate salts of the lanthanide series elements (atomic numbers 58-71); or

yttrium phosphate.

4. The method of any of claims 1-3 wherein said metal is derived from natural mineral ores, in particular wherein said catalyst comprises one or more phosphate salts of rare earth elements derived from natural mineral ores selected from the group consisting of bastnasite, monazite, xenotime, didymium, gadolinite and euxenite.

5. The method of any of claims 1-4 wherein said one or more carbonate salts comprise the carbonates of the following metals in the following quantities: from 8% to 15% Ce, from 44% to 65% La, from 20% to 25% Nd, and from 2% to 10% Pr; or

wherein said one or more carbonate salts are the carbonates of the following metals in the following quantites: 12.5%w Ce, 59.3%w La, 22.4%w Nd and 5.8% Pr.

6. The method of any of claims 1-5 wherein said conditions comprise mixing the one or more carbonate salts of the one or more rare earth metals with a volume of water to form a slurry.

7. The method of claim 6 wherein said conditions comprise preparing an aqueous solution of from 5% to 15% phosphoric acid with agitation at a temperature of from 25 °C. to 80 °C., preferably 25 °C.

8. The method of claim 7 wherein the conditions further comprise adding the carbonate slurry to the aqueous solution of phosphoric acid to produce a reaction mixture; or

wherein the conditions further comprise adding the aqueous phosphoric acid to the carbonate slurry under slurrying conditions effective to produce a reaction mixture.

9. The method of claim 8 further comprising cooling the reaction mixture to a slurrying temperature effective to produce first solids; and

subjecting said first solids to second slurrying conditions effective to separate said first solids from said reaction mixture and to form an aqueous second slurry comprising said first solids.

10. The method of claim 9 wherein said second slurrying conditions comprise stirring at a temperature of from 25 °C to 80 °C to produce a heated second slurry, the method further comprising cooling the heated second slurry, thereby producing a cooled second slurry comprising second solids.

11. The method of claim 10 further comprising subjecting the second solids to neutralizing conditions effective to neutralize the mixture, preferably wherein the neutralizing conditions comprise adding aqueous NH_4OH.

12. A method comprising reacting:

an alkylene oxide,

in particular wherein the alkylene oxide comprises a vicinal alkylene oxide, or

in particular wherein the alkylene oxide is selected from the group consisting of ethylene oxide, propylene oxide, and mixtures thereof;

and an organic compound comprising active hydrogen, in particular an organic compound comprising primary active hydrogen, or in particular one or more compound selected from the group consisting of alkanols, phenols, thiols, amines, polyols, and carboxylic acids, or

in particular the alkoxylate product of a previous alkoxylation of an active hydrogen containing compound, or

in particular an organic compound comprising one or more acyclic aliphatic mono-hydric alkanols having from 1 to 30 carbon atoms, preferably from 6 to 24 carbon atoms, more preferably from 8 to 20 carbon atoms, or

in particular a C_1 to C_{30} primary alkanol;

in the presence of a catalytically effective amount of the carbonate salt derived catalyst of any of claims 1-11.

13. The method of claim 12 wherein the catalyst consists essentially of salts having the formula $L_p(PO_4)q$, in particular LPO_4, wherein L is a rare earth element, the subscripts p and q satisfy the relevant valency relationships, that is, when L is divalent p is 3 and q is 2, and when L is tetravalent p is 3 and q is 4.

INTERNATIONAL SEARCH REPORT

Internat Application No
PCT/US 03/26257

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J27/18 B01J37/28 C07C41/03

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)
IPC 7 B01J C07C

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 057 627 A (EDWARDS CHARLES L) 15 October 1991 (1991-10-15) examples 10,11 claim 1 ---	1-4,6-13
X	US 5 210 325 A (WEIDER PAUL R ET AL) 11 May 1993 (1993-05-11) column 8, line 25 - line 37 ---	1-4,6-13
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search 15 December 2003	Date of mailing of the international search report 05/01/2004
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Besselmann, S

INTERNATIONAL SEARCH REPORT

Internat Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
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