



Cyclohexane oxidation and cyclohexyl hydroperoxide decomposition by poly(4-vinylpyridine-co-divinylbenzene) supported cobalt and chromium complexes

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ABSTRACT

Polymer supported catalysts with Co(II) and Cr(VI) ions were prepared and characterized by means of FTIR, diffuse reflectance UV–vis, nitrogen physisorption, mercury porosimetry and SEM–EDX measurements. The catalytic activity and selectivity of the polymer supported catalysts were tested in aerobic liquid-phase partial oxidation of cyclohexane in a polytetrafluoroethylene lined reactor. The influence of reaction time and temperature, main products addition, mass of the catalyst and different metals loading was investigated. Product yield and cyclohexyl hydroperoxide formation in the catalytic system were used as critical parameters which could be optimized by changing the cobalt content on the polymer and the catalyst mass used in the catalytic runs. By increasing cobalt content, a higher activity and corresponding lower selectivity towards cyclohexanone were obtained. This study indicates that the selectivity towards cyclohexanone and cyclohexanol is mainly defined by the yield and type of the catalyst with minor influence of temperature and main products addition.

In addition catalysts were used for deperoxidation of cyclohexyl hydroperoxide in mild conditions. Nearly the same selectivity towards cyclohexanone and cyclohexanol is achieved using the cobalt containing catalyst, while a higher selectivity towards cyclohexanone is achieved using the chromium containing catalysts.

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1. Introduction

Oxidation of cyclohexane is an industrial chemical process with low efficiency. Conversions are usually in the range of 3–8% with a selectivity ~80% for the cyclohexanone/cyclohexanol mixture. Due to the importance of the large-scale oxidation of cyclohexane to cyclohexanol (ChI) and cyclohexanone (Chn), this process continues to be dealt with and remains a challenge [1,2]. Cyclohexane oxidation products are raw materials in the caprolactam and adipic acid synthesis which are the Nylon 6 and Nylon 66 precursors, respectively. In the present industrial processes, cyclohexane is oxidized in the temperature range between 150 °C and 175 °C and at pressures of 0.8–2 MPa in the presence of a soluble catalyst, i.e. cobalt naphthenate or cobalt octoate under aerobic conditions.

Metal ions act as the initiators of free radical autoxidation which proceeds further via a radical chain reaction [3]. A radical chain

mechanism generally limits the useful reaction yield as the major products are more reactive towards the chain propagation radicals than the substrate. The catalytic activity of some metal ions is based on the acceleration of peroxide decomposition. Most of these catalytic processes involve metal-peroxyl intermediates, i.e. Co(III)-peroxyl, which assist autoxidation reactions [4,5]. According to the Haber–Weiss proposal, the mechanism of decomposition of the hydroperoxide intermediate involves the metal catalyst cycling between two different oxidation states [6].

In the recent years the attention of the scientific community is focused on selective oxidation in solvent-free processes under mild condition with well designed heterogeneous (solid) catalysts of high activity and selectivity [7]. Many heterogeneous catalysts have been developed and generally these catalysts are either oxides, metal cations or metals [8,9] incorporated into inorganic supports such as silica, alumina, titania, zirconia, active carbon, zeolites or aluminophosphates. A great interest for the use of transition metals containing molecular sieves is motivated by their redox ability [10,11], acidity, shape selectivity [11–14] and recyclable properties [3,15]. The strategy for controlling reactions in microporous and macroporous materials includes the design of an effective active center on the surface using certain metal ions, which remain intact

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after the redox processes and the selection of an appropriate porous structure [16,17].

Other types of materials have also been used for oxidation of cyclohexane, i.e. clay minerals attapulgite loaded by cobalt [18], simple porphyrins in absence of reductants [19–21]. Metal aluminophosphates have been used for one-step oxidation of cyclohexane to adipic acid [22].

Chemically modified inorganic materials immobilized with organic ligands allow introducing metal ions to the catalyst and further to the low polarity medium [23–25]. Organic polymers or biopolymers functionalized by a ligand molecule and active metals have been applied for cyclohexane oxidation such as chitosan–Schiff base [26–29]. Especially, nitrogen-containing polymers have been used to generate metal complexes with a transition metal, in which nitrogen atoms are coordinatively bound to metal ions. These complexes are applied in biomolecules separation, as ion conductors, as ion-exchange membranes and as catalysts [30–33].

Cyclohexane oxidation by air on the polymer supported chelated cobalt palmitate catalysts has been investigated [34]. The liquid-phase oxidation of 2,6-di-tert-butylphenol has been studied using a heterogeneous Cu(II)-poly(4-vinylpyridine) catalyst [35]. Iron palladium biocatalyst on copolymer poly(4-vinylpyridine-co-divinylbenzene) has been applied for cyclohexane oxidation with hydrogen-peroxide [36]. Autoxidation of tetralin has been catalyzed by the colloidal poly(4-vinylpyridine)-Co²⁺ complex [37].

The decomposition of cyclohexyl hydroperoxide to Chn and Chl, in the process of deperoxidation, is an important step for the industrial production of adipic acid. In the recent time the interest for testing catalysts for deperoxidation is increasing without Diff41 [38–40].

Besides preparation and characterization of cobalt and chromium supported on a macroporous copolymer poly(4-vinylpyridine-co-divinylbenzene), the subject of the present paper is the investigation of aerobic oxidation of cyclohexane with synthesized catalysts, as well as estimation of activity and selectivity of these catalysts. Separately, with presented cobalt and chromium catalysts the decomposition of the Chhp in mild conditions was tested.

2. Experimental

2.1. Preparation and characterization of the catalysts

Macroporous copolymer poly(4-vinylpyridine-co-divinylbenzene) (PVP) (REILLEX-425, produced by Reilly Tarr & Chemical Corporation) was used as a support. Cobalt catalyst was prepared by wetness impregnation of a degassed support from ethanolic solutions of cobalt(II)-nitrate. PVP (10 g) was mixed with 100 cm³ ethanolic solution of the cobalt nitrate. The suspension was stirred for 3 h at 20 °C and filtered. The solid was washed with ethanol and finally dried at 140 °C for 24 h. The obtained poly(4-vinylpyridine-co-divinylbenzene)-Co²⁺, was denoted as CoPVP-s. The content of cobalt on polymer was 0.52 mass% (CoPVP1), 3.08 mass% (CoPVP2) and 5.72 mass% (CoPVP3).

The preparation of poly(4-vinylpyridinium-co-divinylbenzene) dichromate CrPVP was performed from water suspension: 2.00 g of chromium trioxide was added to the suspension of 20.0 g of cross-linked resin in 200 cm³ of water. The suspension was stirred at 20 °C for several hours according to the procedure proposed by Frechet et al. [41]. After filtration, the catalyst was repeatedly washed with water until the filtrate was colorless and then dried in vacuum at 50 °C. The content of chromium on polymer was 5.03 mass%.

A inductively coupled plasma emission spectroscopy Thermo Scientific iCAP 6500 Duo Series was used to determine the cobalt and chromium contents on polymer and potential leaching of ions from the catalysts.

Scanning electron micrographs were recorded by an automated scanning electron microscope (SEM), JSM-6460LV JOEL, with an energy dispersive X-ray (EDX) detector.

Nitrogen adsorption-desorption isotherms were determined on Sorptomatic 1990 Thermo Finnigan automatic system using nitrogen physisorption at –196 °C. Before measurement the samples were outgassed at 130 °C for 10 h. Specific surface area of the samples (S_{BET}) was calculated from the nitrogen adsorption isotherms according to the Brunauer, Emmett, and Teller method [42]. The micropores were analyzed using Dubinin–Radushkevich method [43]. Pore size, pore volume distribution, bulk density and porosity were determined by mercury intrusion porosimetry (Carlo Erba 2000 porosimeter with Macropores unit 120).

The diffuse reflectance UV–vis spectra were recorded using a Nicolet Evolution 500 spectrometer with a diffuse reflectance accessory. The reflectance (R) data were converted to pseudo-absorbance $f(R)$ using the Kubelka–Munk equation. The samples were grounded, heated overnight at 110 °C and then scanned in the range of 200–800 nm.

Infrared spectra of the samples were recorded in the region of 4000–400 cm^{–1} using a Thermo Nicolet 6700 FTIR spectrometer at a spectral resolution of 2 cm^{–1}, with a Smart Orbit diamond attenuated total reflectance (ATR) accessory.

2.2. Cyclohexane oxidation and Chhp decomposition setup and procedure

Catalyst activity tests were performed in a stainless steel, laboratory scale, Teflon-lined autoclave (100 cm³), produced by Autoclave Engineers. In all experiments the following conditions were used: air pressure 2.8 MPa, stirrer speed 350 rpm, air flow rate 100 cm³ min^{–1} and a temperature in the range of 130–170 °C. The described reactor was charged with 0.27–0.50 g of catalyst and with 35 g of cyclohexane. In the blank experiments, the reactor was only charged with cyclohexane.

The Chhp decomposition tests with cobalt and chromium catalysts were carried out in argon filed Erlenmeyer flask with stopper in the temperature range of 40–70 °C. 14 g of a cyclohexane solution of Chhp was added to a 100-ml Erlenmeyer flask, containing 0.20 g of catalyst (CoPVP3 or CrPVP). Starting concentrations were Chhp: 0.070 mol dm^{–3}; Chn: 0.021 mol dm^{–3}; Chl: 0.027 mol dm^{–3}. Chhp was prepared in non-catalytic run. Obtained liquid was washed three times with water solution of sodium carbonate and dried with anhydrous sodium sulfate.

The products were quantified by gas chromatography (Shimadzu-9A) employing a Carbowax 20M capillary column (30 m × 0.25 mm, 0.25 μm film) and a flame ionization detector by using a variable ramp temperature program from 60 °C to 190 °C. The identity of the products was confirmed on the same column by GC–MS (Hewlett Packard 5890 with MSD 5970). The Chhp concentration was determined by iodometric titration and indirectly by reduction with triphenylphosphine [44].

3. Results and discussion

3.1. Catalysts characterization

The SEM images of the polymer (Fig. 1a) and the supported catalysts (Fig. 1b) show that their surface morphology is uniform. The spherulite surface imperfections are distinguishable, their shape deviating from sphere. A more pronounced smoothness of the poly-

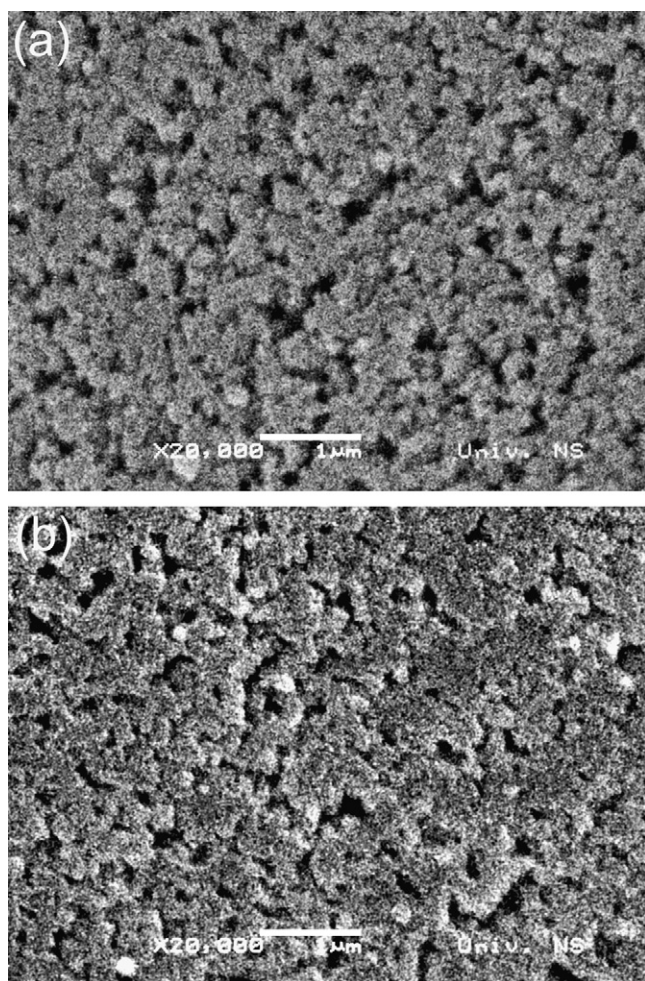


Fig. 1. SEM micrographs of polymer support–PVP (a) and CoPVP3 (b).

mer surface of the supported catalyst CoPVP3 is a consequence of the metal ions loading. Namely, it has been noticed that the grains swell during the process of impregnation in ethanolic solution. Deswelling during drying is not completely reversible, which can be due to the presence of metal ions in the polymer structure. This results in the increased smoothness of the polymer surface after impregnation, as shown in Fig. 1b.

The nitrogen physisorption isotherms for all catalysts are very similar to the one of the polymer support. According to the IUPAC recommendations for classification of adsorption isotherms [45] the obtained isotherms, for all examined catalysts, correspond to Type II isotherm, characteristic for macroporous materials. Hysteresis loops, which appear in the physisorption isotherms, can be classified as Type H1. Origin of this type of hysteresis is characteristic for solids consisting of grains, crossed by nearly cylindrical channels or made by aggregates or agglomerates of spheroidal particles. In this case pores can have uniform size and shape.

Table 1 summarizes the results obtained by nitrogen sorption and mercury porosimetry measurements for the support and for

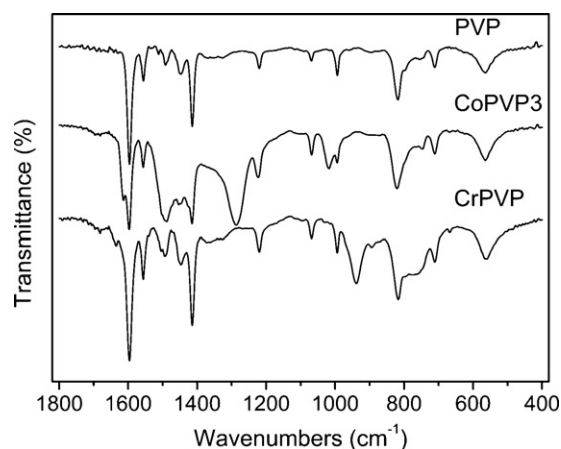


Fig. 2. FTIR spectra of polymer support–PVP, CoPVP3 and CrPVP catalyst.

the catalysts samples. The BET surface area of these materials is between $50 \text{ m}^2 \text{ g}^{-1}$ and $60 \text{ m}^2 \text{ g}^{-1}$. The micropores volume have value in the range of $22\text{--}25 \text{ mm}^3 \text{ g}^{-1}$ for all samples. Pore size distributions for all examined catalysts are in the range of $70\text{--}100 \text{ nm}$ with a mean pore diameter $\sim 85 \text{ nm}$. The differences in the surface areas of these materials are negligible. The minor decrease in the total pore volume observed with the presence of cobalt and chromium on polymer is a consequence of both, the porosity decrease and the bulk density increase. The obtained results show that the metal ions on the polymer support do not significantly affect its pore structure and textural properties.

The FTIR spectra of PVP and two catalysts, CoPVP3 and CrPVP, are presented in Fig. 2. Comparing the spectra of PVP and CoPVP3, changes in the region $1650\text{--}1400 \text{ cm}^{-1}$ can be assigned to the effect of Co^{2+} ions on the pyridine ring. When Co^{2+} ions are introduced into the PVP, a new shoulder appears at 1615 cm^{-1} . A FTIR examination of the similar materials based on vinylpyridine polymers have showed that the pyridine stretching band at 1600 cm^{-1} is shifted towards higher wavenumbers or that a new band is formed. The shift is more or less pronounced depending on metal ion–pyridine interactions. McCurdie and Belfiore [46] noticed that in the PVP– Ru^{2+} complex infrared absorption was at 1615 cm^{-1} . Similar studies for the poly(4-vinylpyridine-co-divinylbenzene)– Cu^{2+} were done by Wu et al. [47]. Therefore, at the molecular level, FTIR of CoPVP3 reveals that the pyridine coordinates to the metal center in the polymeric complex. The characteristic bidentate coordinated nitrate bands 1490 cm^{-1} , 1290 cm^{-1} and 1019 cm^{-1} were detected [48]. The FTIR spectra of CrPVP show bands at 940 cm^{-1} and 760 cm^{-1} , characteristic for the dichromate ion.

DR UV–vis spectra of solid cobalt(II)-nitrate hexahydrate, CoPVP3 and CrPVP samples are presented in Fig. 3. The d–d transition band shifts from 506 nm for solid cobalt(II)-nitrate hexahydrate to 538 nm for coordinate complex in CoPVP3 catalyst. The position of the maxima is consistent with the octahedral configurations for pyridine complex of Co(II) [49]. The spectrum of CrPVP exhibits absorption at 380 nm , characteristic for the dichromate.

Table 1
Basic textural parameters of support and cobalt catalyst samples.

	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)	V_{micro} ($\text{mm}^3 \text{ g}^{-1}$)	V_{meso} ($\text{mm}^3 \text{ g}^{-1}$)	V_{cum} ($\text{mm}^3 \text{ g}^{-1}$)	Mean pore diameter (nm)	Bulk density (g cm^{-3})	Porosity (%)
PVP	52	22	159	748	77	0.66	49
CrPVP	59	24	151	724	85	0.66	47
CoPVP3	53	22	129	671	92	0.67	45

V_{meso} : mesopore volume; V_{cum} : cumulative pore volume; V_{micro} : micropore volume.

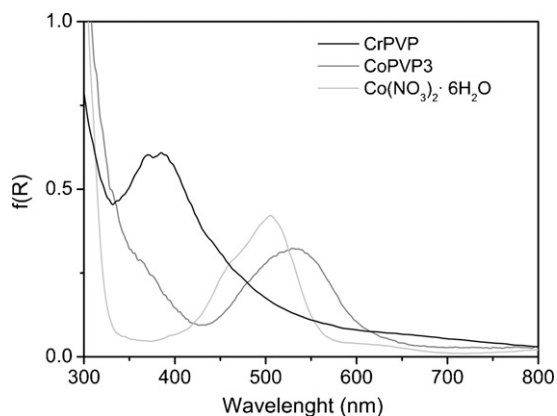


Fig. 3. Diffuse reflectance spectra of CrPVP, CoPVP3 and solid cobalt(II)-nitrate hexahydrate.

According to the DR UV-vis and ATR-FTIR spectra, it can be concluded that cobalt ions are in octahedral coordination with one or more pyridine rings of the polymer support. The nitrogen atom of the pyridine ring is coordinatively bonded to the Co^{2+} center. Chromium is bonded to the pyridine ring via dichromic acid proton.

3.2. Effect of reaction time and temperature

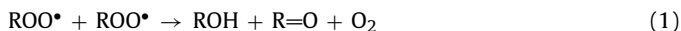
The activity and selectivity of catalyst CoPVP3 were tested at various temperatures (130–170 °C). In a typical non-catalytic cyclohexane oxidation test the three reaction phases are noticeable: short initiation period, followed by a fast increase in product concentration with an approximately constant rate and final phase with a decrease of the reaction rate.

Yields and selectivities to main products Chn and Chl at various temperatures are presented in Fig. 4. With the increase of the temperature and reaction time, the conversion increases, while there is no obvious correlation between selectivity and time at any examined temperature.

The effects of the reaction time and temperature on the products' yield and selectivity are commonly presented separately in most of the papers, as in Fig. 4, but when the radical chain autoxidation is dominant the effect of yield on selectivity should be discussed. The selectivity to Chn and Chl versus yield at different reaction times and temperatures is presented in Fig. 5.

Fig. 5 shows that all experimental points for a particular product are grouped around the corresponding fitting curve and that some points for different temperatures are overlapped, confirming that the selectivity for the used catalyst is correlated by the value of yield, at any used temperature and reaction time.

Generally, selectivity to Chn and Chl of about 50% is a consequence of reaction mechanism, where Chn and Chl are formed in equal quantity according to reaction (1):



In addition, a negligible temperature influence on selectivity towards Chn and Chl is probably a consequence of high and almost equal activation energies for Chn and Chl formation. The Arrhenius plots, the rate constants for oxygen and cyclohexane consumption and Chn and Chl formation were presented and discussed elsewhere [50].

A small change in selectivity around 50% (Fig. 5) can be explained with three segments according to three reaction phases. The segment of the curve corresponding to the lowest yields (up to 1%) was obtained from reaction performed at 130 °C and 140 °C and from initial phase of the reaction performed at 150 °C. The middle seg-

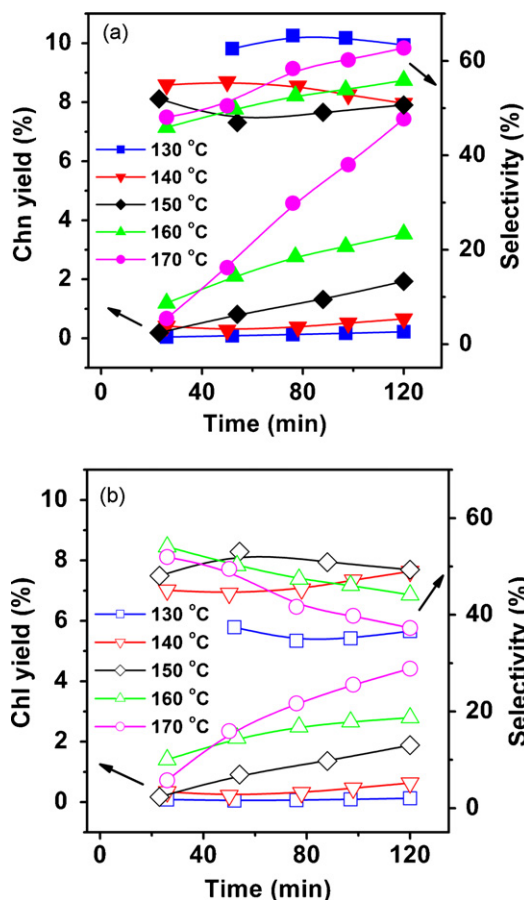


Fig. 4. Influence of temperature on the yield and selectivity of Chn (a) and Chl (b) during partial oxidation of cyclohexane using CoPVP3 catalyst.

ment with a constant selectivity (1–5% of the yield) was obtained from reaction performed at 150 °C and 160 °C, where the reaction rate was nearly constant. Finally, the third segment, with yields higher than 5% was obtained from reaction performed at 160 °C and 170 °C.

The segments of the selectivity–yield curves can be attributed to the different phases of the reaction. The first segment (up to 1% of the yield) represents short initiation period where reactive species

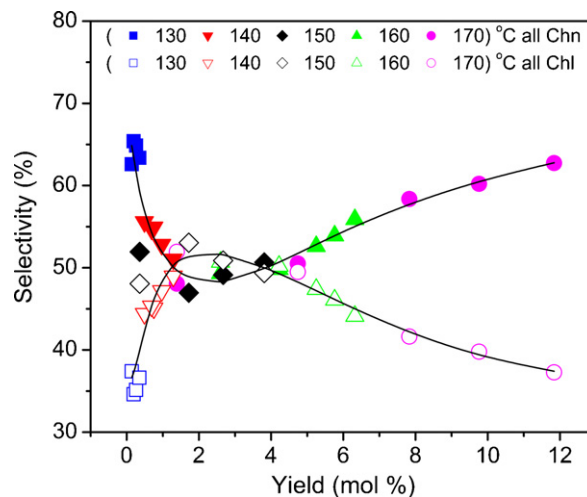


Fig. 5. Selectivity to Chn and Chl versus total yield (Chn + Chl) at different reaction times and temperatures using CoPVP3 catalyst.

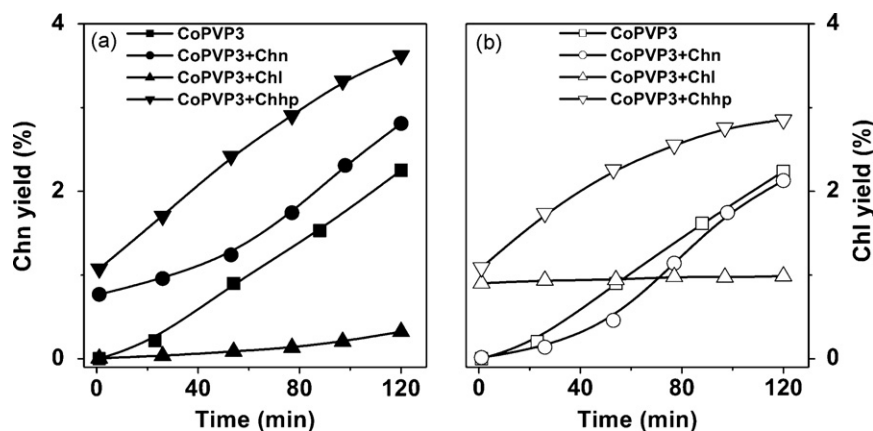


Fig. 6. Effect of Chhp, Chn and Chl addition on Chn (a) Chn yield and (b) Chl yield compared to reference test (catalyst CoPVP3).

and traces of main products are being accumulated. The second segment (from 1% to 5% of the yield) with an almost constant selectivity and constant reaction rate corresponds to the quasi-steady state and propagation as rate determining step (reactions (2) and (3)):



Finally, third segment (the yields higher than 5%) corresponds to the decrease of chain length, oxidation of main product, formation of esters and other deep oxidation products.

According to the Berezin et al. [51] the rate of product formation is mainly governed by the cyclohexylperoxy radical concentration. Three stages of the reaction mechanism exist. Namely, the initial kinetic stage with an increase of the reaction rate corresponds to the chain branching which leads to an increase of the free radical concentration. The central kinetic stage with a constant rate of product formation corresponds to the steady state phase where chain branching is balanced with chain termination and chain propagation dominates over the reaction kinetics. In the last phase, due to decrease of the critical free radical concentration reaction rate is decreasing.

From the obtained results it can be concluded that the changes of reaction rate with time and with temperature are secondary effects on selectivity and a consequence of the reaction mechanism changes. Since the primary effects on selectivity are yield and the nature of applied catalyst, the selectivity of particular catalyst should be given as a function of the yield. If we want to compare selectivity of different catalysts or different experimental conditions, the selectivity should be compared at the same conversions or to present selectivity as a function of yield.

For the CoPVP3 catalyst and applied reaction conditions, the selectivity to Chhp is less than 1%. For the corresponding catalyst the reaction temperature has negligible effect on the total selectivity.

3.3. Effect of main reaction products addition

In order to test reaction course and the influence of the products on reaction kinetics in catalytic reactions, the main products were added to reaction solution at the beginning of the oxidation. In Fig. 6 cyclohexane oxidation with added Chn, Chl and Chhp is compared with reference reaction (CoPVP3 catalyst, 150 °C). The investigated range is 0.5–2.5% of the particular product yield.

Data plotted as solid upside-down triangle, show the kinetic results for the CoPVP3 catalyst with addition of Chhp. The Chhp, present during the initial stages of the reaction, decomposes fast to the primary products, Chn and Chl (90% of the starting Chhp is

decomposed in 5 min). After that period the reaction rates reach the level of the reference catalytic reaction (data plotted as open squares). The concentration of Chn and Chl further increases linearly up to 2.5%. After that period reaction rate decreases, due to their conversion to other products such as acids and esters.

Hence, we can state that the presence of Chhp accelerates the initial step without further influence on the reaction kinetics. This statement is in agreement with a free radical reaction mechanism in which Chhp initiates a free radical process. More precisely, the addition of Chhp does not change the yield–selectivity relation shown in Fig. 5. This confirms the suggested relation between the segments of the kinetic curve and the reaction phases with products formation. Like other hydroperoxides, Chhp is an initiator and essential for branching chain. Especially, decomposition of Chhp by Haber–Weiss mechanism in the presence of metal ions is faster than its thermal decomposition (4):



Data plotted as solid circles show the kinetic results for the CoPVP3 catalyst with addition of Chn. The presence of Chn prolongs the initial step and after about 40 min of the reaction time the reaction proceeds with a kinetic similar to that of the reference reaction. In the presence of both, the catalyst and Chn, the initiated non-catalytic and catalytic reactions are evidently slower than the reference reaction. Obviously, Chn partially deactivates the CoPVP3 in its initiation role. In initial phase of reaction, at about 1% of the conversion, the presence of Chn or Chl prolongs initial period by trapping radicals by alpha hydrogen which is more reactive than cyclohexane hydrogen. Formed radicals further react and form acids or other non-radical species, without peroxy radical or Chhp formation, which are essential for chain length increase. Besides, like in the case of Chhp, an addition of Chn does not change process selectivity.

Data plotted as solid triangle show the kinetic results for the CoPVP3 catalyst with addition of Chl. It can be seen that the presence of Chl prolongs the initial period in comparison with the reference reaction, and hinders the formation of both Chn and Chl. Chl reacts with cyclohexylperoxy radical producing α -hydroxycyclohexylperoxy radical which decompose to cyclohexanone and hydroxyperoxy radical. Hydroxyperoxy radical is terminated by other cyclohexylperoxy radicals slowing down the overall cyclohexane oxidation [52].

The obtained results show that addition of Chhp, Chl and Chn leads to a different initial reaction rate. After the initial period, the steady state is reached, and after that the reaction rates and selectivity are independent of products addition.

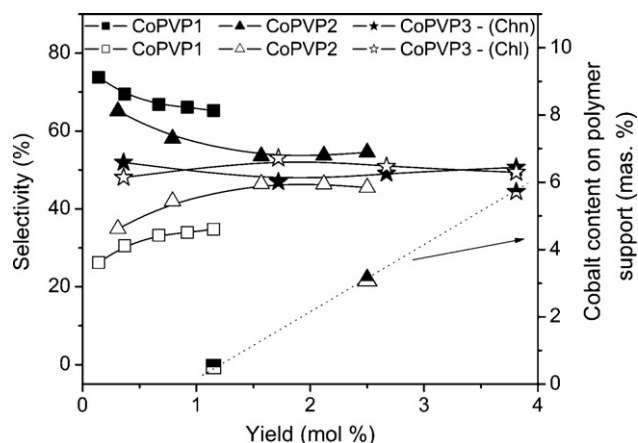


Fig. 7. Selectivity versus yield for catalyst with different cobalt contents (left ordinate) and effect of cobalt content on yield (right ordinate).

Addition of Chl and Chn is slowing down the initial reaction rate by trapping radicals in initial phase. Comparing to Chn, Chl decreases reaction rate in higher extent due to more reactive hydrogen. Only Chhp can initiate reaction faster than the catalyst itself by producing more radicals for initiation.

3.4. Effects of cobalt content and catalyst mass

The results of kinetic tests obtained using cobalt supported catalysts with different cobalt contents are shown in Fig. 7 and Table 2 (entries 3, 4, 6). It can be seen that the conversion (given as the total yield after 120 min) increases linearly in the range of 1–4%, with an increase of the cobalt content from 0.52% to 5.72% (shown in right ordinate). However, higher selectivity to Chn is obtained by decreasing the cobalt content on the polymer. If we compare the selectivity–yield curves for all examined cobalt catalysts, it can be noted, that all curves have the same shape.

According to the presented results, an increase in the cobalt content results in conversion increase and in an associated decrease in selectivity to Chn. The range in which we can vary cobalt content is limited from both sides. The maximum polymer capacity for cobalt loading is ~6%. On the other hand, a decrease of the cobalt content below 0.5% leads to incomplete decomposition of the Chhp, which results in an increased autocatalytic processes observed in initial stage of reaction and significant support effects.

Significant amounts of Chhp were determined in the blank tests and tests with support only (Table 2, entries 1 and 2), whereas only traces were found using cobalt catalysts. The selectivity towards products (Chl, Chn and Chhp) was changed in the presence of a polymer supported cobalt catalyst. It is evident that Chhp selectiv-

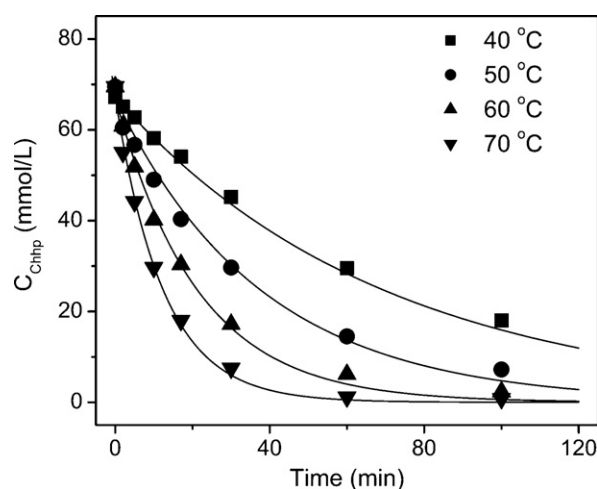


Fig. 8. Effect of reaction temperature on Chhp decomposition using CoPVP3 catalyst.

ity shows the most pronounced difference between catalytic and non-catalytic reaction systems. The effect of the catalyst mass is also presented in Table 2 (entries 5, 6, 7). It can be seen that the conversion is decreasing with an increase of the catalyst mass in system. The increase of the catalyst mass leads to an increased cobalt amount in the system, but also to an increased mass of the polymer itself, which further results in inhibition or retardation of the cyclohexane oxidation. In general, in comparison to the blank tests, presence of some solid supports results in inhibition of free radical reactions and in conversion lowering. Since, the increase in cobalt content results in linear increase of activity, while the increase in catalyst mass results in the activity decrease Table 2 (entries 5–7), it can be concluded that support has inhibition effects on activity. On the other side, when decreasing the catalyst mass, Chhp content increases, especially in initial phase of the reaction, as a consequence of autocatalytic reaction.

According to the results presented in Figs. 5 and 7, the selectivity is directly related to the yield. Hence, the yield and Chhp formation can be considered as critical parameters, which can be optimized by changing the cobalt content on the polymer support and the catalyst mass used in the catalytic run. The optimization should be balanced between the activation of the initiation through a decomposition of Chhp with a Co²⁺ ion and the inhibition of the bulk free radical reaction by the polymer or other support. The sequence should be (i) preparation of catalyst with maximum cobalt content allowed by the support properties, and (ii) gradual decrease of the prepared catalyst mass until a substantial amount of Chhp is formed in the reaction system.

Table 2
Oxidation of cyclohexane^a over various polymer supported catalysts.

Entry	Catalyst	Metal ion content (%)	Catalyst mass (g)	Yield (mol%)	Selectivity		
					Chn (mol%)	Chl (mol%)	Chhp (mol%)
1	Blank		0.00	0.52	3.3	18.3	78
2	PVP		0.50	0.62	15.4	16.7	68
3	CoPVP1	0.52	0.50	1.15	65.2	34.8	<1
4	CoPVP2	3.08	0.50	2.50	54.5	45.5	<1
5	CoPVP3	5.72	0.27	4.64	51.0	48.9	<1
6	CoPVP3	5.72	0.50	3.65	50.4	49.2	<1
7	CoPVP3	5.72	0.89	3.77	54.1	45.9	<1
8	CrPVP	5.03	0.50	0.52	74.4	23.9	2
9	CoPVP3 + CrPVP		0.27 + 0.23	2.69	52.0	46.2	2
10	CoPVP3 + CrPVP		0.02 + 0.48	0.49	73.1	24.5	2

^a Reaction conditions: 150 °C, 120 min, air pressure 2.8 MPa, and 35 g cyclohexane.

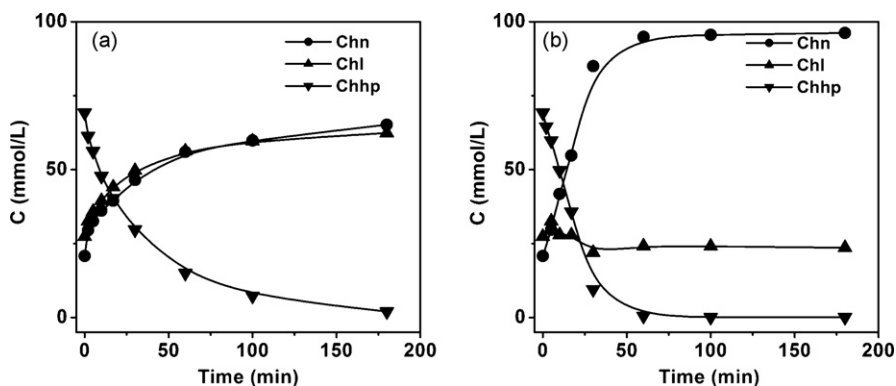


Fig. 9. Chhp decomposition and Chn, Chl formation using CoPVP3 (a) and CrPVP (b) catalysts.

3.5. Decomposition of cyclohexyl hydroperoxide

Due to the importance of the Chhp decomposition to the overall cyclohexane oxidation this process was tested separately. Namely, in order to maximize the amount of Chhp and to minimize its decomposition, oxidation was carried out as an uncatalyzed first step [53]. In this case, the subsequent decomposition of Chhp to Chl and Chn was performed in a separate catalytic step with various catalysts.

In our study the Chhp decomposition with cobalt catalyst, CoPVP3, and blank experiments were tested in the range of 40–70 °C. In this temperature range blank tests showed no activity. The first-order reaction law was applied to determine the basic kinetic parameters. The catalytic activity was expressed by a first-order decomposition rate constant. The activation energy and the corresponding frequency factor, obtained from Arrhenius plot, are 50 kJ mol⁻¹ and 8.7 × 10⁴ s⁻¹, respectively. The kinetic curves calculated from the obtained activation energy and the frequency factor for experimental data points obtained using cobalt catalyst are presented in Fig. 8.

The kinetic plots for Chhp decomposition and main product formation, using cobalt and chromium catalysts, are presented in Fig. 9. It can be seen that the Chhp decomposition is faster using a chromium catalyst than cobalt catalyst.

Nearly the same selectivity towards Chn and Chl is achieved using cobalt supported catalyst, while a higher selectivity towards Chn is achieved using chromium supported catalysts. Namely, Co²⁺ shows homolitic Chhp decomposition while Cr⁶⁺ shows heterolitic Chhp decomposition [54,55]. The chromium catalyst shows no activity in the oxidation of Chl.

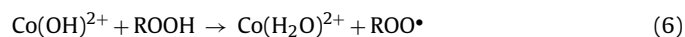
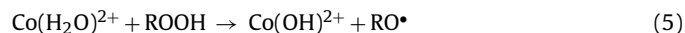
3.6. Effect of different metals

The yields and selectivities to Chl and Chn after 120 min, for cobalt and chromium catalysts are compared in Table 2 (entries 6 and 8). CrPVP catalyst shows higher selectivity to Chn, while CoPVP3 catalyst shows higher catalytic activity. The results from non-catalytic tests (entries 1 and 2) show a higher selectivity to Chhp and a low activity.

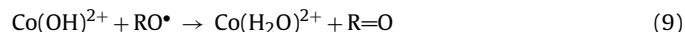
According to the presented results, CrPVP increases selectivity to Chn, while CoPVP3 is better initiator. In order to achieve good selectivity to Chn and high activity, mixed catalyst system (CoPVP3 + CrPVP) was tested (entries 9 and 10). Catalytic tests were done with different mass ratios of CoPVP3 and CrPVP. The results from first test (entry 9) suggest that chromium catalyst suppresses activity initiated by cobalt catalyst with no significant changes in selectivity (entry 9). The results from second test (entry 10) suggest that the presence of cobalt catalyst does not increase the activity of chromium catalyst with no significant changes in selectivity.

According to previous results (Section 3.5) and Table 2 (entry 8), it would be expected that the chromium catalyst contributes more significantly to Chn selectivity even in the presence of the cobalt catalyst. But the obtained results indicate that decomposition of Chhp is faster using the cobalt catalyst than the chromium catalyst or that there is no Chhp forming, so higher selectivity to Chn could not be achieved. In addition results show that, using the cobalt catalyst, the products Chl and Chn are not formed directly from Chhp, but from the free radical intermediary according to reaction (1).

Only if some quantity of Chhp, formed by autocatalytic process, is not decomposed by cobalt, it can be than decomposed by chromium. Since both cobalt and chromium catalysts are equally active in process of decomposition and cobalt catalyst is more active in aerobic oxidation, it can be concluded that cobalt catalyst is better initiator. Beside cobalt, other metals also decompose Chhp by Haber–Weiss mechanism (reactions (5) and (6)), but since they do not have high oxidation potential as cobalt, they are less efficient in reactions of initiation. Among other reactions, the one with Co³⁺ was suggested as reaction of initiation (reaction (7)):



Cyclohexyloxy radical mainly produces Chl (reaction (8)) and from proposed reactions and from Haber–Weiss mechanism (reactions (5) and (6)) it cannot be deduced why there is higher selectivity to Chn at the first phase of the reaction. One of the reactions that could explain higher selectivity to Chn at the beginning of the oxidation is reaction (9):



3.7. Leaching test and reuse of the catalyst

The possible leaching of active metal ion and reuse of the catalyst CoPVP3 were tested. The recycling efficiency of the used catalyst was determined by its reuse two more times under the same conditions. At the end of the oxidation cycles, catalyst was filtered, washed with acetone, and dried. The first reuse of the catalyst showed ~5% lower activity than in the first run. The catalyst activity in the second reuse was similar with the activity in the first reuse.

In order to estimate possible activity of leached metal ions, catalyst was separated from the solution by filtration, at the reaction temperature, before completion of the reaction. Tested filtrate shows activity similar to the one in the case of non-catalytic test

with characteristic formation of Chhp. As there was no formation of Chhp in tests with catalyst, the obtained results indicated that the decomposition of Chhp proceeds as heterogeneous. Additionally, the hot filtered solution from the catalytic tests was analyzed with aim to quantify amount of leached cobalt ions. For the samples taken in 80 min and 120 min of the reaction time, the detected amount of cobalt ions was 9 ppb and 20 ppb, respectively.

4. Concluding

The polymer supported catalysts with Co(II) and Cr(VI) ions were prepared and characterized and their catalytic activity and selectivity were tested in aerobic liquid-phase partial oxidation of cyclohexane and cyclohexyl hydroperoxide deperoxidation in mild conditions.

The polymer support functionalization by metal ions did not significantly affect its pore structure and textural properties. Cobalt ions in the catalyst are in octahedral coordination with one or more pyridine rings of the polymer support.

The results of catalytic tests showed that the change in selectivity towards cyclohexanone and cyclohexanol is mainly defined by the yield and the type of the catalyst with minor influence of temperature as a consequence of the reaction mechanism. The segments of the selectivity–yield curves for particular catalyst can be attributed to the reaction phases.

Testing the influence of the main products (Chn, Chl and Chhp) addition at the beginning of the oxidation on the reaction kinetics showed that the addition of Chl and Chn has detrimental effect on the initial reaction rate, while Chhp initiated the reaction faster than the catalyst itself by producing more radicals for the initiation. After the initial period the reaction rates and selectivity were independent of products addition.

An increase in the cobalt content results in an increase of conversion and in an associated decrease in selectivity to Chn. Product yield and Chhp formation in the catalytic system are used as critical parameters which can be optimized by changing the cobalt content on the polymer and the catalyst mass used in the catalytic run.

Chromium catalyst showed higher selectivity to Chn, while cobalt catalyst showed higher catalytic activity. The results for mixed catalyst system (CoPVP3 + CrPVP) showed that the chromium catalyst suppresses the activity initiated by cobalt catalyst with no significant changes in selectivity, while the presence of the cobalt catalyst does not increase the activity of the chromium catalyst with no significant changes in selectivity.

Leaching of cobalt ions was negligible and the catalyst can be reused without significant loss of activity indicating that the examined catalytic reactions proceed as heterogeneous.

The deperoxidation tests showed that the cobalt and chromium supported catalysts are very efficient in the decomposition of Chhp. Cobalt showed homolytic Chhp decomposition while chromium showed heterolytic Chhp decomposition with almost complete selectivity to cyclohexanone.

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