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O.N. Chupakhin on his 70th Anniversary

Homogeneous and Polymer-Supported Catalysts in the Oxidation of α -Pinene with Oxygen

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Received January 10, 2004

Abstract—The catalytic activities of nitrogen-containing cobalt complexes, polymer (AN-251 anion exchanger)-supported cobalt complex, and a polymer–salt composition containing molybdenum salt and non-ionogenic water-soluble polymers were compared in the oxidation of α -pinene.

Oxidation of α -pinene with oxygen attracts researchers' attention, for it utilizes an accessible and ecologically clean oxidant [1]. This reaction leads to practically important oxygen-containing compounds which can be obtained with a fairly high selectivity, especially in the presence of transition metal salts and complexes [2]. However, analysis of published data shows that the results of using transition metal compounds as catalysts should be considered with some criticism [3]. In particular, insufficient attention was given to possible isomerization of the substrate and formation of active radical intermediates. For example, in the presence of dibromo(4-methylpyridine)cobalt(II) [(4-MeC₅H₄N)₂CoBr₂] at 72°C, the yield of verbenone in the crude product attained 76% (the conversion of α -pinene was complete); with (4-MeC₅H₄N)₂CoCl₂ as catalyst (65°C), the conversion of α -pinene was 53%, the yield of verbenone was as low as 12%, and 10% of verbenol and 26.5% of 2,3-epoxypinane were obtained. Presumably, the formation of the latter is responsible for the poor yield of verbenone. In the above cases, the oxidation of α -pinene was carried out by bubbling air or oxygen at a flow rate of about 40–60 ml/min. On the other hand, oxidation of α -pinene in the presence of cobalt(II) abietate in a static system at room temperature [4] was accompanied by gradual decrease in the rate of oxygen absorption (which was controlled using a gas burette), and addition of 10 fresh

portions of the catalyst was necessary to keep the process running. Here, the yield of verbenol was 26.5%, and the yield of verbenone was 11%.

Kuznetsova *et al.* [5] reported on the oxidation of α -pinene with a 1:2 oxygen–hydrogen gas mixture in the presence of a two-component heterogeneous catalytic system based on platinum metals and heteropolycompounds. The authors showed that the reaction involves several types of active intermediates having a radical or electrophilic nature. For example, such heteropolycompounds as PW₁₁ and especially PW₁₁Ti and PW₁₁Zr are capable of producing peroxy intermediates which are responsible for the transformation of alkenes into epoxy derivatives; heteropolytungstates containing Fe, Mn, Cr, and Co, as well as compounds like PMo₁₂ and PMo_{12-n}V_n, give rise to radical oxygen species which promote allylic oxidation.

The activity of a series of homogeneous catalysts and immobilized molybdenum and cobalt salts and complexes in the oxidation of α -pinene can be estimated by the rate of oxygen absorption under static conditions [6]. We previously reported on successful peroxide oxidation of anthracene with the use of acetylacetonato VO(II) and Co(II) complexes immobilized on chloromethylated styrene–divinylbenzene copolymer [7, 8] and of metallic molybdenum with polyvinyl alcohol [9]. It seemed reasonable to

Catalytic activity of homogeneous and polymer-supported heterogeneous catalytic systems^a (50°C)

Run no.	Catalyst ^b	Molar ratio α -pinene–solvent–metal	$-v_0$, mol l ⁻¹ min ⁻¹	$-v_{sp}$	$-W_r \times 10^6$
1	CoSalen	1:3.03:0.0095	0.00149	4.975	13.1
2	Co(acac) ₂	1:3.03:0.0095	0.00126	4.2	10.6
3	(2-MeC ₅ H ₄ N) ₂ CuCl ₂	1:3.03:0.0096	0.000612	2.05	5.3
4	(2-MeC ₅ H ₄ N) ₂ CoCl ₂	1:3.03:0.0096	0.00182	6.3	15.3
5	AHM (4.5%) + PVA	1:0:0.0031	0.000063	0.67	0.075
6	AHM (4.5%) + PVA + UV	1:0:0.0031	0.00013	1.3	0.13
7	AHM (9%) + PVA	1:0:0.0063	0.000109	0.88	0.08
8	AHM (9%) + PVA ^c	1:0:0.0042	0.00013	0.99	0.11
9	AN-251 + CoCl ₂	1:3.03:0.021	0.00021	0.337	0.375

^a v_0 is the initial oxidation rate, v_{sp} is the specific oxidation rate, mol l⁻¹ min⁻¹ [M]⁻¹; and W_r is the reduced oxidation rate, m³(O₂) × g⁻¹(M) mol⁻¹(α -pinene) s⁻¹.

^b AHM stands for ammonium heptamolybdate, and PVA, for polyvinyl alcohol.

^c Reused catalyst.

examine the activity of polymer-supported heterogeneous catalysts with a view to elucidate the possibility for their repeated use. As such polymeric catalysts we used cross-linked wide-pore styrene–2-methyl-5-vinylpyridine copolymer (which is a large-scale product) containing adsorbed Co(II) and Cu(II) ions and a heterophase polymer–salt composition consisting of polyvinyl alcohol and ammonium heptamolybdate (NH₄)₆Mo₇O₂₄·4H₂O (an aqueous solution). Both these systems can readily be separated from the oxidation products.

A possible catalytic activity in redox reactions of compositions including water-soluble non-ionogenic polymers and oxygen-containing molybdenum, tungsten, and vanadium salts was noted in several publications [10, 11]. An important specific feature of these systems (which are used as solutions, gels, films, or grains) is the occurrence therein of reversible photochemical reactions leading to partial reduction of *d*-metals under UV irradiation, which makes it possible to control the catalytic process with participation of molecular oxygen.

The results of our kinetic studies showed that, among the examined homogeneous systems, the catalytic properties of 2-methylpyridine Co(II) complexes ensure the highest initial rate v_0 of α -pinene oxidation (see table). Their activity changes in the following series: (2-MeC₅H₄N)₂CuCl₂ < Co(acac)₂ < CoSalen < (2-MeC₅H₄N)₂CoCl₂. The initial parts of the $\log c = f(\tau)$ plots (Fig. 1) are close to linear, indicating that pseudofirst-order equation (1) (see

below) can be applied to estimate (at least roughly) the kinetics of α -pinene oxidation with molecular oxygen. The data of volumetric and titrimetric (iodometry) analyses showed a considerable discrepancy which attained ~40%. Presumably, this is the result of partial decomposition of hydroperoxides in the presence of transition metal ions.

A common criterion of the efficiency of homogeneous and polymer-supported heterogeneous catalysts under the given oxidation conditions is the specific rate of oxidation, which is calculated by dividing the initial reaction rate v_0 by the molar concentration of metal ions (M) in solution. Some difference between the reaction volumes with the use of a fairly large amount of the catalyst based on polyvinyl alcohol (without solvent addition, for in the presence of acetonitrile as solvent coagulation of polyvinyl alcohol occurs) and those of homogeneous systems formally leads to higher initial concentration of oxygen in the reaction solution and hence to lower values of the specific initial oxidation rate.

Although the amount of the substrate was the same in all experiments, the substrate-to-metal ion molar ratio was varied over a wide range. Therefore, it was more reasonable to compare the specific initial rates of oxidation of different samples in the presence of polyvinyl alcohol-based catalysts only with each other. For example, twofold increase of the concentration of ammonium heptamolybdate in polyvinyl alcohol (from 4.5 to 9 wt %) leads to only ~20% increase in the specific initial oxidation rate. On the other hand, UV

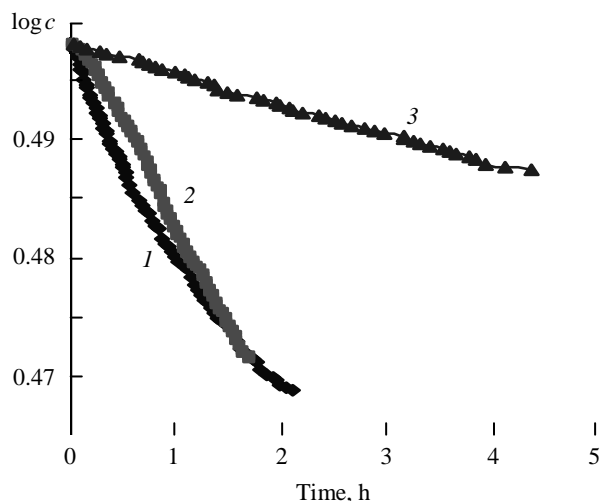


Fig. 1. Variation of the concentration of oxygen ($\log c$) with time in the presence of (1) cobalt(II) complex with 2-methylpyridine, (2) cobalt(II) complex with 1,2-bis(salicylidene-amino)ethane, and (3) polymer (AN-251)-supported CoCl_2 complex.

irradiation of the reaction mixture containing the same sample over a period of 2 h results in more than 90% increase of the specific initial rate. An analogous situation was observed when so-called reduced oxidation rate W (m^3/s), which is related to 1 g of the metal and 1 mol of the substrate, was used as parameter characterizing the catalytic activity. Here, the rate of oxidation in homogeneous catalytic systems was considerably higher, while the reduced oxidation rates for heterogeneous polymer-supported catalysts were fairly similar. It should be noted that the catalyst containing 9% of ammonium heptamolybdate can be reused without loss of catalytic activity (see table).

While performing the oxidation under UV irradiation, we found that the consumption of oxygen increased after the UV lamp was turned off (with account taken of the temperature conditions). Simultaneously, the optical density D (λ 740 nm) of the catalytic solution increased (Fig. 2). The optical density depends on the concentration of polymer-salt complexes containing partially reduced Mo [10, 11]. Their concentration can increase as a result of reduction of Mo ions in the dark due to greater stability of radical ions whose formation and disappearance are controlled by dynamic equilibrium under UV irradiation. The character of variation of the optical density indicates the occurrence of a "pulsating" reaction. Probably, the catalytic activity of such compositions depends on the concentration ratio of the initial metal ions $[\text{M(VI)}]$ and the reduced species.

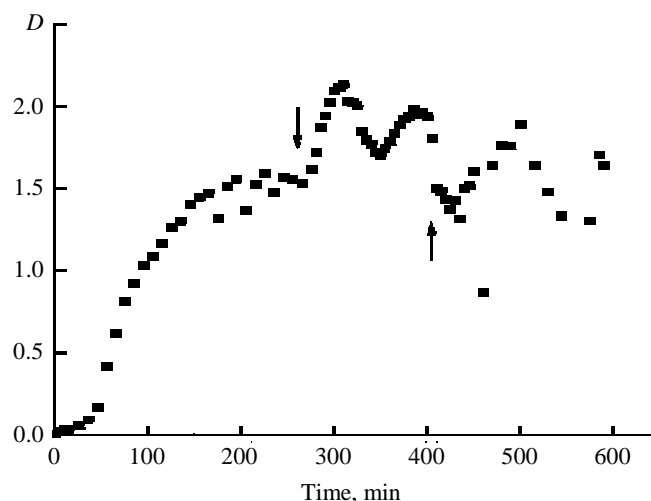


Fig. 2. Variation of the optical density D (Specol-11) of solutions containing 2 wt % of polyvinyl alcohol and 1 wt % of ammonium heptamolybdate at 0°C . Down and up arrows correspond to the moments of turning UV lamp off and on, respectively.

Thus, the oxidation of α -pinene under the given mild conditions is characterized by low conversion of the substrate and good selectivity for verbenol (according to the GLC data); verbenone is formed in trace amounts. Polymer-supported metal-complex catalyst can be used repeatedly. The results confirmed the previously presumed catalytic activity of a composition based on polyvinyl alcohol and ammonium heptamolybdate and the possibility for controlling the catalytic process by UV irradiation. Prolonged periodical UV irradiation and barbotage technique are necessary to raise the substrate conversion. The oxidation catalyzed by metal complexes immobilized on a poly(vinylpyridine) matrix should be performed under pressure, for barbotage technique could lead to mechanical degradation of samples.

EXPERIMENTAL

The optical densities of solutions were measured on a Specol-11 spectrophotometer. Ultraviolet irradiation was generated using an HGOK-125 lamp. Samples were analyzed by GLC on an LKhM-8MD gas chromatograph equipped with a thermal conductivity detector; a 3000×1.5 -mm steel column was packed with Chromaton N-AW (0.16–0.20 mm) which was preliminarily washed with an acid and impregnated with 15% of Apiezon L as stationary liquid phase.

The catalytic activity in the oxidation of α -pinene with molecular oxygen was determined using a glass

reactor consisting of two parts where particular components of the reaction mixture (substrate and catalyst) could be stored without mixing until preliminary operations were complete. The reactor was hermetically sealed and purged with oxygen (5 times), the components were mixed, and the reaction was carried out by continuous shaking at 50°C, measuring the amount of absorbed oxygen. The resulting mixture was then analyzed by GLC. All original kinetic data for a nonzero-order reaction were treated in a simplified version using pseudofirst-order equation (1):

$$c_{\tau} = c_0 \exp(-k\tau), \quad (1)$$

where c_0 and c_{τ} are, respectively, the initial and current concentrations of oxygen, and k is the rate constant. The first derivative

$$v_{\tau} = \partial c_{\tau} / \partial \tau = -c_{\tau} k \exp(-k\tau) \quad (2)$$

was extrapolated to $\tau = 0$ to obtain the initial reaction rate v_0 . The current oxygen absorption measured by a gas burette was converted into the consumed oxygen concentration in an oxygen-saturated solution:

$$c_{\tau} = (n[\text{O}_2]_{\text{max}} - n[\text{O}_2]_{\tau}) / V_{\text{R}}$$

Here, $n[\text{O}_2]_{\text{max}}$ is the maximally possible amount of absorbed oxygen (mol), $n[\text{O}_2]_{\tau}$ is the current amount of absorbed oxygen (measured by a burette), and V_{R} is the volume of the reaction solution. The substrate conversion was also monitored by iodometric titration (formation of hydroperoxides) [12].

Copper(II) and cobalt(II) complexes with 2-methylpyridine were synthesized by the procedure described in [13].

Dichlorobis(2-methylpyridine)copper(II) ($(2\text{-MeC}_5\text{H}_4\text{N})_2\text{CuCl}_2$). A solution of 11.617 g (0.0681 mol) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 25 ml of ethanol was added to a solution of 15.828 g (0.17 mol) of 2-methylpyridine in 25 ml of ethanol, heated to 50°C. After cooling, 15.215 g (0.0475 mol) of the complex was isolated. Yield 70%. Found, %: C 42.98; H 4.14; N 8.58. $\text{C}_{12}\text{H}_{14}\text{Cl}_2\text{CuN}_2$. Calculated, %: C 44.04; H 4.40; N 8.73.

Dichlorobis(2-methylpyridine)cobalt(II) ($(2\text{-MeC}_5\text{H}_4\text{N})_2\text{CoCl}_2$). Found, %: C 44.10; H 4.31; N 8.26. $\text{C}_{12}\text{H}_{14}\text{Cl}_2\text{CoN}_2$. Calculated, %: C 45.59; H 4.46; N 8.86.

Cobalt(II) complexes with a commercial sample of styrene–2-methyl-5-vinylpyridine copolymer (AN-251) were prepared by heating (50°C) a required amount of the anion exchanger with 3 equiv of CoCl_2 over a period of 24 h. The product was washed in a Soxhlet apparatus and dried. Cobalt(II) complexes with 1,2-bis-(salicylideneamino)ethane (CoSalen) were prepared by the procedure reported in [14]. Polymer–salt compositions containing polyvinyl alcohol and ammonium heptamolybdate were prepared as described in [10, 11].

The authors are grateful to Corresponding Member of the Russian Academy of Sciences, Prof. A.V. Kuchin for providing samples of α -pinene and its oxidation products used as reference compounds for GLC analysis, as well as for discussing the results. This study was performed under financial support by the Russian Foundation for Basic Research (project no. № 02-03-32777) and by the Ministry of Education of the Russian Federation (program for support of research by post-graduate students at higher school, project no. A 03-2.11-853).

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