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(54) CATALYST FOR LIQUID-PHASE OXIDATION OF OLEFINS AND A METHOD OF PREPARING SAME

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KAUCHUKA, both Russian corporate bodies, of Novosibirsk, prospekt Nauki, 5,
USSR and Omsk, USSR, respectively, do hereby declare the invention, for which we
pray that a patent may be granted to us, and the method by which it is to be performed,
to be particularly described in and by the following statement:—

This invention relates to a catalyst for the liquid-phase oxidation of olefins, to a
method of preparing the catalyst, and to a process for the liquid-phase oxidation of
olefins using the catalyst.

Among the principal products of the oxidation of olefins are carbonyl compounds
which have many industrial uses. Thus, acetaldehyde is used for producing butanol,
acetic acid and oil-resistant rubbers, while methyl ethyl ketone is an excellent de-
paraffinizing agent for lubricating oils, and acetone is one of the most widely used
organic solvents.

Catalysts have been proposed for the heterogenous oxidation of olefins to the
corresponding aldehydes, for example, supported PdO, metallic Pd supported on
alumina or a supported contact agent as disclosed in British Specification 1,025,679,
which contact agent comprises molybdenum trioxide or a hetero-polyacid (or a salt
thereof) and metallic Pd or Pt (or a salt thereof). Such heterogeneous oxidation
necessarily involves the use of explosive mixtures of ethylene and oxygen.

This danger can only be avoided by carrying out the oxidation in the liquid phase
using a catalyst containing a reversible oxidant. Such catalysts include those known
as Wacker-type catalysts (because they were developed in the 1950's by Wacker Co.),
which comprise, for example, aqueous solutions of palladium chloride, an alkali metal
chloride and, as reversible oxidant, copper chloride.

Wacker-type catalysts have the serious disadvantages that the presence therein of
chloride ions gives rise to corrosion of the plant (necessitating the use of expensive
titanium plant) and undesirable side-reactions involving the formation of chloro-
organic compounds, which are difficult to separate from the desired product and difficult
to dispose of. The chlorinating ability of Wacker-type catalysts increases rapidly with
increasing chain length of the olefin, as follows:

Olefin:	ethylene	propylene	n-butenes
Percentage of chloro-organic compounds:	2	7	25

Because of this, oxidation of higher olefins (beginning from C₃) using a Wacker-type catalyst has proved to be uneconomical and, indeed, such catalysts are not even used for the oxidation of propylene to acetone and of n-butenes to methyl ethyl ketone.

5 It has been proposed to decrease the concentration of chloride ions in the catalyst by the use of zinc and cadmium chlorides or cadmium chloride alone, whereby the cadmium ions and, when present, zinc ions, form strong complexes with chloride ions and so decrease the concentration of free chloride ions. However, the catalyst solution is still highly corrosive. 5

10 Studies in the kinetics and ethylene oxidation mechanism on a Wacker-type catalyst have made it clear that the overall process comprises three inter-related reactions: 10



In the absence of chloride ions, the redox potential of the system Pd²⁺/Pd⁰ is too high, being from 0.6 to 0.987 volt, while that of the system Cu²⁺/Cu⁺ is too low, i.e. 0.153 volt. That is why reaction (2) and, hence, the entire catalytic process, are thermodynamically impossible in solutions free from chloride ions. In other words, bivalent copper cannot serve as an oxidant of Pd⁰ if no chloride ions are present. 20

Therefore, elimination of chloride ions from the catalyst necessitates a simultaneous replacement of bivalent copper as the oxidant in reaction (2). What is required is a reversibly acting oxidant capable of reacting in the absence of chloride ions in the following reactions:



(Ox and Red are abbreviations for an oxidant and its reduced form, respectively.)

It is suggested in the above-mentioned British Specification 1,025,679 that a contact agent comprising molybdenum trioxide or a hetero-polyacid (or a salt thereof) and metallic Pd or Pt (or a salt thereof) can be used as a homogeneous catalyst for the liquid-phase oxidation of olefins. In such a catalyst, the molybdenum oxide or hetero-polyacid would apparently function as the reversibly acting oxidant indicated in the above reactions (4) and (5). 30

We have now found that only certain hetero-polyacids (and certain mixed iso-polyacids as defined herein) function satisfactorily as reversibly acting oxidants in the above reaction. Such hetero-polyacids and mixed iso-polyacids have a redox potential in excess of 0.5 volt and contain both molybdenum and vanadium. We have also found that the activity and stability of catalysts comprising an aqueous solution of a palladium compound and a hetero-polyacid or a mixed iso-polyacid as mentioned above are enhanced without making the solution more corrosive by the addition of certain acids to the solution. 35

Accordingly, in one aspect the invention provides a catalyst for the liquid-phase oxidation of olefins, which comprises an aqueous solution of a palladium compound, a reversible oxidant which has a redox potential in excess of 0.5 volt and which is a mixed iso-polyacid (as defined herein) or a hetero-polyacid containing both molybdenum and vanadium, or a salt of the polyacid, and an organic or inorganic acid other than the mixed iso-polyacid or hetero-polyacid, which acid is free of halide ions and is unreactive or at most weakly reactive with the palladium compound. 40

The expression "mixed iso-polyacid" is defined herein as an iso-polymolybdate in which one or more of the molybdenum atoms are replaced by vanadium or an iso-polyvanadate in which one or more of the vanadium atoms are replaced by molybdenum. 45

Mixed iso-polyacids do not contain a central hetero-atom having vanadate and molybdate groups arranged around the heteroatom. 50

The polyacid used contains vanadium atoms, for example from 1 to 8, more preferably 6 atoms, in a molecule, and molybdenum. As the number of vanadium atoms 55

in the polyacid increases, for example from 1 to 6, the principal characteristics of the catalyst, such as its activity, stability and olefin capacity, increase. Further increases in the vanadium content in the catalyst likewise increase the activity and capacity of the latter but make it thermally less stable.

Typical polyacids for use in the present invention are represented by the following general formula:



in which

X is B, Si, Ge, P, As, Se, He or I;

M is W, Nb, Ta or Re;

m , a , b and z are integers;

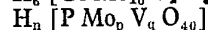
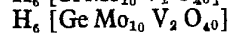
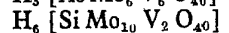
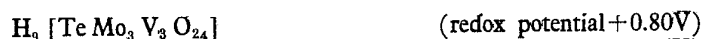
x is zero (for mixed isopolyacids or an integer (for hetero-polyacids);

and y is zero or an integer such that

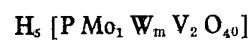
$$6 < \frac{y+a+b}{z} < 12$$

and $m + Nx + 6a + 5b + N'y < 2z$;

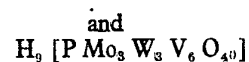
in which N and N' is each the number of the group of the periodic table to which X and M respectively belong. Examples of typical heteropolyacids are as follows:



in which $n=3+q$, $p=12-q$,
 $q=1$ to 10 ; the redox
potentials of these
polyacids are given
hereinafter.



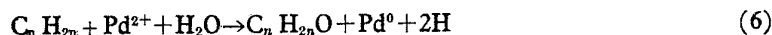
in which $m=2, 4, 6$ or 8 and
 $1=10-m$.



(redox potential +0.70V)

Hereinafter, the terms mixed iso-polyacid and hetero-polyacid will both be denoted as HPA.

The action of the catalysts of the invention can be represented by the following scheme:



Two stages can be distinguished in the catalyst operation: stage I consists in oxidation of an olefin with palladium to a carbonyl compound (6), whereupon HPA oxidizes the reduced palladium (Pd⁰) to regenerate Pd²⁺ for the initial state (7). Stage I will hereinafter be called the olefinic reaction. Stage II consists in oxidation of the reduced HPA (H₂HPA) with oxygen, accompanied by regeneration of the initial HPA (8). This stage will hereinafter be called the oxygen reaction. When in combination, stages I and II give catalytic oxidation of olefins with oxygen (9). A once-through olefinic and oxygen reaction will hereinafter be called a cycle.

The catalysts of the invention have advantages over the Wacker-type catalyst. The catalysts of the invention are more active, up to 30 to 100 times more active, in the olefin oxidation, while the activity in the reaction with atmospheric oxygen is of the same order as in the Wacker-type catalyst. The catalysts of the invention are highly selective towards the formation of carbonyl compounds:

Olefin:	ethylene	propylene	n-butenes
Main product:	acetaldehyde	acetone	methyl ethyl ketone
Yield of product, percent:	97	95	98

- 5 It is especially notable that the reaction products are completely free from those chloro-organic derivatives which are separable only with great difficulty from carbonyl compounds. 5
- 10 The capacity of the catalysts of the invention is about double that of the Wacker-type catalyst (the catalyst capacity being the maximum number of mols of olefin oxidizable by 1 litre of the catalyst solution without O₂ that does not provoke irreversible changes in the catalyst properties). The catalyst throughput rate expressed, say, in grams of CH₃CHO/litre per hour, is twice as high as for the known catalyst. 10
- 15 The catalysts of the invention are much less corrosive than the Wacker-type catalyst. 15
- 20 The redox potential of HPA in the catalysts of the invention must be in excess of 0.5 volt. If HPA of a lower redox potential is used, the catalyst is unstable, has a low activity and possesses only a low capacity with respect to the olefin. An increase in the redox potential makes the catalyst more stable and active both in the olefinic and oxygen reactions, and also adds to its capacity. 20
- 25 The palladium concentration in the catalyst can vary widely, but it is desirable to keep it within 10⁻⁶ to 0.5 g-atom/litre, preferably at about 2 × 10⁻³ g-atom/litre. With lower Pd concentrations, the rate of the olefinic reaction is too low, whereas with higher Pd concentrations the reaction is so accelerated that the process is diffusion controlled, so that high palladium concentrations are not desirable. 25
- 30 The concentration of HPA may also be varied within a broad range but it is best to maintain the concentration within 10⁻³ to 1.0 g-mole/litre, preferably at about 0.2 g-mole/litre. With lower HPA concentrations, the catalyst is of low activity and has low capacity, while with higher HPA concentrations, the specific gravity and viscosity of the catalyst are greatly increased, which adversely affects mass-transfer in the catalyst solution and involves the extra expense of providing stirring. 30
- 35 One example of a catalyst of the invention is that consisting of PdCl₂, phospho-6-molybdo-6-vanadic acid (H₃[PMo₆V₆O₄₀]), and an acid as set forth above. The specific gravity of this catalyst at 90° C. is 1.485; its viscosity is 1.775; its surface tension is 1.0; its boiling point is +103° C.; and its freezing point is -4° C. 35
- 40 According to the invention, the activity and stability of the catalyst is increased by doping it with a mineral or organic acid (e.g. H₂SO₄, HNO₃, H₃PO₄ or CH₃COOH), which acid does not react, or only reacts feebly, with palladium and which acid contains no halide ions. The most preferable of the above acids is sulphuric acid, which increases the activity and stability of the catalyst whilst not seriously increasing the corrosivity of the solution. The amount of acid is such as to maintain the pH of the solution at not more than 3, preferably at 1.0. Up to 2 percent of the acid is generally used. With higher pH values, the catalyst is not sufficiently stable against hydrolysis and palladium precipitation, and is of low activity in the olefinic reaction. At lower pH values, the rate of the oxygen reaction is appreciably diminished. 40
- 45 To reduce the corrosivity of the catalyst solution, a corrosion inhibitor which does not react, or reacts only weakly, with palladium and HPA, may be included in the catalyst. The inhibitor must not reduce the activity and stability of the catalyst. One suitable inhibitor is polyethylsiloxane, added in a concentration of 0.06 to 0.30 weight percent of the catalyst solution. Lower concentrations of the inhibitor may not be enough to suppress corrosion, while with a concentration of 0.30 weight percent practically no corrosion is encountered. 45
- 50 The invention also provides a method of preparing a catalyst for the liquid-phase oxidation of olefins, which comprises introducing palladium, in the form of a salt, a complex or the metal (preferably in an amount sufficient to provide a concentration in the solution of from 10⁻⁶ to 0.5 g-atom/litre) into an aqueous solution of a heteropolyacid or mixed iso-polyacid or a salt thereof, which polyacid has a redox potential in excess of 0.5 volt and contains both molybdenum and vanadium, said solution having been prepared by dissolving in water at 50 to 100°C oxides, salts and/or acids of the elements forming the polyacid, in a ratio corresponding or close to the stoichiometric composition of the polyacid (the oxides, salts or acids preferably being used in an amount sufficient to provide a concentration of the polyacid in the solution of from 10⁻³ to 1.0 g-mole/litre) and adding to the solution an organic or mineral acid as specified above. 50
- 55 55
- 60 60

A preferred catalyst is prepared by dissolving in water Na_3PO_4 , MoO_3 , V_2O_5 and Na_2CO_3 to form a solution, adding PdCl_2 to the solution of molybdovanadophosphoric acid, and then adding the acid. It should be noted that Na_3PO_4 can be replaced by Na_2HPO_4 , or NaH_2PO_4 , or H_3PO_4 , or P_2O_5 . MoO_3 can be replaced by Na_2MoO_4 , or H_2MoO_4 ; V_2O_5 can be replaced by NaVO_3 ; and Na_2CO_3 , by NaOH , for example. In all cases, such replacement should be effected in equiatomic quantities, according to the number of gram-atoms of P, Mo and V. It is best that the total number of Na atoms per atom of P be not in excess of 7 or 8 and not less than 6. The atomic ratio of P, Mo and V is governed by the composition of the HPA being synthesized. Thus, to obtain a heteropolyacid in the series $\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$ — $\text{H}_{11}[\text{PMo}_4\text{V}_8\text{O}_{40}]$ use is made of the following atomic ratios of heteroatoms:

HPA	Radox Potential (volts)	P	Mo	V	Excess V_2O_5 , percent of theory
$\text{H}_4[\text{PMo}_{11}\text{VO}_{40}]$	+0.65	I	II	I	—
$\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]$	+0.70	I	10	2.1	5
$\text{H}_6[\text{PMo}_9\text{V}_3\text{O}_{40}]$	+0.72	I	9	3.3	10
$\text{H}_7[\text{PMo}_8\text{V}_4\text{O}_{40}]$	+0.75	I	8	4.6	15
$\text{H}_8[\text{PMo}_7\text{V}_5\text{O}_{40}]$	+0.76	I	7	6.0	20
$\text{H}_9[\text{PMo}_6\text{V}_6\text{O}_{40}]$	+0.77	I	6	7.5	25
$\text{H}_{10}[\text{PMo}_5\text{V}_7\text{O}_{40}]$	+0.79	I	5	9.1	30
$\text{H}_{11}[\text{PMo}_4\text{V}_8\text{O}_{40}]$	+0.80	I	4	10.8	35

Synthesis of the HPA consists in dissolving a mixture of components in water at 50 to 100°C.

In preparing the catalyst, there is no need to produce crystalline HPA for example by ether extraction. Aqueous solutions of the components of HPA can be used.

The invention also includes a process for the liquid-phase oxidation of olefins wherein there is used a catalyst of the invention.

In order that the invention may be more fully understood, the following Examples are given by way of illustration only.

Example 1.

A catalyst containing PdCl_2 and phospho-6-molybdo-6-vanadic HPA $\text{H}_9[\text{PMo}_6\text{V}_6\text{O}_{40}]$ was used in an ethylene oxidation process.

To prepare the catalyst the following components were taken: 11.4 g $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (0.03 g-mole); 25.9 g MoO_3 (0.18 g-mole); 20.5 g V_2O_5 (0.226 g-atom V); 13.0 g $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$; the components were dissolved in 150 ml of water with vigorous stirring and boiled for 40 minutes. In the course of the reaction all the components dissolved, to form an intense brownish-red solution. Then the solution was evaporated down to 100 ml and cooled down to room temperature, the pH of the solution adjusted to 1.0 by adding 10 to 15N H_2SO_4 and the solution boiled for another 20 minutes and twice filtered while hot. Thereupon 35 mg PdCl_2 were poured into the solution and the latter was boiled for 20 to 30 minutes, while maintaining the volume thereof at 100 ml. The thus prepared catalyst contained $[\text{H}_9[\text{PMo}_6\text{V}_6\text{O}_{40}]]$ in an amount of 0.3 g-mole/litre and $[\text{Pd}]$ in an amount of 2.10^{-3} g-atom/litre.

50 ml of the prepared catalyst solution was tested for activity, capacity, stability and selectivity in ethylene oxidation. Tests were carried out in a completely temperature-controlled circulation-static installation with a shaking glass reactor, ensuring elimination of acetaldehyde thus formed from the gaseous phase. The solution reacted alternately with ethylene and oxygen. The rate of the ethylene and oxygen reactions was

determined by the rate of absorption of C_2H_4 and O_2 by the catalyst solution, respectively. Use was made of pure ethylene (99.8 percent) and oxygen (99 percent). The catalyst stability was assessed according to any change in its activity and composition, with cycles repeatedly run on the same catalyst specimen. 50 ml of the catalyst solution thus prepared were tested in an ethylene oxidation process at $90^\circ C$ under partial ethylene and oxygen pressure of 230 mm Hg for 30 cycles. The catalyst acted stably at an average rate of ethylene reaction (hereinafter abbreviated as $W_{C_2H_4}$) of 143 ml/litre per minute (ml at $P = 750$ mm Hg and $23^\circ C$), at an average rate of oxygen reaction (hereinafter abbreviated as W_{O_2}) of 115 ml/litre per minute (ml at $P = 750$ mm Hg and $23^\circ C$ and a capacity with respect to ethylene of 0.6 mole C_2H_4 /litre. The yield of acetaldehyde was 97 percent for the reacted ethylene. 2.4 percent of ethylene was converted into acetic acid and 0.6 percent, into non-volatile organic substances.

Example 2.

A catalyst containing $PdCl_2$ and phospho-4-molybdo-8-vanadic acid $H_{11}[PMo_4V_8O_{40}]$ was used in an ethylene oxidation process.

The catalyst production process was as described in Example 1, the ingredients being as follows: $Na_3PO_4 \cdot 12H_2O$, 11.4 g; MoO_3 , 17.3 g; V_2O_5 , 29.5 g; $Na_2CO_3 \cdot 10H_2O$, 13.0 g. To the resultant solution was added $PdCl_2$, as in Example 1, to give a solution having the same concentrations of Pd and HPA and pH as in Example 1.

50 ml of the thus-prepared catalyst solution, which contained $H_{11}[PMo_4V_8O_{40}]$ in an amount of 0.3 g-mole/litre and [Pd] in an amount of 2.10^{-3} g-atom/litre; and had a $pH = 1.0$, were tested in an ethylene oxidation process, following the test procedure of Example 1 for 10 cycles. The catalyst acted stably at $W_{C_2H_4} = 248$ ml/litre per minute and had a capacity of 0.8 mole C_2H_4 /litre. The yield of acetaldehyde was 96 percent for the reacted ethylene. Further operation of the catalyst resulted in hydrolytic decomposition of $H_{11}[PMo_4V_8O_{40}]$ with gradual formation of a precipitate of VO_2 . The catalyst was applicable for processes at temperatures of up to $80^\circ C$.

Example 3.

A catalyst containing $PdSO_4$ and phospho-8-molybdo-4-vanadic acid $H_7[PMo_8V_4O_{40}]$ was used in an ethylene oxidation process.

The catalyst production process was as described in Example 1, the ingredients being as follows: $Na_3PO_4 \cdot 12H_2O$, 11.4 g; MoO_3 , 34.5 g; V_2O_5 , 12.6 g; $Na_2CO_3 \cdot 10H_2O$, 13.0 g; $PdSO_4$, 40 mg. The thus-obtained solution had the same concentration of HPA and pH as in Example 1.

50 ml of the thus-prepared solution which contained $H_7[PMo_8V_4O_{40}]$ in an amount of 0.3 g-mole/litre and [Pd] in an amount of 2.10^{-3} g-atom/litre and which had a $pH = 1.0$ were tested in an ethylene oxidation process according to the test procedure of Example 1 for 10 cycles. The catalyst acted stably at $W_{C_2H_4} = 128$ ml/litre per minute, $W_{O_2} = 105$ ml/litre per minute and a capacity of 0.36 mole C_2H_4 /litre. The yield of acetaldehyde was 98 percent for the reacted ethylene.

Example 4.

A catalyst containing $PdCl_2$ and $H_6[PMo_4V_3O_{40}]$ was used in an ethylene oxidation process.

The catalyst production process was as described in Example 1, the ingredients being as follows: $Na_3PO_4 \cdot 12H_2O$, 11.4 g; MoO_3 , 38.9 g; V_2O_5 , 9.1 g; $Na_2CO_3 \cdot 10H_2O$, 13.0 g. The concentration of Pd and HPA and pH of the solution were as in Example 1.

50 ml of the thus-prepared catalyst solution which had the following composition: $H_6[PMo_4V_3O_{40}] = 0.3$ g-mole/litre, [Pd] = 2.10^{-3} , $pH = 1.0$ were tested in oxidation of ethylene as described in Example 1 for 10 cycles. The catalyst acted stably at $W_{C_2H_4} = 120$ ml/litre per minute, $W_{O_2} = 70$ ml/litre per minute and a capacity of 0.25 mole C_2H_4 /litre. The yield of acetaldehyde was 98 percent for the reacted ethylene.

Example 5.

A catalyst containing $PdCl_2$ and $H_5[PMo_{10}V_2O_{40}]$ was used in an ethylene oxidation process.

The catalyst production was as described in Example 1, the ingredients being as follows: $Na_3PO_4 \cdot 12H_2O$, 11.4 g; MoO_3 , 43.2 g; V_2O_5 , 5.7 g; $Na_2CO_3 \cdot 10H_2O$,

13.0 g. Palladium was introduced as PdSO_4 , as in Example 3. The concentration of Pd, HPA and pH of the solution were as in Example 1.

50 ml of the thus-obtained solution, which contained $[\text{H}_5[\text{PMo}_{10}\text{V}_2\text{O}_{40}]]$ in an amount of 0.3 g-mole/litre, and $[\text{Pd}]$ in an amount of 2.10^{-3} g-atom/litre and had a pH=1.0 were tested in an ethylene oxidation process as described in Example 1 for 30 cycles. The catalyst acted stably at $\bar{W}_{\text{C}_2\text{H}_4}=210$ ml/litre per minute, $\bar{W}_{\text{O}_2}=50$ ml/litre per minute and a capacity of 0.15 mole C_2H_4 /litre. The yield of acetaldehyde was 98 percent for the reacted ethylene.

Example 6.

A catalyst containing PdCl_2 and $\text{H}_9[\text{PMo}_6\text{V}_6\text{O}_{40}]$ was used in an ethylene oxidation process.

Weighed quantities of the following ingredients: $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 31.2 g; MoO_3 , 173.0 g; V_2O_5 , 136.3 g; NaHCO_3 , 117.6 g were dissolved in 1.5 litres of water and boiled with vigorous stirring for 40 to 60 minutes. Within this time, a homogeneous intense brownish-red solution was formed. The solution was evaporated to 1.0 litre and cooled to room temperature, while its pH was adjusted to 1.0 by adding 50% by weight H_2SO_4 , whereupon the solution was boiled for another 30 minutes and twice filtered while hot. The resulting solution of HPA of composition $[\text{H}_9[\text{PMo}_6\text{V}_6\text{O}_{40}]]$ had a concentration of 0.2 g-mole/litre. In an activity test of the resulting catalyst, sufficient PdCl_2 was introduced that the concentration of palladium was 2.10^{-3} g-atom/litre.

50 ml of the thus-prepared catalyst solution, which contained $[\text{H}_9[\text{PMo}_6\text{V}_6\text{O}_{40}]]$ in an amount of 0.2 g-mole/litre and $[\text{Pd}]$ in an amount of 2.10^{-3} g-atom/litre and which had a pH=1.0 were tested in an ethylene oxidation process as described in Example 1, for 90 cycles. The catalyst functioned stably at $\bar{W}_{\text{C}_2\text{H}_4}=190$ ml/litre per minute, $\bar{W}_{\text{O}_2}=60$ ml/litre per minute and a capacity of 0.30 mole C_2H_4 /litre. The yield of acetaldehyde was 97 percent for the reacted ethylene, while 3 percent thereof was converted into acetic acid. Addition of acetic acid (10 weight percent) did not affect $\bar{W}_{\text{C}_2\text{H}_4}$, \bar{W}_{O_2} capacity or stability of the catalyst.

400 ml of the solution of the above catalyst were tested for 150 cycles in ethylene oxidation process at 110°C and a partial ethylene and oxygen pressure of 6 atm and 3.5 atm, respectively. The tests were performed in a temperature-controlled reaction vessel made of stainless steel. Acetaldehyde, accumulated in the solution in the course of ethylene reaction and was removed therefrom after the reaction was terminated. The reaction rate was determined from the pressure drop in the system with time. The catalyst functioned stably at $\bar{W}_{\text{C}_2\text{H}_4}=900$ ml/litre per minute, $\bar{W}_{\text{O}_2}=450$ ml/litre per minute (ml at $P=750$ mm Hg and 23°C) and a capacity of 0.3 mole C_2H_4 /litre. The yield of acetaldehyde under these conditions was industrially useful (about 95% based on the weight of ethylene, while about 3% of the ethylene was converted to acetic acid and the remainder into non-volatile organic substances). Chloride ions introduced into the catalyst solution (as PdCl_2) in concentrations up to 10^{-2} g-ion/litre, did not cause the formation of chloro-organic compounds.

It was established that the catalyst retained its principal characteristics (activity, capacity, selectivity, stability) after having been heated at 150°C for 20 hours.

Example 7.

A catalyst containing PdCl_2 and one of the phosphomolybdo-vanadic acids specified in the table below was used in an ethylene oxidation process.

The catalyst production process was performed as described in Example 1 except that $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ was replaced by $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, MoO_3 by H_2MoO_4 , and $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, by NaHCO_3 .

The weight of the ingredients used for the synthesis of 100 ml of HPA solution with [HPA] concentration of 0.2 mole/l are tabulated below:

HPA being synthesized	$\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$	H_2MoO_4	V_2O_5	NaHCO_3
$\text{H}_{11}[\text{PMo}_4\text{V}_8\text{O}_{40}]$	3.12	13.0	14.55	10.1
$\text{H}_{10}[\text{PMo}_5\text{V}_7\text{O}_{40}]$	3.12	16.2	12.75	10.1
$\text{H}_8[\text{PMo}_7\text{V}_5\text{O}_{40}]$	3.12	22.6	9.10	10.1
$\text{H}_7[\text{PMo}_8\text{V}_4\text{O}_{40}]$	3.12	25.9	7.26	10.1

The concentration of HPA and pH of the solution obtained were as in Example 1. For testing the catalyst the required amounts of the solution thereof were taken, into which were introduced weighed quantities of PdCl₂ or PdSO₄ such that the palladium concentration was 2.10⁻³ g-atom/litre.

5 Results of testing the catalysts containing PdCl₂ and H₁₁[PMo₄V₈O₄₀] or PdSO₄ and H₇[PMo₃V₄O₄₀] in ethylene oxidation process were identical to those employed in Examples 2 and 3. 5

Example 8.

10 A catalyst containing PdCl₂ and H₉[PMo₆V₆O₄₀] was used in an ethylene oxidation process. 10

To 100 ml of a solution of the above HPA, obtained according to Example 1, were added 5 mg of PdCl₂, whereupon the solution was diluted 300-fold. The thus-obtained catalyst solution contained [H₉[PMo₆V₆O₄₀]] in an amount of 1.10⁻³ g-mole/litre and [Pd] in an amount of 1.10⁻⁶ g-atom/litre; the pH of the solution was adjusted to 1.0 by adding 10N H₂SO₄. The solution was initially orange, but upon passing ethylene therethrough, the solution turned first green, then indigo which indicated that the ethylene oxidation reaction was proceeding, while a regenerated catalyst solution was green or indigo depending upon the degree of catalyst regeneration. The solution was found to contain acetaldehyde. When a regenerated solution was heated in air, a reaction with oxygen took place, and the solution turned orange again. Upon subsequent passing of ethylene the solution was regenerated once more and became green. With such low concentrations of Pd and HPA as stated above W_{C₂H₄} and W_{O₂} as well as the capacity of the catalyst solution were low and it is therefore desirable that the catalyst contains Pd and HPA in greater concentration. 15 20

Example 9.

25 A catalyst containing PdCl₂ and H₉[PMo₆V₆O₄₀] was used for ethylene oxidation. The catalyst was prepared as described in Example 1, the quantities of the precursors being as follows: Na₃PO₄ · 12H₂O, 38.0 g; MoO₃, 86.2 g; V₂O₅, 68.2 g; Na₂CO₃ · 10H₂O, 43.3 g. Then 8.85 g PdCl₂ were added to the resulting HPA solution which was then boiled for 30 to 40 minutes while maintaining its volume at 100 ml. The thus-obtained catalyst solution contained [H₉[PMo₆V₆O₄₀]] in an amount of 1.0 g-mole/litre; and [Pd] in an amount of 0.5 g-atom/litre. 25 30

50 ml of the thus-prepared catalyst solution were tested in an ethylene oxidation process using the procedure of Example 1 for 5 cycles. The catalyst functioned stably at W_{C₂H₄} = 300 ml/litre per minute, W_{O₂} = 210 ml/litre per minute (which values are underestimates) and a capacity of 3.0 mole C₂H₄/litre. The yield of acetaldehyde was 90 percent based on ethylene supplied. The viscosity of the catalyst solution with such a high concentration of HPA was 100 times the viscosity of water, the specific gravity thereof being 2.5. Owing to these high values of viscosity and specific gravity, the mass transfer conditions in the solution were adversely affected and the process was diffusion controlled. For the same reasons, application of catalyst solutions having high viscosity and specific gravity is uneconomical since it involves high power consumption for stirring and circulation of the reaction solution. 35 40

Example 10.

45 A catalyst derived from metallic Pd and H₉[PMo₆V₆O₄₀] was used in an ethylene oxidation process. 45

Into a solution of the HPA produced as in Example 6 (25 ml) were introduced 0.0032 g metallic Pd (which corresponds to a Pd content [Pd] of 1.10⁻³ g-atom/litre, if all the palladium is dissolved. The thus-obtained catalyst solution was tested in an ethylene oxidation process using the procedure of Example 1, W_{C₂H₄} being equal to 150 ml/litre per minute, W_{O₂} to 100 ml/litre per minute at a capacity of 0.2 mole C₂H₄/litre. The yield of acetaldehyde was 97 percent, based on the reacted ethylene. 50

Example 11.

55 A catalyst containing PdSO₄, H₉[PMo₆V₆O₄₀] and polyethylsiloxane as a corrosion-inhibitor was used in an ethylene oxidation process. 55

To 50 ml of a catalyst solution prepared as in Example 1 were added 0.3 percent of polyethylsiloxane, whereupon the solution was tested in an ethylene oxidation process using the procedure of Example 1 for 50 cycles. The catalyst functioned stably at W_{C₂H₄} = 140 ml/litre per minute, W_{O₂} = 120 ml/litre per minute and a capacity of 0.6 mole C₂H₄/litre. 60

The yield of acetaldehyde was 97 percent based on the reacted ethylene.

Example 12.

A catalyst containing PdSO_4 and $\text{H}_9[\text{PMo}_3\text{W}_3\text{V}_6\text{O}_{40}]$ was used in an ethylene oxidation process.

22.4 g H_2WO_4 were dissolved in 100 ml boiling water and to the hot solution were added 14.6 g H_2MoO_4 and 11.4 g of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, and the mixture was boiled with vigorous stirring till the ingredients had completely dissolved, whereupon 16.4 g V_2O_5 were added and the solution was boiled with stirring for another 2.5 hours. Then the solution was cooled and the pH adjusted to 3.0 by adding 50% H_2SO_4 . The solution was boiled again for 30 minutes, cooled, diluted to 100 ml and its pH adjusted to 1.0 by adding 50% H_2SO_4 . Thereupon 20 mg PdSO_4 were added into the thus-prepared solution. The resulting solution contained [Pd] in an amount of 1.10^{-3} g-atom/litre and $[\text{H}_9[\text{PMo}_3\text{W}_3\text{V}_6\text{O}_{40}]]$ in an amount of 0.2 g.mole/litre.

A further 25 ml of the above solution were tested in ethylene oxidation process described in Example 1 for 7 cycles. The catalyst functioned stably at $W_{\text{C}_2\text{H}_4} = 110$ ml/litre per minute, $W_{\text{O}_2} = 50$ ml/litre per minute and a capacity of 0.4 mole C_2H_4 /litre. The yield of acetaldehyde was 97 percent based on the reacted ethylene.

Example 13.

A catalyst containing PdCl_2 and a mixture of $\text{H}_4\text{As}_2\text{Mo}_{12}\text{V}_6\text{O}_{61}$ and $\text{H}_3\text{AsMo}_6\text{V}_6\text{O}_{40}$ in a molar ratio of 1:2 was used in an ethylene oxidation process.

7.2 g KH_2AsO_4 ; 11.5 g MoO_3 ; 10.9 g V_2O_5 ; and 10 g NaHCO_3 were mixed with 70 ml water, the resulting mixture was brought to boiling point with vigorous stirring and 5 ml 50% H_2SO_4 were added in succession thereto at 20 minute intervals, whereupon the mixture was boiled for another 20 minutes to form a black-red solution. Then the solution was cooled to room temperature, filtered and the volume of the filtrate adjusted to 100 ml. The pH of the solution was then 1.15. Into the obtained solution of HPA were introduced 35 mg PdCl_2 and the solution was boiled for another 20 minutes, its volume being kept at 100 ml. The thus obtained catalyst solution contained [Pd] in an amount of 2.10^{-3} g-atom/litre and had a total concentration of HPA of 0.2 g mole/litre.

100 ml of the solution were tested in an ethylene oxidation process for 6 cycles by following the procedure of Example 1. During the initial 4 cycles the catalyst functioned stably at $W_{\text{C}_2\text{H}_4} = 66$ ml/litre per minute, $W_{\text{O}_2} = 62$ ml/litre per minute and a capacity of 0.6 mole C_2H_4 /litre. Then the rate of ethylene and oxygen reactions decreased owing to hydrolytic decomposition of the HPA.

Example 14.

A catalyst containing PdCl_2 and $\text{H}_9[\text{TeMo}_3\text{V}_3\text{O}_{24}]$ was used in an ethylene oxidation process.

11 g Na_2TeO_4 ; 13 g MoO_3 ; and 14.6 g NaVO_3 were mixed with 70 ml water, the mixture was brought to boiling point and 8 ml of 50% H_2SO_4 were added thereto. The solution was then boiled for 20 minutes, cooled to room temperature and filtered. The volume of the filtrate was adjusted to 100 ml, when its pH was 1.12. Into the resulting homogeneous solution of HPA was introduced PdCl_2 as in Example 9. The thus obtained catalyst solution contained Pd in an amount of 2.10^{-3} g atom/litre and $\text{H}_9[\text{TeMo}_3\text{V}_3\text{O}_{24}]$ in an amount of 0.2 g mole/litre.

100 ml of the resulting solution were tested in an ethylene oxidation process for 5 cycles according to the procedure adopted in Example 1. During the initial cycle $W_{\text{C}_2\text{H}_4}$ was 74 ml/litre per minute, W_{O_2} was 40 ml/litre per minute and the capacity was 0.6 ml C_2H_4 /litre. Then the rate of ethylene and oxygen reactions decreased owing to hydrolytic decomposition of the HPA.

Example 15.

A catalyst containing PdCl_2 and $\text{H}_9[\text{PMo}_6\text{V}_6\text{O}_{40}]$ was used in a propylene oxidation process.

20 ml of the catalyst solution prepared as in Example 1 were tested in a propylene oxidation process by the procedure of Example 1 for 5 cycles, the purity of propylene used being 99.8 percent. The catalyst functioned stably at $W_{\text{C}_3\text{H}_6} = 200$ ml/litre per minute, $W_{\text{O}_2} = 50$ ml/litre per minute and a capacity of 0.5 mole C_3H_6 /litre. The yield of acetone was 95 percent, based on the reacted propylene.

Example 16.

A catalyst containing PdCl_2 and $\text{H}_9[\text{PMo}_6\text{V}_6\text{O}_{40}]$ was used for the oxidation of n-butenes.

20 ml of the catalyst solution prepared as in Example 1 were tested in oxidation of n-butenes by the procedure of Example 1 for 5 cycles, use being made of butylene fraction of the following composition: butene-1, 10.8 percent; cis-butene-2, 38.0 percent; trans-butene-2, 49.6 percent; admixtures of O₂, CO, N₂. The catalyst functioned stably at W_{C₄H₈} = 50 ml/litre per minute, W_{O₂} = 30 ml/litre per minute and a capacity of 0.25 mole C₄H₈/litre. The yield of methyl ethyl ketone was 98 percent, based on the reacted n-butenes.

Example 17.

A catalyst containing H₂[PMo₆V₆O₄₀] and PdCl₂ was used in a hexene-1 oxidation process.

200 ml of the catalyst solution prepared as in Example 6 were placed into a flask having a mechanical stirrer, heated with boiling acetone vapour, at its boiling point (56°C), whereupon 5 ml (40 moles) of hexene-1 were added thereto. After stirring for 3 hours in a nitrogen atmosphere, the solution was cooled to room temperature and 50 ml of it were extracted four times with 50 ml heptane. From the heptane extract could be obtained methyl butyl ketone in a yield of 80 percent, based on the reacted hexene-1.

WHAT WE CLAIM IS:—

1. A catalyst for the liquid-phase oxidation of olefins, which comprises an aqueous solution of a palladium compound; a reversible oxidant which has a redox potential in excess of 0.5 volt and which is a mixed iso-polyacid (as defined herein) or a hetero-polyacid containing both molybdenum and vanadium, or a salt of said polyacid, and an organic or mineral acid other than said mixed iso-polyacid or hetero-polyacid, which organic or mineral acid is free of halide ions and is unreactive or at most weakly reactive with the palladium compound.
2. A catalyst as claimed in claim 1, wherein the palladium concentration is from 10⁻⁶ to 0.5 g-atom/litre, the concentration of the polyacid is from 10⁻³ to 1.0 g-mole/litre and the concentration of the organic acid or mineral acid is such that the solution has a pH of from 0 to 3.
3. A catalyst as claimed in claim 2, wherein the palladium concentration is substantially 2 × 10⁻³ g-atom/litre and the concentration of the polyacid is substantially 0.2 g-mole/litre.
4. A catalyst as claimed in any of claims 1 to 3, wherein the hetero-polyacid or mixed iso-polyacid contains from 1 to 8 vanadium atoms per molecule.
5. A catalyst as claimed in any of claims 1 to 4, wherein the palladium compound is PdCl₂ and the hetero-polyacid is a phospho-6-molybdo-6-vanadic heteropolyacid.
6. A catalyst as claimed in any of claims 1 to 5, wherein the mineral acid is sulphuric acid.
7. A method of preparing a catalyst as claimed in any of claims 1 to 6, which comprises introducing palladium, in the form of a salt, a complex or the metal, into an aqueous solution of the reversible oxidant prepared by dissolving in water at 50 to 100°C the necessary oxides, salts and/or acids of the elements forming the hetero-polyacid or mixed iso-polyacid, in a molar ratio close to the stoichiometric value of the elements in the hetero-polyacid or mixed iso-polyacid, and adding to the solution the organic or mineral acid.
8. A catalyst for the liquid-phase oxidation of olefins, prepared according to the method as claimed in claim 7.
9. A catalyst as claimed in any of claims 1 to 6 or 8, which also contains a corrosion inhibitor which is unreactive or at most weakly reactive with the palladium compound, the polyacid and the organic or mineral acid.
10. A catalyst as claimed in claim 9, wherein the corrosion inhibitor is polyethylsiloxane in an amount of 1 to 5 g/litre.
11. A catalyst for the liquid-phase oxidation of olefins substantially as herein described in any one of Examples 1 to 14.
12. A process for the liquid-phase oxidation of olefins to carbonyl compounds wherein there is used a catalyst as claimed in any of claims 1 to 6 or 8 to 11.

13. A process according to claim 12, substantially as herein described in any one of the Examples.

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