Alkanes are converted to unsaturated carboxylic acids by contacting an alkane with an oxidizing agent and a Wells–Dawson type heteropolyacid supported on wide pore polyoxometallate salts.
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WELLS-DAWSON TYPE HETEROPYLACIDS, THEIR PREPARATION AND USE AS OXIDATION CATALYSTS

This application is a continuation-in-part of applications Serial No. 09/002,816, filed January 5, 1998, and Serial No. 09/002,845, filed January 5, 1998.

FIELD OF THE INVENTION

This invention relates to compositions comprising Wells-Dawson type heteropolyacids on supports, such as wide pore polyanion salt salts, methods for the preparation of such compositions, and the use of supported Wells-Dawson type heteropolyacids for the direct catalytic oxidation of alkanes to unsaturated carboxylic acids.

BACKGROUND OF THE INVENTION

Polyoxometallates and heteropolyacids, both in general and those which can be used to prepare some of the catalysts used in our invention, and their preparation are described in Pope et al., Heteropoly and Isopoly Oxometalates, Springer-Verlag, New York (1983).

Polyoxometallates and heteropolyacids consist of a polyhedral cage structure or framework bearing a negative charge (e.g., [PMo$_{12}$O$_{40}$]$^3-$; [P$_2$Mo$_{18}$O$_{62}$]$^6-$) which is balanced by cations that are external to the cage. If the cations are protons, then the compound is a heteropolyacid (HPA) (e.g., H$_6$[P$_2$Mo$_{18}$O$_{62}$]). If the cations were not all hydrogen, but either metals such as an alkali metal, potassium, sodium, or lithium, as in K$_2$P$_2$W$_{18}$O$_{62}$, or ammonium, as in (NH$_4$)$_6$P$_2$Mo$_{18}$O$_{62}$, then it is referred to as a polyoxometallate (POM). In earlier patents, we have used the term “polyoxoanion” to describe compounds in which some or all of the cations are not hydrogen (e.g., K$_3$PMo$_{12}$O$_{40}$); in the present case, however, these compounds are referred to as polyoxometallates and the term polyoxoanion is reserved for describing the anionic cage-like portion of the compound (e.g., [P$_2$Mo$_{18}$O$_{62}$]$^6-$).

As described in Pope et al., supra, heteropolyacids and polyoxometallates are cage-like structures with a primary, generally centrally located atom(s) surrounded by a cage framework, which framework contains a plurality of metal atoms, the same or different, bonded to oxygen atoms. The central element of
heteropolyacids and polyoxometallates is different from metal atoms of the framework and is sometimes referred to as the "hetero" element or atom; the condensed coordination elements are referred to as the "framework" elements or metals. The framework metal atoms are ordinarily transition metals. As described by Pope et al., supra, the majority of heteropolyacids and polyoxometallates have a centrally located heteroatom ("X") usually bonded in a tetrahedral fashion through four oxygen atoms to the "framework" metals ("M"). The framework metals, in turn, (i) are usually bonded to the central atom in an octahedral fashion through oxygens ("O"), and (ii) are bonded to four other framework metals through oxygen atoms and (iii) have a sixth non-bridging oxygen atom known as the "terminal oxygen" atom. This can be illustrated as shown below:

\[
\begin{align*}
M & \equiv O \quad O \quad O \quad M \\
\uparrow \quad \uparrow \quad \downarrow \\
M & \equiv O \quad M \quad O \quad M \\
\quad \downarrow \\
\quad O \\
\quad \downarrow \\
\quad X
\end{align*}
\]

The principal framework metal, M, is effectively limited to only a handful of metals including molybdenum, tungsten, vanadium, niobium and tantalum. According to Pope et al., supra, this is due to the necessary condition that suitable metals have appropriate cation radius and be good oxygen π-electron acceptors.

Among the successful candidates, molybdenum and tungsten share a common feature; namely, the expansion of valences of their metal cations from four to six. The coincidence of these characteristics allow these metals to form stable heteropolyacids and polyoxometallates.

Conventional heteropolyacids (and polyxoations thereeto can be described by the general formula \(H_n(X_\text{metal}O_y)^z\). In this formula, X, the central atom, is
frequently phosphorus. However, other suitable central atoms include Group IIIB-VIB elements, such as antimony, silicon and boron. Further, the subscript k is preferably 2, but can be from 1 to 5. M is molybdenum tungsten, or vanadium and n will vary from 5-20. The subscript y may be as low as 18 or as high as 62. The notation e is the negative charge, on the \((X_{k}M_{n}O_{y})\) polyoxoanion and will vary from case to case, but e is always the number of protons needed to balance the formula. In a typical such heteropolyacid, \(k=2, \ n=18\) and \(y=62\), as in \(H_{6}P_{2}Mo_{18}O_{62}\) and the polyoxometallate \(H_{2}(VO)_{2}[P_{2}Mo_{18}O_{62}]\).

As described in Pope et al., supra, heteropolyacids are known to exist in a variety of structures including the Keggin, Wells-Dawson and Anderson structures. The different structures correspond to the specific geometry of particular heteropolyacid compositions and vary according to the coordination chemistry and atomic radii of the metals present. These compounds may be substituted at various framework sites as disclosed, *inter alia*, in our prior patents. The present invention focuses on compounds of the Wells-Dawson type structure.

In our U.S. Patent 4,803,187, issued February 7, 1989, we taught how to prepare heteropolyacids and polyoxometallates with random substitution of framework metals, such as \(H_{3}(PMo_{8}V_{4}O_{40})\); \(K_{6}(SiMo_{11}MnO_{39})\) and \(K_{2}(PW_{11}VO_{40})\). The preparation of framework-substituted heteropolyacids or polyoxometallates as described in our 4,803,187 patent, supra, is adequate for random substitution, but will not provide the regiospecific, trilacunary substitution as described in our 4,898,989 patent, supra; i.e., replacement of three \(M\) in a single, triangular face with three \(M'\). The teaching of

As described in Pope et al., supra, heteropolyacids and polyoxometallates have found a variety of applications. In the area of catalysis, Keggin ion catalysts have been used in connection with the oxidation of propylene and isobutylene to acrylic and methacrylic acids, oxidation of aromatic hydrocarbons; olefin polymerization; olefin epoxidation; and hydrodesulfurization processes. See, for example, M. Ai. “Partial Oxidation of n-Butane with Heteropoly Compound-based Catalysts”, Proceedings of the 18th International Congress on Catalysis, Berlin 1984, Verlag Chemie, Vol. 5, page 475; Lyons et al., U.S. Patent 4,803,187, issued February 7, 1989; Lyons et al. U.S. Patent 4,859,798, issued August 22, 1989; Ellis et al., U.S. Patent 4,898,989, issued February 6, 1990; Lyons et al., U.S. Patent 4,916,101, issued April 10, 1990; Ellis et al., U.S. Patent 5,091,354, issued February 25, 1992; and Shaikh et al., U.S. Patent 5,334,780, issued August 2, 1994; each of which is incorporated herein by reference.

Framework-substituted Keggin heteropolyacids have been disclosed as catalysts for oxidation of aldehydes, cyclohexene and cyclohexane, and for hydrogen peroxide decomposition. N. Mizuno et al., “Synthesis of [PW\(_x\)O\(_{37}\)(Fe\(_{3+x}\)Ni\(_x\)(OAc\(_3\))\(_{2}\)]^{(9+x)-} (x=predominantly 1) and Oxidation Catalysts by the Catalyst Precursors”, J. Mol. Cat., 88, L125-31 (1994); and Wu et al., “Catalytic Behavior of Metal Ions Located at Different Sites of Heteropoly Compounds”, Catalysis Letters, 23, 195-205 (1994).

Non-framework substituted Keggin polyoxometallates and heteropolyacids are known in the art as catalysts for oxidation of isobutane to

The references cited above primarily employed non-framework substituted Keggin-type heteropolyacids as catalysts in manufacture of unsaturated carboxylic acids, for example acrylic acid and methacrylic acid, from alkanes, for example propane and isobutane. There is no known use of Wells-Dawson-type heteropolyacids for catalysis of these reactions.

Wells-Dawson-type heteropolyacids are more difficult to prepare than the Keggin compounds. This may explain the paucity of published works regarding their activity. In fact, work relating to Wells-Dawson structures is primarily limited to their use for certain homogeneous liquid-phase reactions (Hill et al., Coord.Chem.Rev., 143, 407 (1995)) and in the decomposition of hydrogen peroxide (Wu et al., Cat.Lett., 23, 195 (1994)). Comuzzi et al., Cat.Lett., 36, 75 (1996), investigated the gas-phase oxidative dehydrogenation of isobutane to isobutene catalyzed by K$_6$P$_2$W$_{18}$O$_{62}$, a Wells-Dawson-type phosphotungstate. However, despite the literature on Keggin-type compounds,
there has been no disclosure of the use of the acid form of the Wells-Dawson-type compounds (i.e., or use of Wells-Dawson-type phosphomolybdates (e.g., K₂P₂W₁₈O₆₃), for example, for the heterogeneous gas-phase oxidation of alkanes to unsaturated carboxylic acids.

Given the value and industrial importance of acrylic acid and methacrylic acid, it has been recognized that the one-step conversion of alkanes to unsaturated carboxylic acids would be a useful process with important commercial applications, provided that sufficient yield can be obtained. To date, no efficient catalysts have been developed for the commercial production of acrylic acid from propane or methacrylic acid from isobutane. As a result, acrylic acid is manufactured from propylene, a raw material which is over three times more expensive than propane.

The process of the present invention provides such a one-step process for the conversion of alkane to carboxylic acid catalyzed by Wells-Dawson type HPAs. These catalysts have been found to yield superior results to Keggin-type HPAs having similar metals. Through electrochemical experiments, we have demonstrated that Wells-Dawson HPAs have superior redox properties to Keggin HPAs. At the same time, we have found that Wells-Dawson HPAs are more efficient catalysts for the oxidation of alkanes to α-β-unsaturated oxidation products than Keggin HPAs in comparable experiments. These advantages make the process more attractive than the prior art processes for practical use and potential commercial interest.

**SUMMARY OF THE INVENTION**

The present invention relates to the oxidation of alkanes to unsaturated carboxylic acids or nitrites catalyzed by supported or unsupported, fully or partially
protonated Wells-Dawson-type polyoxoanions (heteropolyacids (HPAs)) which may also
have been promoted or otherwise modified to improve their effectiveness. The support
is preferably a wide pore cation salt of a heteropolyacid (polyoxometallate (POM)), for
example, a wide pore polyoxometallate salt, but other supports are also suitable for use
according to the invention. The process of the invention is useful, for example, for the
conversions of propane acrylic acid or acrylonitrile, and isobutane to methacrylic acid or
methacrylonitrile. In one embodiment, the process of the present invention involves the
conversion of alkane to unsaturated carboxylic acid at a temperature in the range of
about 225°C to 450°C by contacting the alkane with an oxidizing agent in the presence
of a supported Wells-Dawson-type heteropolyacid catalyst, where the support
comprises a wide pore cesium heteropolyoxometallate salt. The process of the
invention is also applicable to the conversion of alkanes to unsaturated nitriles.

The invention comprises a process for the conversion of alkanes to
unsaturated carboxylic acids which comprises contacting an alkane with an oxidizing
agent under oxidation conditions with a Wells-Dawson type heteropolyacid (HPA)
supported on a wide-pore polyoxometallate (POM). Thus the catalyst of this process
can be defined as a HPA/POM catalyst. The HPA component of the catalysts useful in
the process of the present invention has the general formula:

$$H_{(c\cdot d\cdot e\cdot f)}G(A_{2}M_{m}^{+}M'_{x}M''_{y}O_{z})^{x}$$

where G is Cu, Fe, Co, Mn, Ni, La, Li, Na, K or Rb, or an oxy ion of Ti, V, Cr, Mo, U,
As, Bi, Sb, Nb, or ammonium, tetraalkylammonium, pyridinium, quinolinium,
protonated aromatic amines or protonated aliphatic amines, or combinations thereof, or
is absent; X is a Group IIIB, IVB, VB, VIB or transition element, such as phosphorus,
silicon, gallium, aluminum, arsenic, germanium, boron, cobalt, cerium, praseodymium, uranium and thorium; M is molybdenum or tungsten or combinations thereof, M' is vanadium, M'" is independently zinc or a transition metal different from M and M', such as titanium, zirconium, hafnium, niobium, tantalum, chromium, manganese, rhenium, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper or combination thereof, z' is the charge on said cation G; m' is 12 to 18, x' is 0 to 6, n' is 0 to 3, where m' + x' + n' = 18; y' is 48 to 62; and e' is the charge of the anion of the polyoxometallate. The support component comprises an insoluble polyoxometallate salt having the formula:

\[ C_{x}H_{(e-2z)}(X_{i}M_{m}M'_{m}M''_{n}O_{y})^{e} \]

where cation C is selected from the group consisting of potassium, rubidium, cesium, magnesium calcium, strontium, barium, vanadium, chromium, lanthanum, manganese, iron, cobalt, ruthenium, copper, actinide metal, lanthanide metal, metal oxy ion, ammonium, tetraalkylammonium, pyridinium, quinolinium, protonated aromatic amines and protonated aliphatic amines, or combinations thereof, X is a Group IIIB, IVB, VB, VIB or transition metal; M is molybdenum or tungsten or combinations thereof, M' is vanadium; M'" is independently zinc or a transition metal different from M and M', or combination thereof; z is the charge on said cation C; k is 1 to 5, in is 5 to 18, x is 0 to 6, n is 0 to 3, y is 18 to 62.

A preferred cation for the POM support is cesium; for example, Cs_{3+x}(PMo_{12-x}V_{x}O_{40}), where x is 0 to 2. Thus, the HPA/POM catalysts which have been found to be effective have the general formula:

\[ H_{(e'-2z')}G_{b}(X_{2}M_{m}M'_{m}M''_{n}O_{y})^{e'}/C_{x}H_{(e-2z)}(X_{i}M_{m}M'_{m}M''_{n}O_{y})^{e} \]
An example of an HPA/POM catalyst is \( \text{H}_6(\text{P}_2\text{Mo}_{12}\text{O}_{40})/\text{Cs}_3(\text{PMo}_{12}\text{O}_{40}) \). In one embodiment, the POM support comprises a combination of two POMs, for example, a Cs-POM and a K-POM; e.g., \( \text{Cs}_3(\text{PMo}_{12}\text{O}_{40}) \) and \( \text{K}_6(\text{P}_2\text{W}_{18}\text{O}_{62}) \).

The conversion process is carried out at a temperature in the range from 225°C to 450°C, preferably in the range from 350°C to 400°C. The pressure used in the process of the invention is not critical and may, for example, be atmospheric pressure or such other pressure as is within the ability of the person skilled in the art to determine.

**BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 shows the relative reduction potential of framework metals of a Wells-Dawson-type HPA and a Keggin-type BPA.

Figure 2 shows the effect of catalyst support pore volume (in ml/g), for pores with radii greater than 100Å, on Wells-Dawson-type and Keggin-type catalyst performance as a function of acrylic acid yield.

**DETAILED DESCRIPTION OF THE INVENTION**

The present invention relates to the oxidation of alkanes to unsaturated carboxylic acids or nitrites catalyzed by heteropolyacids (HPAs) supported on wide pore polyoxometallates (POMs) which may have been promoted or otherwise modified to improve their effectiveness. The process of the invention is useful, for example for the conversions of propane to acrylic acid or acrylonitrile and isobutane to methacrylic acid or methacrylonitrile.
Reaction Conditions

The temperature used in the process of the invention is that which favors the formation of unsaturated carboxylic acids or nitrites as reaction products. The conversion process is generally carried out at a temperature in the range from about 225°C to about 450°C, preferably at a temperature in the range from about 350°C to 400°C. Notwithstanding this, certain catalysts within the scope of the present invention particularly those HPAs supported on phosphotungststate Keggin ion (e.g., Cs₃(PW₁₂O₄₀)) have been found to maintain their physical and structural integrity at temperatures up to approximately 500°C. These catalysts in particular may be used in the oxidation process of the present inventory at temperatures in the range of 350°C to 500°C where propane activation occurs more readily. The determination of the most desirable temperature for a given reaction and given catalyst within the scope of the invention is within the ability of the person skilled in the art.

The process may be carried out at atmospheric pressure. Other pressures may be used, and the determination of the most desirable pressure for a given reaction within the scope of the invention is within the ability of the person skilled in the art.

The process of the invention may be carried out in any suitable reactor configuration. For example, the reaction may be performed in a fixed-bed, moving bed, ebullating bed reactor, or other as is within the ability of the person skilled in the art to determine.

The process of the invention is preferably carried out in vapor phase. Preferably, the feedstock is an alkane gas. The reaction may be carried out in the
presence or absence of steam. An inert gas, such as nitrogen, argon, helium or the like, may so be used. When an inert, diluting gas is used in the process of the invention, determination of the molar ratio of alkane, oxidant, diluting gas and water (steam), if present, in the starting, reaction gas mixture is within the ability of the skilled practitioner in the art. Determination of the gas space velocity used in the process of the invention is within the ability of the skilled practitioner in the art.

**Feedstocks**

The alkane starting materials include straight and branched-chain compounds suitable for conversion to unsaturated carboxylic acids or combinations thereof, or to unsaturated nitriles or combinations thereof. Preferred among these are light alkanes comprising three to seven carbon atoms. More preferred feedstocks for the process of the present invention are propane and isobutane which may be oxidized by the process of the present invention to form acrylic acid and methacrylic acid, respectively, or, when ammonia is present in the feed, to form acrylonitrile and methacrylonitrile, respectively.

As noted above, the feedstock may comprise a combination of alkanes, preferably C_3-C_7 alkanes. In addition, the purity of the starting material is not critical, though it is preferable to avoid the presence of compounds which may poison the catalyst. As a result, the feedstock may, in addition to the alkane or alkanes of interest, further comprise methane or ethane as well as impurities such as air or carbon dioxide.

Suitable oxidants for use in the process of the invention comprise air, molecular oxygen and other oxidants, such as nitrogen oxides. Preferred among these are air and molecular oxygen.
In one embodiment of the invention, an alkane is contacted with an oxidizing agent in the presence of a supported Wells-Dawson heteropolyacid catalyst. For example propane is contacted with an oxidizing agent in the presence of a supported Wells-Dawson heteropolyacid catalyst according to the invention, to produce acrylic acid. Similarly, isobutane is converted to methacrylic acid. The support comprises a wide pore polyoxometallate salt. The supported heteropolyacid may be framework-substituted as described elsewhere herein.

Catalyst

The catalysts useful in the process of the present invention comprise supported Wells-Dawson type heteropolyacids. Effective catalysts comprise Wells-Dawson HPAs on a support comprising at least one wide-pore polyoxometallate. These catalysts are novel compositions of matter. The soluble heteropolyacid component of the catalysts useful in the process of the present invention has the general formula:

\[ H_{(c-hy)}G_k(X_{2M_{m}M'_{n}M''_{p}O_{y})^{x^{\theta}}\}

where cation G is Cu\(^{++}\), Fe\(^{+++}\), Co, Mn, Ni, La, Li, Na, K or Rb, or an oxy ion of Ti, V, Cr, Mo, U, As, Bi, Sb, Nb, or ammonium, tetraalkylammonium, pyridinium, quinolinium, protonated aromatic amines or protonated aliphatic amines, or combinations thereof, or is absent; X is a Group IIIB, IVB, VB, VIB or transition element, such as phosphorus, silicon, gallium, aluminum, arsenic, germanium, boron, cobalt, cerium, praseodymium, uranium and thorium; M is molybdenum or tungsten, or combinations thereof; M' is vanadium; M'' is independently zinc or a transition metal different from M and M', such as titanium, zirconium, hafnium, niobium, tantalum, chromium, manganese, rhenium, iron, cobalt, nickel, ruthenium, rhodium, palladium,
osmium, iridium, platinum, copper or combination thereof, \( z' \) is the charge on said
cation G; \( m' \) is 12 to 18, \( x' \) is 0 to 6, \( n' \) is 0 to 3, where \( m' + x' + n' = 18; y' \) is 48 to 62;
and \( e' \) is the charge of the anion of the polyoxometallate.

The catalysts used in the process of the invention are heteropolyacids

5 supported on at least one wide pore polyoxometallate salt. A preferred support

comprises an insoluble polyoxometallate salt having the formula:

\[
C_{x}H_{e+az}(X_{k}M_{m}M'_{n}M''_{n}O_{y})^{e}
\]

where cation \( C \) is selected from the group consisting of potassium, rubidium, cesium,
magnesium, calcium, strontium, barium; transition metal, such as vanadium, chromium,
lanthanum, manganese, iron, cobalt, ruthenium, copper and the like; actinide metal;
lanthanide metal; metal oxy ion, such as oxy ions of vanadium, chromium and uranium
and the like; ammonium, tetraalkylammonium, pyridinium, quinolinium, protonated
aromatic amines and protonated aliphatic amines, or combinations thereof; \( X \) is a Group

10 IIIB, IVB, VB, VIB or transition metal; \( M \) is molybdenum or tungsten or combinations
thereof, \( M' \) is vanadium; \( M'' \) is independently zinc or a transition metal different from \( M \nand M' \), or combination thereof, \( z \) is the charge on said cation \( C \); \( k \) is 1 to 5, \( m \) is 5 to

18, \( x \) is 0 to 6, \( n \) is 0 to 3, \( y \) is 18 to 62. When “az” equals “e”, then there are no
protons present in the polyoxometallate support.

Suitable cations in the POMs useful in the process of the invention

20 comprise alkali metal, including, but not limited to, potassium, sodium, cesium and the
like; magnesium, calcium, strontium, barium; transition metal, such as vanadium,
chromium, lanthanum, manganese, iron, cobalt, ruthenium, copper and the like; actinide
metal; lanthanide metal; metal oxy ion, such as oxy ions of vanadium chromium and
uranium and the like, for example, vanadyl, chromyl, uranyl and the like; or other cation such as ammonium, \( R_N^+ \) ("tetraalkylammonium") and the like; pyridinium, quinolinium and protonated aromatic amines and protonated aliphatic amines. Of these cations, preferred cations comprise potassium, rubidium, cesium, magnesium, calcium, strontium, barium, lanthanum, ammonium, tetraalkylammonium, pyridinium, quinolinium, protonated aromatic amines and protonated aliphatic amines, or combinations thereof. The presence of vanadyl has been found to result in a particularly effective compound.

A preferred cation for the support POM is cesium; for example,

\[
Cs_{3+x}(PMo_{12}V_xO_{40}) , \text{ where } x \text{ is } 0 \text{ to } 3.
\]

Preferred embodiments of the support include

\[
Cs_3(PMo_{12}O_{40}), Cs_4(PMo_{11}VO_{40}), Cs_5(PMo_{11}V_2O_{40}), Cs_5(PW_{12}O_{40}), Cs_6(P_2Mo_{16}O_{62}),
\]

\[
Cs_6(P_2W_{18}O_{62}) \text{ or combinations thereof. Other suitable supports include wide pore salts,}
\]

for example wide pore cesium salts of the various substituted polyoxometallates described below and in Lyons et al., U.S. Patent 5,705,685, issued January 6, 1998,

which is incorporated by reference herein for all purposes. The support for the catalyst may comprise more than one POM composition; for example, the support may comprise a mixture of two or more POMs; for example, a Cs-POM and a K-POM; e.g.,

\[
Cs_3(PMo_{12}O_{40}) \text{ and } K_6(P_2W_{18}O_{62}). \text{ Other suitable supports comprise silicas, silicalites, zeolites, aluminas and the like, preferably coated on with a suitable POM of the types described herein.}
\]

The support is a porous material having pore volumes in the range from 0.01 to 0.25 ml/g and a pore size distribution in which more than approximately 60% of the pores have a pore radius of greater than or equal to approximately 75 Å, preferably
greater than or equal to approximately 100Å, more preferably, greater than or equal to approximately 150Å, still more preferably greater than or equal to approximately 200Å. More preferably, the support has pore volumes in the range from 0.05 to 0.25 ml/g and a pore size distribution in which more than approximately 60% of the pores have a pore radius of greater than or equal to approximately 75Å. In a preferred embodiment, the support material has pore volumes in the range from 0.01 to 0.25 ml/g and a pore size distribution in which more than approximately 80% of the pores have a pore radius of greater than or equal to approximately 200Å; more preferably, the support material has pore volumes greater than 0.15 ml/g and a pore size distribution in which more than approximately 80% of the pores have a pore radius of greater than approximately 250Å.

Preferably, the pores in the support have pore radii of greater than 75Å and pore volumes greater than 0.05 ml/g; more preferably, the pore radii are greater than 100Å, and independently, the pore volumes are greater than 0.1 ml/g. It has been found that supports with pore volumes greater than 0.02 ml/g result in catalysts with superior activity, provided the pores are wide (i.e., radii greater than approximately 75Å). These supported catalysts may be further modified by pretreatment with water and by formation in the presence of vanadyl acetylacetonate or VOSO₄.

Typically, the POM support component of the catalyst may be prepared by adding a soluble salt of the desired cation, for example Cs₂CO₃ or CsNO₃ or the like for a cesium salt support, to the desired soluble heteropolyacid, for example H₃(PMo₁₂O₄₀), to form the insoluble POM example Cs₅(PMo₁₂O₄₀). The salt solution is preferably added slowly into the heteropolyacid solution to precipitate the cation heteropolymetallate salt. The following reactions exemplify the process:
\[ 3 \text{Cs}_2\text{CO}_3 + 2 \text{H}_3(\text{PMo}_{12}\text{O}_{40}) \rightarrow 2 \text{Cs}_3(\text{PMo}_{11}\text{O}_{40}) + 3 \text{H}_2\text{O} + 2 \text{CO}_2 \]

\[ 3 \text{Cs}_2\text{CO}_3 + \text{H}_6(\text{P}_2\text{Mo}_{90}\text{O}_{62}) \rightarrow 3 \text{Cs}_6(\text{P}_2\text{Mo}_{18}\text{O}_{62}) + 3 \text{H}_2\text{O} + 3 \text{CO}_2 \]

The precipitation may be performed at an elevated temperature (e.g., 25-100°C) and CO₂ is evolved during the reaction. The resulting POM salt forms a fine suspension in water and may be evaporated to dryness, for example by rotary evaporation, or by heating at 50°C or below. The dried material may be calcined (e.g., at 275°C). POMs having the formula \( \text{Cs}_n\text{H}_{(e-a)}(\text{X}_2\text{M}_{m-x}\text{M'}_{x}\text{M''}_y\text{O}_{z})^e \), as described more fully herein, may be prepared according to this process.

After calcination, the physical properties of the POM salt may be determined, for example the surface area, the pore volume and the pore size distribution (PSD). It has been found that the preparation process can influence these physical characteristics. For example, slow addition of the cation salt to the HPA solution results in a material with few small pores and many large pores. In contrast, rapid addition of the cation salt yields a broad PSD with many small pores and some intermediate and large pores. For the present invention, slow addition to form mainly wide pores is preferable; for example, at a rate of 2 ml/minute particularly when using solution concentrations of approximately 0.1 mole/liter. More generally, the salt solution may have a concentration in the range from approximately 0.05 to 1 mole/liter, preferably 0.1 to 0.2 mole/liter, and the HPA solution may have a concentration in the range from approximately 0.05 to 1 mole/liter, preferably 0.1 to 0.2 mole/liter, and more preferably 0.1 mole/liter. The solutions may be mixed at a rate in this range from 0.5 to 20 ml/minute, preferably 1 to 10 ml/minute, more preferably 2 ml/minute. More
preferably, particularly for the preparation of large quantities of material, the solutions of the cation salt and the HPA may be added simultaneously to a reaction vessel.

A further factor influencing the PSD was found to be the temperature of the reaction medium during the precipitation step. Precipitation at room temperature, yielded a narrow PSD with a median pore radius of about 90Å, whereas precipitation at 65°C was found to result in a broader PSD with a greater median pore radius (≥120Å).

The precipitation step may be carried out at a temperature in the range from approximately 25°C to 100°C; preferably in the range from 50°C to 80°C; more preferably in the range from 60°C to 65°C.

Additionally, it has been found that aging of the slurry containing the polyoxometallate salt, followed by slow evaporation to dryness, is beneficial to the production of wide pore materials. Preferably, the slurry is allowed to remain at room temperature or at a temperature in the range from approximately 25°C to 45°C, preferably 35°C to 45°C, for an extended period of time and is then slowly dried. The aging and drying process may extend for a period of 12 to 72 hours or longer. This forms a wide-pore material. Finally, use of excess cation salt (relative to the stoichiometric amount) has been found to promote formation of the desired wide-pore support material. While the support material can be prepared using stoichiometric ratios of starting materials, it is preferred to use an excess of the cation salt.

It has been found that certain POM salts, particularly for example Cs₃(PMo₁₂O₄₀), are produced with greater pore sizes and pore volumes than certain other comparably prepared materials, such as Cs₄(PMo₁₁VO₄₀), Cs₃(PW₁₂O₄₀) and Cs₃(AsMo₁₂O₄₀). However, we have developed a novel preparation method involving
the simultaneous precipitation of Cs₅(PMo₁₂O₄₀) along with the desired POM salt which yields materials with comparable pore sizes and pore volumes to the Cs₅(PMo₁₂O₄₀) material.

The following procedure has been found to yield POM salts with comparable desirable pore sizes and pore volumes as Cs₅(PMo₁₂O₄₀). According to this process, Cs₅(PMo₁₂O₄₀) is in solution with the desired salt of Cs₅(PM₁₂ₓM'₄O₄₀) and is simultaneously precipitated with the desired POM salt. Examples of suitable materials for preparation according to this process include, for example, Cs₅(PMo₁₁VO₄₀), Cs₅(PMo₁₀V₂O₄₀), Cs₅(PW₁₂O₄₀), Cs₆(P₂Mo₁₈O₆₂) and Cs₆(P₂W₁₈O₆₂). In order to precipitate the two POM salts simultaneously, a solution of the two HPAs, or two separate solutions of the two BPAS, are slowly mixed with a solution of the salt of the desired cation, for example Cs₅CO₃. The solution concentration, the mixing rate, the reaction temperature and the time of drying and aging of the precipitate are the same as that described above. It is believed that this process is applicable as well to the preparation of other POM salts described herein. For Cs-POM supports of the Wells-Dawson type, lower precipitation temperatures (i.e., room temperature) are preferable.

The Wells-Dawson heteropolyacids supported on such supports comprise heteropolyacids, which may have been framework-substituted as described below. Likewise, the polyoxometallate comprising the support may have been framework-substituted as described below. The substitution may, for example, be monosubstitution, regio-disubstitution or regio-trisubstitution, all of which produce effective compositions for use as the supported HPA and the support POM in the process of the present invention. The catalysts may be further promoted by a variety of
means described below. The present invention encompasses unsubstituted and
substituted HPAs supported on wide pore salts of unsubstituted and substituted POMs.

In one embodiment, the catalyst, a modified HPA supported on a wide-
pore POM as described above, has the general formula:

\[ H_{(c-bx)}G_b(X_{2}M_{m-n}M'_nM''_nO_y)_{\gamma}/C_{x}H_{(e-bz)}(X_{k}M_{m-n}M'_nM''_nO_y)_{\gamma} \]

where, in the HPA \( H_{(c-bx)}G_b(X_{2}M_{m-n}M'_nM''_nO_y)_{\gamma} \), \( G \), the cation, is \( \text{Cu}^{++}, \text{Fe}^{+++}, \text{lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cobalt (Co), manganese (Mn), nickel (Ni), or lanthanum (La), or an oxy ion of titanium (Ti), vanadium (V), chromium (Cr), uranium (U), arsenic (As), bismuth (Bi), tin (Sn), niobium (Nb), or ammonium, tetraalkylammonium, pyridinium, quinolinium, protonated aromatic amines or protonated aliphatic amines, or combinations thereof, or is absent; X, the central or hetero atom, is a Group IIIB, IVB, VB or transition element, such as phosphorus, silicon, gallium, aluminum, arsenic, germanium, boron, cobalt, cerium, praseodymium, uranium and thorium; M, the first framework metal, is molybdenum or tungsten of combinations thereof; M' is vanadium substituted for first framework metal M; M'', the second framework metal, is different from M and is independently zinc or a transition metal, such as titanium, zirconium, hafnium, niobium, tantalum, chromium, manganese, rhenium, iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper or combination thereof; m' is 12 to 18, x' is 0 to 6, n' is 0 to 3 where m' + x' + n' = 18; y' is 48 to 62; e' is the charge of the anion of the heteropolyacid; and z' is the charge on the cation G; and where, in the POM \( C_{x}H_{(e-bz)}(X_{k}M_{m-n}M'_nM''_nO_y)_{\gamma} \), C is selected from the group consisting of potassium, rubidium, cesium, magnesium, calcium, strontium, barium, lanthanum, ammonium, tetraalkylammonium, pyridinium,
quinolinium, protonated aromatic amines and protonated aliphatic amines, or combinations thereof; X is a Group IIIB, IVB, VB, VIB or transition metal; M is molybdenum or tungsten or combinations thereof; M' is vanadium; M'' is independently zinc or a transition metal different from M and M', or combination thereof, z is the charge on said cation C; k is 1 to 5, m is 5 to 18, x is 0 to 6, n is 0 to 3; y is 18 to 62; and when "az" equals "e", there are no protons present in the polyoxometallate support.

The catalysts useful in the process of the present invention may be promoted by various means including preparing the HPA in the presence of vanadyl acetylacetonate or the like. In addition, exchange of iron or other transition metals, actinide and lanthanide metals, and other groups, G, has been found to promote the activity of the Wells-Dawson HPAs of the catalysts used in the process of the invention.

The invention comprises a process for conversion of alkanes to unsaturated carboxylic acids by contacting an alkane with an oxidizing agent under partial oxidation and dehydrogenation conditions with an HPA supported on a POM salt, thereby to convert said alkane to an unsaturated carboxylic acid or, when ammonia is added to the feed, an unsaturated nitrile. Either or both of the HPA and the POM independently, may be framework substituted or not as described herein. In one embodiment comprising a substituted POM support, the POM may comprise (1) at least 11 atoms of a first framework metal or metals comprising molybdenum or tungsten or combinations thereof and (2) at least one atom of a second framework metal or metals comprising zinc or a transition metal other than molybdenum or tungsten. When there is more than one second framework metal, they may comprise a combination of zinc and the available transition metals. Independently of the composition of the POM support,
the HPA may comprise 18 atoms or less of molybdenum as framework metal, or may
contain a combination (totalling 18 atoms or less) of molybdenum framework atoms and
tungsten framework atoms. If the HPA contains fewer than 18 atoms of Mo and/or W,
it will also comprise one or more second framework metal or metals, comprising zinc or
a transition metal (other than Mo or W) or combination thereof.

In one embodiment, either or both of the HPA and POM support used in
the process of the invention may independently comprise 12 to 17 atoms of a first
framework metal selected from the group consisting of molybdenum or tungsten, or
combinations thereof, and 1 to 6 atoms if a second framework metal such as titanium,
zirconium, vanadium, niobium, tantalum, chromium, manganese, rhenium, iron, cobalt,
nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper or zinc. The
second framework metals (M) may be site-specific, regioselective substitutions or may
be essentially randomly substituted in the framework. When the substituted POM
support is a Keggin-type POM it may comprise 9 to 11 atoms of a first framework
metal and 1 to 3 atoms of a second framework metal, with the metals as described
above.

The central or hetero element, X, of the POM and HPA components of
the catalyst useful in the process of the present invention is selected from the elements
of Group IIIB, IVB, VB, VIB of the Periodic Table or from the transition elements; it
may, for example, be phosphorus, silicon, aluminum, germanium or the like. In these
embodiments, the first framework element comprises molybdenum, tungsten, or a
combination thereof. An example of such heteropolyacid is $\text{H}_m\text{P}_{2}\text{W}_{18-n}\text{M}^\nu\text{O}_{62}$, in which
phosphorus (P) is the hetero atom and tungsten (W) is the first framework metal and M' is the second framework metal as described below.

The POM or HPA component used in the process of the invention may contain second framework metals which have been substituted into the framework thereof, replacing an equivalent number of the first framework metals. Such substituting metals may, for example, be titanium, zirconium, hafnium, vanadium, niobium, tantalum, chromium, manganese, rhenium iron, cobalt, nickel, ruthenium, rhodium, palladium, osmium, iridium, platinum, copper, zinc or combinations thereof.

The atoms which have been replaced in such substitution may be for example molybdenum or tungsten, or combinations thereof, as disclosed in Ellis and Lyons U.S. Patent 4,898,989; supra; J.P. Ciabrini, et al., Polyhedron, 2, 1229 (1983); M. Abbessi et al., Inorg. Chem., 30, 1695 (1991); D.K. Lyons et al., J. Am. Chem. Soc., 113, 7209 (1991). The number of framework atoms replaced may be from 1 to 3 or more, and the substituting metals, which are different from the replaced metal, may each be the same metal, for example iron, or may be different from each other, for example, two or three different metal atoms; e.g., one iron atom may replace one tungsten atom; two iron atoms may replace two tungsten atoms; three iron atoms may replace three tungsten atoms; two atoms, different from each other, for example molybdenum and vanadium, may replace two tungsten atoms; three atoms, different from each other, for example manganese, molybdenum and vanadium, may replace three tungsten atoms. In one embodiment, three framework atoms of a POM or HPA are replaced by three atoms, different from the framework atoms, one of which replacing atoms is selected from the group consisting of iron, chromium, manganese or ruthenium, and two of
which are different from the one just referred to and are the same or different transition metals.

Examples of such HPAs are \( H_3[P_2W_{17}FeO_{61}] \), wherein \( P \) is the heteroatom, \( W \) is the first framework metal, and \( Fe \) is the second framework metal;

\[ H_3[P_2W_{15}Mo_{6}O_{32}] \], wherein \( P \) is the heteroatom, \( W \) is the first framework metal, and \( Mo \) is the second framework metal; and \( H_3[P_2W_{13}Mo_{5}MoO_{62}] \), wherein \( P \) is the heteroatom, \( W \) is the first framework metal, and \( Mo \) is the second framework metal, and \( M' \) is the third framework metal, \( M' \) being a transition metal, preferably selected from the group consisting of \( Fe, Mn, V, Co \) and \( Ni \). These compositions, as well as their promoted forms, for example with \( VO^{2+} \) in the cationic positions, are useful as the HPA component of the supported catalysts.

The supported catalyst comprising a Wells-Dawson-type heteropolyacid (HPA) supported on POM salt may be prepared, for example, by incipient wetness techniques in which a solution of HPA is sprayed on solid support matrix and then dried, or by adding support material to a solution of HPA and evaporating the solution to dryness. The HPA may be dissolved in water or other solvent, such as acetonitrile. The resulting material is then calcined.

The following process illustrates the catalyst preparation using incipient wetness technique. The amounts of POM support and HPA used are determined on the basis of the total pore volume of the support (typically, 0.13-0.18 ml/g) and the desired catalyst loading (typically about 30 wt.%). The desired amount of HPA is dissolved in solvent (typically water or acetonitrile) which may be as much as approximately 25% in excess of the total pore volume of the support material. The solution is sprayed evenly
on the support material and the supported catalyst is dried, for example at 100°C for 1 hour when using water, or 70°C for 1 hour when using acetonitrile. Repeated spraying and drying steps may be used to modify dispersion characteristics. The final supported catalyst material is then calcined. The calcination temperature is preferably between 250°C and 450°C, and is not so severe as to damage the catalyst structure. The calcination may be performed, for example, at 275°C for 3 to 6 hours, or at 420°C for 1 to 2 hours.

The HPA may usefully be supported on a catalyst support comprising wide pore POM salt. Supported catalysts with HPA loading of approximately 30 weight percent (i.e., 30 wt.% HPA and 70 wt.% support) may be prepared by standard incipient wetness techniques. Modification of this ratio for purposes of manipulating the activity or other characteristics of the catalyst or the process is within the ability of the practitioner of the art. The amount of HPA and POM support used to prepare the supported catalyst may be varied according to the pore volume of the solid support and the degree of catalyst loading desired. These supported catalysts may be prepared, for example, by slurring the solid support with a solution of the HPA, or by spraying the HPA dissolved in water onto the dried support or by means known in the art. Preferably, the supported catalyst is dried and calcined prior to use.

In one embodiment of the invention, the catalyst is prepared by reacting an HPA with VO(acac),, isolating the product, and then applying a solution of the product to the support. The supported catalyst is then dried and calcined prior to use.

A variety of in situ techniques can be used to generate a supported Wells-Dawson HPA catalyst, including, for example, precipitating some of the HPA, as
its cesium salt with cesium carbonate, followed by evaporation to leave the Wells-Dawson HPA on the Cs-POM surface. Another technique is to acidify the surface of a Wells-Dawson POM to generate surface HPA. Regardless of the method used, any Wells-Dawson HPA on a suitable support will be an effective catalyst for converting, for example, propane to acrylic acid. Pure crystalline Wells-Dawson HPAs themselves are active catalysts, but because of their hydrolytic instability and solubility, supported catalysts are preferred.

The catalysts of the present invention have been found to be highly active in the conversion of alkanes to unsaturated carboxylic acids. One important aspect of oxidation catalysts is the redox potential of their active metal sites. Through electrochemical experiments, we have demonstrated that Wells-Dawson HPAs have superior redox properties than Keggin HPAs. Figure 1 shows the relative reduction potential of Wells-Dawson-type HPAs and Keggin-type HPAs with framework metal substitutions. It can be seen that the Wells-Dawson-type HPA has a wave of more positive reduction potential than the Keggin HPA. In oxidation experiments, we have found that Wells-Dawson HPAs are more efficient catalysts for the oxidation of alkanes to α-β-unsaturated oxidation products than certain Keggin HPAs in comparable experiments. This is consistent with the concept that complexes with more positive reduction potentials lead to active oxidation catalysts. See also, J.E. Lyons et al., *J. Catal.*, 155, 59 (1995); A. Bottcher et al., *J. Mol. Catal. A*, 113, 191 (1996); T.P. Wijesekera et al., *Catal. Lett.*, 36, 69 (1996).

The data in Figure 1 show the more positive reduction potential of Wells-Dawson-type Cs-POMs relative to Keggin-type Cs-POMs. Carbon paste
electrodes were prepared containing Cs₃H₆ₓ(PO₆)₂ and Cs₃(PMo₁₂O₃₉). As is
illustrated in the figure, comparison of the surface electrochemistry of these Cs-POMs
showed that the most positive potential of the Wells-Dawson-type ion was over 150 mV
more positive than that of the Keggin-type ion.

The data in Figure 2 shows the effect of catalyst support pore volume (in
ml/g), for pores with radii greater than 100 Å, on Wells-Dawson type and Keggin-type
catalyst performance as a function of acrylic acid yield. The catalysts, designated in the
figure, were prepared as described herein. The figure illustrates that the increase in
acrylic acid yield with increasing volume of wide pores is steeper with Wells-Dawson
type HPA catalysts than with Keggin-type HPA catalysts. In addition, the figure shows
that supported Wells-Dawson type HPA catalysts achieve higher yield values than
supported Keggin-type HPA catalysts of the same pore size. This is a comparison of
the PSD of the finished catalysts.

EXAMPLES

Example 1

The following procedure for the synthesis of (NH₄)₆[P₂Mo₁₈O₆₂] is an
adaptation of that described by Wu (H. Wu, J. Biol. Chem., 189, 43 (1920)). In a 1 L rb
flask, 100 g
Na₃MoO₄·2H₂O was dissolved in 400 ml deionized water; 15 ml phosphoric acid were
added, followed by 80 ml concentrated hydrochloric acid. The contents of the flask
were refluxed for 8 hours; then cooled to room temperature. One drop of 30% H₂O₂
was added and the solution was allowed to stir overnight.
NH₄Cl (100 g) was added to the above solution, stirred for 10 minutes and the yellow product was filtered under suction. The solid was redissolved in a minimum of warm water and refiltered to remove any insoluble material. The filtrate was concentrated in vacuo and diluted with approximately four times its volume of 1,4-dioxane. The solid was washed with dioxane-water (3:1), and diethyl ether and dried in air protected from light. FTIR (v; KBr): 1406, 1077, 1003, 936, 906, 769 cm⁻¹. ³¹P NMR (δ; H₂O/D₂O): -2.50 ppm (ref: H₃PO₄ at 0).

Example 2

The following procedure for the synthesis of K₆[P₂W₁₈O₆₂] is an adaptation of that described in the literature: R.G. Finke, et al., Inorg. Chem., 26, 3886 (1987). In a 1L rb flask, Na₂WO₄⋅2H₂O (100g) was dissolved in 350 ml of water, and heated to near reflux. Phosphoric acid (85%; 150 ml) was added dropwise over 30 minutes and continued heating at reflux for 8-12 hours. The reaction mixture was cooled to room temperature, treated with 2 drops of bromine and allowed to stir for 30 minutes. Solid KCl (100 g) was stirred in and K₆P₂W₁₈O₆₂ was collected by filtration and dried under suction.

The crude product prepared above was redissolved in approximately 200 ml of hot water and filtered through a celite pad. An equal volume of dioxane was added and the solution was allowed to cool overnight. The product was collected by filtration, washed with dioxane-water (1:4), followed by diethyl ether, and then air dried. The yield was 70-75g. FTIR (v, KBr): 1090, 1023, 962, 917, 788 cm⁻¹. ³¹P NMR (δ; H₂O/D₂O): -12.4, -10.8, -11.6 ppm (ref: H₃PO₄ at 0).
Example 3

\( \text{H}_6[\text{P}_2\text{Mo}_{18}\text{O}_{62}] \) was synthesized as follows: A solution of 50 g (NH\(_4\))\(_6[\text{P}_2\text{Mo}_{18}\text{O}_{62}] \) dissolved in minimum cold water was passed through 150 g of strongly acidic ion exchange resin (e.g. Dowex HCR-W2, H\(^+\) form) packed in an ice-water cooled glass column. The eluate was evaporated to dryness and the residue was further dried on the vacuum-line overnight. FTIR (\(\nu\); KBr): 1079, 1004, 948, 903, 771 cm\(^{-1}\). \(^{31}\)P NMR (\(\delta\); H\(_2\)O/D\(_2\)O): -2.55 ppm (ref: H\(_3\)PO\(_4\) at 0).

Example 4

\( \text{H}_2(\text{VO})_2[\text{P}_2\text{Mo}_{18}\text{O}_{62}] \) was synthesized as follows: A solution of \( \text{H}_6[\text{P}_2\text{Mo}_{18}\text{O}_{62}] \) (29.84 g) in acetonitrile (325 ml) was treated with a solution of vanadyl acetylacetonate (5.3 g) in acetonitrile (325 ml). The solution was allowed to stir for 1 hour and evaporated to dryness in vacuo. The residual solvent was removed on the vacuum-line overnight and the product was dried in the vacuum-oven at 60\(^\circ\)C for 3 hours and then at 100\(^\circ\)C for 4 hours. FTIR (\(\nu\); KBr): 1076, 1004, 953, 892, 830 cm\(^{-1}\).

\(^{31}\)P NMR (\(\delta\); H\(_2\)O/D\(_2\)O): -4.06 ppm (ref: H\(_3\)PO\(_4\) at 0).

Example 5

The catalysts \( \text{H}_2(\text{VO})_2[\text{P}_2\text{Mo}_{18}\text{O}_{62}] \) on Cs\(_2\)PMo\(_{12}\)O\(_{40}\) and \( \text{H}_6[\text{P}_2\text{Mo}_{18}\text{O}_{62}] \) on Cs\(_2\)PMo\(_{12}\)O\(_{40}\) were synthesized as follows: A solution of the active material \( \text{H}_6[\text{P}_2\text{Mo}_{18}\text{O}_{62}] \) or \( \text{H}_2(\text{VO})_2[\text{P}_2\text{Mo}_{18}\text{O}_{62}] \) (quantity required for the desired loading level) in water was coated on finely ground Cs\(_2\)PMo\(_{12}\)O\(_{40}\) to incipient wetness. The material was dried in an oven at 100\(^\circ\)C for 1 hour, ground again and the procedure repeated until the entire solution was impregnated on the support. The catalyst was finally dried in a vacuum-oven at 100\(^\circ\)C overnight and calcined at 275\(^\circ\)C for 2 hours prior to testing.
Example 6

The catalyst $\text{H}_2(\text{VO})_2[\text{P}_2\text{Mo}_{18}\text{O}_{62}]$ on the mixed POM support, $\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ and $\text{Cs}_6\text{PMo}_{12}\text{O}_{40}$ was prepared as follows: Finely powdered $\text{Cs}_6\text{PMo}_{12}\text{O}_{40}$ was slurried in a solution of $\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62}$ in water (10% $\text{K}_6\text{P}_2\text{W}_{18}\text{O}_{62}$, 90% $\text{Cs}_6\text{PMo}_{12}\text{O}_{40}$ by weight) and allowed to stir for 2 hours. The solvent was evaporated and the residue was dried in a vacuum oven at 120°C overnight. The mixed POM thus prepared, was used to support $\text{H}_2(\text{VO})_2[\text{P}_2\text{Mo}_{18}\text{O}_{62}]$ at a desired level of loading as described in the Example 5 above. The catalyst was dried (100°C in a vacuum oven overnight), and calcined at 275°C in air, or at 420°C under $\text{N}_2$, for 2 hours prior to testing.

Example 7

The $\text{H}(\text{VO})(\text{PMo}_{12}\text{O}_{40})$ on $\text{Cs}_3(\text{PMo}_{12}\text{O}_{40})$ catalyst was prepared according to the following process. The amounts of support and heteropolyacid used are determined on the basis of the total pore volume of the support (typically, 0.13-0.18 ml/g) and the desired catalyst loading (typically about 30 wt.%). The desired amount of $\text{Cs}_3(\text{PMo}_{12}\text{O}_{40})$ powder is weighed into a Pyrex dish. The total pore volume of the powder is calculated from the BET pore volume. A certain amount of HPA, based on the desired catalyst loading of approximately 30 wt.%, is placed in a beaker and water is added with stirring. After the HPA is dissolved, the solution is sprayed evenly on the support material with a syringe and the supported catalyst is dried at 80°C for 8 hours.

Repeated spraying and drying steps are used to modify dispersion characteristics. The final supported catalyst material is then calcined at 275°C for 3 to 6 hours.

Likewise, the $\text{H}_3(\text{PMo}_{12}\text{O}_{40})$ on $\text{Cs}_3(\text{PMo}_{12}\text{O}_{40})$ catalyst was prepared according to the following process. $\text{H}_3(\text{PMo}_{12}\text{O}_{40})$ (Fluka) was supported on a wide
pore Cs$_3$(PMo$_{13}$O$_{40}$) at the 30% level by incipient wetness from an aqueous solution.

The catalyst was dried at 100°C in vacuo overnight followed by heating in air at 275°C for 2 hours.

Table 1 shows comparative data for the oxidation of propane catalyzed by Keggin and Wells-Dawson type heteropolyacids supported on Cs-POMs. We have found that the Wells-Dawson-type HPAs produce higher yields of acrylic acid than compositionally comparable Keggin-type HPAs.
TABLE I
Propane Oxidation to Acrylic Acid

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Propane Conv. %</th>
<th>AA Yield %</th>
<th>AA</th>
<th>C₃⁻</th>
<th>ACR</th>
<th>Acetic Acid</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₃[PMO₁₂O₄₉] on Cs₃PMO₁₂O₄₀ *</td>
<td>6</td>
<td>0.3</td>
<td>4.5</td>
<td>15.2</td>
<td>0</td>
<td>10.1</td>
<td>69.7</td>
</tr>
<tr>
<td>H₃[PMO₁₂O₄₉] on Cs₃PMO₁₂O₄₀ *</td>
<td>35</td>
<td>4.1</td>
<td>11.8</td>
<td>2.9</td>
<td>0.2</td>
<td>17.4</td>
<td>67.5</td>
</tr>
<tr>
<td>H(VO)[PMO₁₀O₄₀] on Cs₃PMO₁₀O₄₀ *</td>
<td>27</td>
<td>7.8</td>
<td>28.4</td>
<td>3.5</td>
<td>0.4</td>
<td>23.3</td>
<td>48.9</td>
</tr>
<tr>
<td>H₃(VO)₂[PMO₁₀O₄₀] on Cs₃PMO₁₀O₄₀</td>
<td>33</td>
<td>9.2</td>
<td>28.4</td>
<td>1.6</td>
<td>0.2</td>
<td>21.5</td>
<td>48.1</td>
</tr>
</tbody>
</table>

Propane is oxidized in a stream of propane (55ml/min) and air (28 ml/min) for 24 hours at 350°C. After this time, the flows are changed to propane (3.2 ml/min), air (16 ml/min) and nitrogen (9.6 ml/min), and propane is oxidized at 370°C. **[After this time, the flows are changed to propane (1.76 ml/min), air (15.8 ml/min) and nitrogen (9.6 ml/min), and propane is oxidized at 375°C.]** After a 2 hour equilibration period, gases and liquids are collected and analyzed at 4 hour intervals.

AA = Acrylic Acid; C₃⁻ Propylene; ACR = Acrolein; CO₄ = CO₂ + CO

The molecular formula as determined prior to drying at elevated temperatures, impregnation on the support, and calcination.
What is claimed is:

1. A composition of matter comprising at least one heteropolyacid having the formula

$$H_{(\nu \cdot \delta \gamma)}G_{0}(X_{2}M_{m}M'_{x}M''_{n}O_{y})^{x}$$
on a support comprising at least one polyoxometallate having the formula

$$C_{2}H_{(\alpha \cdot \beta \gamma)}(X_{k}M_{m}M'_{x}M''_{n}O_{y})^{y},$$

where

(a) in the formula of said heteropolyacid, cation $G$ is $Cu^{++}$, $Fe^{+++}$, Co, Mn, Ni, La, Li, Na, K or Rb, or an oxy ion of Ti, V, Cr, Mo, U, As, Bi, Sb, Nb, or ammonium, tetraalkylammonium, pyridinium, quinolinium, protonated aromatic amines or protonated aliphatic amines, or combinations thereof; or is absent; $X$ is a Group IIIB, IVB, VB, VIIIB or transition metal; M is molybdenum or tungsten, or combinations thereof; $M'$ is vanadium; $M''$ is independently zinc or a transition metal different from $M$ and $M'$, or combination thereof; $z'$ is the charge on said cation $G$; $m'$ is 12 to 18, $x'$ is 0 to 6, $n'$ is 0 to 3 where $m' + x' + n' = 18$, and $y'$ is 48 to 62; and

(b) in the formula of said support, cation $C$ is selected from the group consisting of potassium, rubidium, cesium, magnesium, calcium, strontium, barium, vanadium, chromium, lanthanum, manganese, iron, cobalt, ruthenium, copper, actinide metal, lanthanide metal, metal oxy ion, ammonium, tetraalkylammonium, pyridinium,
quinolinium, protonated aromatic amines and protonated aliphatic amines, or combinations thereof. X is a Group IIIB, IVB, VB, VIB or transition metal; M is molybdenum or tungsten or combinations thereof; M' is vanadium; M'' is independently zinc or a transition metal different from M and M', or combination thereof; z is the charge on said cation C; k is 1 to 5, m is 5 to 18, x is 0 to 6, n is 0 to 3 and y is 18 to 62; and said support is a porous material with pores, which material has pore volumes in the range from 0.01 to 0.25 ml/g and a pore size distribution in which more than approximately 60% of said pores have a pore radius of greater than or equal to approximately 75 Å.

2. The composition of Claim 1 wherein said cation of said heteropolyacid comprises oxy ion of vanadium.

3. The composition of Claim 1 wherein said heteropolyacid comprises
   \[ H_2(\text{VO})_2(P_2\text{Mo}_{18}O_{62}) \] or \[ H_4(P_2\text{Mo}_{18}O_{62}) \] or combination thereof

4. The composition of Claim 3 wherein said heteropolyacid comprises
   \[ H_2(\text{VO})_2(P_2\text{Mo}_{18}O_{62}) \] and said support comprises \( \text{Cs}_3(\text{PMo}_{12}O_{40}) \).
5. The composition of Claim 3 wherein said heteropolyacid comprises
   \( H_4(VO)(P_2Mo_{18}O_{62}). \)

6. The composition of Claim 3 wherein said heteropolyacid comprises
   \( H_2(VO)_2(P_2W_{12}Mo_3O_{62}) \) and said support comprises \( Cs_5(PMo_{12}O_{40}). \)

7. The composition of Claim 3 wherein said heteropolyacid comprises
   \( H_2(VO)_2(P_2W_{12}Mo_2VO_{40}) \) and said support comprises \( Cs_5(PMo_{12}O_{40}). \)

8. The composition of Claim 3 wherein said heteropolyacid comprises
   \( H_2(VO)_2(P_2Mo_{18}O_{62}) \) and said support comprises \( Cs_6(P_2Mo_{18}O_{62}). \)

9. The composition of Claim 3 wherein said heteropolyacid comprises
   \( H_4(P_2Mo_{18}O_{62}) \) and said support comprises \( Cs_6(P_2Mo_{18}O_{62}). \)

10. The composition of Claim 1 wherein said cation of said support
    composes potassium, rubidium, cesium, magnesium, calcium, strontium,
    barium, lanthanum, ammonium, tetraalkylammonium, pyridium,
    quinolinium, protonated aromatic amines and protonated aliphatic
    amines, or combinations thereof.

11. The composition of Claim 1 wherein said support comprises
    \( Cs_6(P_2Mo_{18}O_{62}). \)
12. The composition of Claim 1 comprising a heteropolyacid having the
formula \( \text{H}_2(\text{VO})_2(\text{P}_2\text{Mo}_{18}\text{O}_{62}) \) and a polyoxometallate support comprising
\( \text{Cs}_3(\text{PMo}_{12}\text{O}_{40}) \) and \( \text{K}_6(\text{P}_2\text{W}_{18}\text{O}_{62}) \).

13. A process for the conversion of alkanes to unsaturated carboxylic acids
comprising contacting said alkanes with an oxidizing agent in the
presence of a catalyst comprising a heteropolyacid having the formula
\( \text{H}_{(\text{c}-\text{bz})}\text{G}_{\text{e}}(\text{X}_2\text{M}_\text{m}\text{M}'_\text{x}\text{M}''_\text{y}\text{O}_\text{z}) \)^{\text{e}} \) on a support comprising at least one
polyoxometallate having the formula \( \text{C}_\text{a}\text{H}_{(\text{c}-\text{ad})}(\text{X}_\text{n}'\text{M}_\text{m}'\text{M}'_\text{x}\text{M}''_\text{y}\text{O}_\text{z}) \)^{\text{e}} \), where
in the formula of said heteropolyacid, cation \( \text{G} \) is \( \text{Cu}^{++} \),
Fe\(^{+++}\), Co, Mn, Ni, La, Li, Na, K or Rb, or an oxy ion of
Ti, V, Cr, Mo, U, As, Bi, Sb, Nb, or ammonium,
tetraalkylammonium, pyridinium, quinolinium, protonated
aromatic amines or protonated aliphatic amines, or
combinations thereof, or is absent; \( \text{X} \) is a Group IIIB,
IVB, VB, VIB or transition metal; \( \text{M} \) is molybdenum or
tungsten, or combinations thereof, \( \text{M}' \) is vanadium; \( \text{M}'' \) is
independently zinc or a transition metal different from \( \text{M} 
\text{and M}', or combination thereof, \( \text{z}' \) is the charge on said
cation \( \text{G} \); \( \text{m}' \) is 12 to 18, \( \text{x}' \) is 0 to 6, \( \text{n}' \) is 0 to 3 where \( \text{m}' + \text{x}' + \text{n}' = 18 \), and \( \text{y}' \) is 48 to 62; and
in the formula of said support, cation \( \text{C} \) is selected from
the group consisting of potassium, rubidium, cesium,
magnesium, calcium, strontium, barium, vanadium, chromium, lanthanum, manganese, iron, cobalt, ruthenium, copper, actinide metal, lanthanide metal, metal oxy ion, ammonium, tetraalkylammonium, pyridinium, quinolinium, protonated aromatic amines and protonated aliphatic amines, or combinations thereof, X is a Group IIIB, IVB, VB, VIB or transition metal; M is molybdenum or tungsten or combinations thereof; M' is vanadium; M'' is independently zinc or a transition metal different from M and M', or combination thereof; z is the charge on said cation C; k is 1 to 5, m is 5 to 18, x is 0 to 6, n is 0 to 3 and y is 18 to 62; and said support is a porous material with pores, which material has pore volumes in the range from 0.01 to 0.25 ml/g and a pore size distribution in which more than approximately 60% of said pores have a pore radius of greater than or equal to approximately 75Å.

14. The process of Claim 13 wherein said cation of said heteropolyacid comprises oxy ion of vanadium.

15. The process of Claim 13 wherein said heteropolyacid comprises $\text{H}_x(\text{VO})_y(\text{P}_2\text{Mo}_{13}\text{O}_{62})$ or $\text{H}_z(\text{P}_2\text{Mo}_{12}\text{O}_{62})$ or combination thereof.
16. The process of Claim 15 wherein said heteropolyacid comprises
\[ H_2(VO)_2(P_2Mo_{18}O_{62}) \] and said support comprises \( Cs_5(\text{PMo}_{12}O_{40}) \).

17. The process of Claim 15 wherein said heteropolyacid comprises
\[ H_4(VO)(P_2Mo_{18}O_{62}) \] and said support comprises \( Cs_3(\text{PMo}_{12}O_{40}) \).

18. The process of Claim 15 wherein said heteropolyacid
\[ H_2(VO)_2(P_2W_{15}Mo_{5}O_{62}) \] and said support comprises \( Cs_3(\text{PMo}_{12}O_{40}) \).

19. The process of Claim 15 wherein said heteropolyacid comprises
\[ H_2(VO)_2(P_2W_{15}Mo_{5}VO_{40}) \] and said support comprises \( Cs_3(\text{PMo}_{12}O_{40}) \).

20. The process of Claim 15 wherein heteropolyacid comprises
\[ H_2(VO)_2(P_2Mo_{18}O_{62}) \] and said support comprises \( Cs_6(\text{P}_2\text{Mo}_{18}O_{62}) \).

21. The process of Claim 15 wherein said heteropolyacid comprises
\[ H_6(P_2Mo_{18}O_{62}) \] and said support comprises \( Cs_6(\text{P}_2\text{Mo}_{18}O_{62}) \).

22. The process of Claim 13 wherein said cation of said support comprises potassium, rubidium, cesium, magnesium, calcium, strontium, barium, lanthanum, ammonium, tetraalkylammonium, pyridinium, quinolinium, protonated aromatic amines and protonated aliphatic amines, or combinations thereof.
23. The process of Claim 13 wherein said support comprises 
   $\text{Cs}_6(\text{P}_2\text{Mo}_{18}\text{O}_{62})$.

24. The process of Claim 13 wherein said catalyst comprises a 
heteropolyacid having the formula $\text{H}_2(\text{VO})_2(\text{P}_2\text{Mo}_{18}\text{O}_{62})$ and a 
   polyoxometallate support comprising $\text{Cs}_3(\text{PMo}_{12}\text{O}_{40})$ and $\text{K}_6(\text{P}_2\text{W}_{18}\text{O}_{62})$.

25. The process of Claim 13 wherein said conversion is carried out at a 
temperature in the range from 225°C to 450°C.

26. The process of Claim 25 wherein said temperature is in the range from 
   350°C to 400°C.

27. The process of Claim 13 wherein said conversion is carried out in vapor 
   phase.

28. The process of Claim 13 wherein said alkanes are selected from the 
group consisting of alkanes comprising four to seven carbon atoms.

29. The process of Claim 28 wherein said alkanes comprise propane or 
isobutane.
FIGURE 2

H4[PMo11VO40], 30% on Cs-Keggin

HxCu.1As.1[PMo11VO40], 30% on Cs-Keggin

H(VO)[PMo12O40], 30% on Cs-Keggin

H2(VO)2[P2Mo18O62], 30% on Cs-Keggin

H2(VO)2[P2Mo18O62], 23%+K6[P2W18O62], 7% on Cs-KA

H2(VO)2[P2Mo18O62], 30% on Cs-Dawson
### A. CLASSIFICATION OF SUBJECT MATTER
IPC 7  B01J27/188  C07C51/215

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)

### C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>A</td>
<td>EP 0 757 027 A (BP CHEM INT LTD) 5 February 1997 (1997-02-05) claims 1,4-16 page 2, line 31 -page 3, line 41</td>
<td>1, 3, 9-12</td>
</tr>
<tr>
<td>A</td>
<td>EP 0 063 956 A (ATLANTIC RICHFIELD CO) 3 November 1982 (1982-11-03) the whole document</td>
<td>1, 3, 9</td>
</tr>
<tr>
<td>A</td>
<td>WO 96 12695 A (DU PONT) 2 May 1996 (1996-05-02)</td>
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</tr>
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* Further documents are listed in the continuation of box C.

© Patent family members are listed in annex.

* Special categories of cited documents:
  - "A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search
19 November 1999

Date of mailing of the international search report
08.12.99

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk
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Authorized officer
Zuurdeeg, B

Form PCT/ISA/210 (second sheet) (July 1990)
INTERNATIONAL SEARCH REPORT

Box I  Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.: because they relate to subject matter not required to be searched by this Authority, namely:

2. ☑ Claims Nos.: because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
   see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.: because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II  Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest
☐ The additional search fees were accompanied by the applicant's protest.
☐ No protest accompanied the payment of additional search fees.
Continuation of Box 1.2

Present claims 1-29 relate to an extremely large number of possible compounds and use thereof in a conversion process of alkanes into carboxylic acids. Support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT is to be found, however, for only a very small proportion of the compounds claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be supported and disclosed, namely those parts relating to the compounds mentioned in claims 3-9, 12, 15-21 and 24, and closely related homologous compounds.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.
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<th>Publication date</th>
<th>Patent family member(s)</th>
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<tr>
<td>US 4192951 A</td>
<td>11-03-1980</td>
<td>NONE</td>
<td></td>
</tr>
<tr>
<td>EP 0757027 A</td>
<td>05-02-1997</td>
<td>CA 2182558 A</td>
<td>03-02-1997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CN 1150585 A</td>
<td>28-05-1997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 9118647 A</td>
<td>06-05-1997</td>
</tr>
<tr>
<td></td>
<td></td>
<td>SG 49973 A</td>
<td>15-06-1998</td>
</tr>
<tr>
<td></td>
<td></td>
<td>US 5861530 A</td>
<td>19-01-1999</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CA 1208238 A</td>
<td>22-07-1986</td>
</tr>
<tr>
<td></td>
<td></td>
<td>JP 57209248 A</td>
<td>22-12-1982</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EP 0787118 A</td>
<td>06-08-1997</td>
</tr>
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