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Homogeneous catalytic oxidation of propene to acetone and butene-1 to butanone in the presence of palladium and molybdovanadophosphoric heteropoly acid

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Abstract

Oxidation of propene to acetone and butene-1 to butanone in aqueous solutions was studied in the presence of homogeneous catalysts Pd + HPA-x (HPA-x = $H_{3+x}PV_xMo_{12-x}O_{40}$ having Keggin composition, x = 1–4). The reaction order with respect to alkenes is 1, to palladium is 0.5 for propene and 0.66 for butene-1, respectively. The rate of alkene oxidation does not depend on concentration of HPA-x and acidity of catalyst solution. Alkenes are also successfully oxidized in the presence of new catalysts Pd + HPA-x' containing modified high-vanadium non-Keggin HPA-x' ($x' > 4$). The HPA-x' solutions have improved thermal stability and are very promising for oxidation of the lower alkenes. Kinetic peculiarities of oxidation of both alkenes in the presence of solutions of HPA-x' and HPA-x are similar.

Keywords: Catalytic oxidation; Propene; Acetone; Butene-1; Butanone; Heteropoly acids

1. Introduction

Selective oxidation of alkenes with dioxygen to yield oxygenated compounds is widely used both in organic synthesis and industrial chemistry. Dioxygen is the best oxidant due to its environmental friendliness. The Wacker homogeneous catalytic system $PdCl_2 + CuCl_2$ is the efficient catalyst of selective oxidation of lower alkenes to ketones by O_2 [1–4]. Unfortunately, $CuCl_2$ provides formation of detrimental chlorine byproducts.

In Refs. [5,6], the authors suggested a number of chloride-free solutions of the Keggin-type Pd + Mo-V-phosphoric heteropoly acids ($H_{3+x}PV_xMo_{12-x}O_{40}$ = HPA-x, x = 2–6) as very efficient homogeneous catalysts for oxidation of alkenes. Later [7], catalysts Pd + HPA-x (x = 2–4) with low chloride concentration ($[Cl^-]/[Pd]$ = 5–50) were suggested, which did not find an industrial application because of their chlorinating action.

In the presence of Pd + HPA-x solutions, processes (3) are usually performed via two steps (1)–(2) in different reactors using the non-stationary catalysis method [8]. In such processes, HPA-x is a reversible oxidant.

$$\tfrac{m}{2}\mathrm{R{-}CH{=}CH_2} + \text{HPA-}x + \tfrac{m}{2}\mathrm{H_2O} \xrightarrow{\mathrm{Pd}} \tfrac{m}{2}\mathrm{R{-}CO{-}CH_3} + \mathrm{H}_m\text{HPA-}x \quad (1)$$

$$\mathrm{H}_m\text{HPA-}x + \tfrac{m}{4}\mathrm{O_2} \rightarrow \text{HPA-}x + \tfrac{m}{2}\mathrm{H_2O} \quad (2)$$

$$\mathrm{R{-}CH{=}CH_2} + \tfrac{1}{2}\mathrm{O_2} \xrightarrow{\mathrm{Pd+HPA-}x} \mathrm{R{-}CO{-}CH_3} \quad (3)$$

Here $R = CH_3$ or C_2H_5, and H_mHPA-x ($H_{3+x+m}PV_m{}^{IV}V_{x-m}{}^{V}Mo_{12-x}O_{40}$) is the HPA-$x$ form reduced by m electrons ($m = [V(IV)]_\Sigma$: [HPA-x]). Acetaldehyde is the product of reaction (1) at R = H.

In contrast to the known methods of ketone production from alkenes, the above chloride-free processes (3) are characterized by high selectivity and absence of waste products. However, the industrial use of processes (3) depends on the duration of catalyst regeneration via reaction (2). Note that reaction (2) proceeds slower than reaction (1) and it never comes to a full completion [9]. The rate and depth of catalyst regeneration

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depend on the total number of vanadium atoms in HPA-*x* (*i.e.* *x*) as well as temperature and pressure of O_2 [9].

Aqueous solutions of HPA-*x* are complex equilibrium systems containing different anions $H_{x-1}PV_xMo_{12-x}O_{40}{}^{4-}$ (HPAn-*x*) and cations $VO_2{}^+$ [10–12], which act as oxidants in reaction (1). Note that partially reduced solutions H_mHPA-*x* are even more complex systems, which contain both oxidants and their reduced forms, *i.e.* anions $H_{x+m-1}PV_m{}^{IV}V_{x-m}{}^{V}Mo_{12-x}O_{40}{}^{4-}$ and cations VO^{2+} [13]. Concentrations of the above particles change during redox conversions of HPA-*x*. So investigations of different redox reactions (1) and (2) occurring in HPA-*x* solutions become more difficult.

The purpose of the present work is the development of industrial homogeneous catalysts based on Mo-V-phosphoric heteropoly acids for oxidation of lower alkenes. These catalysts must be thermostable and ready regenerable.

2. Experimental

2.1. Materials

Aqueous HPA-*x* solutions (0.10–0.35 M, *x* = 1–4) of the Keggin composition and modified non-Keggin composition were prepared by the methods described elsewhere [14,15]. Catalysts Pd^{2+} + HPA-*x* ($[Pd^{2+}] = 5 \times 10^{-4}$ to 4×10^{-3} M) were prepared by introducing $PdSO_4$ into solutions of HPA-*x*. In the experiments, we used high-purity propene (≥99.9%) and butene-1 (99.5%) samples containing only inert impurities.

2.2. Reduction degree *m* and redox potential *E* of the partially reduced HPA solutions

During reaction (1), reduction degree *m* of any HPA-*x* solution increases, and redox potential *E* of the catalyst solution decreases. In the course of reaction (2), *m* decreases and *E* increases. The value of *m* was usually determined from the empirical dependence of redox potential *E* on *m* [16]. *E* was measured using a digital ion meter I-130.2 M (Soyuzanalitpribor, USSR) with platinum and silver chloride electrodes. The values of *E* are given with respect to the normal hydrogen electrode (NHE). The same instrument was used to measure pH of solutions of HPA using glass and silver chloride electrodes.

2.3. Oxidation of alkenes (C_3H_6 and C_4H_8) via reaction (1)

Reaction (1) was studied at atmospheric pressure and temperature range 303–343 K in a thermostated shaken glass reactor (volume 170 mL). First, the reactor containing 20 mL of catalyst Pd + HPA-*x* was blown out with C_3H_6 (or C_4H_8) without bubbling. Then the reactor was connected to a burette filled with the same alkene. The reaction was carried out at shaking with frequency 1200 min^{-1} in kinetic region. Note that the reaction rate did not depend on frequency of shaking above 800 min^{-1}. The volumes of the alkene absorbed by solutions of Pd + HPA-*x* *versus* time are shown in Fig. 1 (for C_3H_6) and Fig. 2 (for C_4H_8). The reaction rate $W_1 = dV_{C_nH_{2n}}/dt$ (in moles C_nH_{2n}/L min) was determined at the initial part of the kinetic curve $V_{C_nH_{2n}} = f(\tau)$, where W_1 was constant. To obtain average values of W_1, each run was repeated two or three times using a fresh catalyst portion.

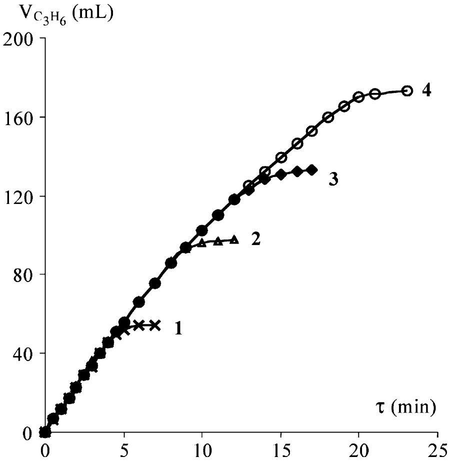

Fig. 1. Volume of propene absorbed by the Pd + HPA-*x* solutions as a function of time at 318 K. $[PdSO_4] = 1 \times 10^{-3}$ M, [HPA-*x*] = 0.2 M. **1**: *x* = 1; **2**: *x* = 2; **3**: *x* = 3; **4**: *x* = 4.

Gas mixtures $C_nH_{2n} + N_2$ were used in the runs with varied partial pressures of C_nH_{2n} ($P_{C_nH_{2n}}$). Taking into account the fact that partial pressure of C_nH_{2n} over aqueous solution of the catalyst decreases with increasing temperature, all values of W_1 were recalculated for $P_{C_nH_{2n}} = 1$ atm (101.3 kPa).

Selectivity of reaction (1) was determined by the GLC method using a capillary column containing SE-30 (length 40 m, diameter 0.25 mm).

2.4. Regeneration of the catalyst by dioxygen via reaction (2)

Reaction (2) was studied in a stainless steel temperature-controlled autoclave (volume 150 mL) equipped by a glass beaker with a magnetic core and a backflow condenser. Prior to the run, 20 mL of the catalyst solution was poured into the glass

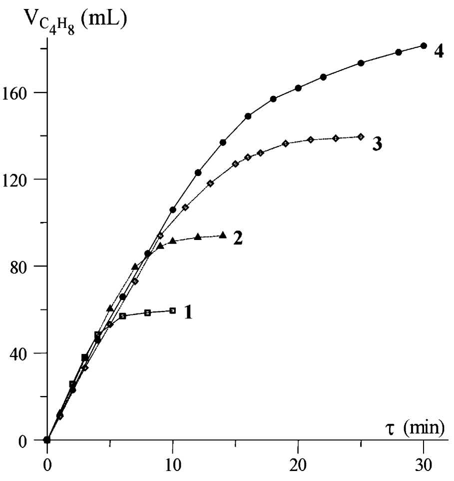

Fig. 2. Volume of butene-1 absorbed by the Pd + HPA-*x* solutions as a function of time at 333 K. $[PdSO_4] = 5 \times 10^{-4}$ M, [HPA-*x*] = 0.2 M. **1**: *x* = 1; **2**: *x* = 2; **3**: *x* = 3; **4**: *x* = 4.