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2-Propen-1-ol hydrogenation and isomerisation on polymer-palladium complexes — effect of polymer matrix

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Abstract

Palladium complexes with different polymer ligands have been studied in hydrogenation and isomerisation of 2-propen-1-ol. Isomerisation of 2-propen-1-ol into propanal under hydrogenation conditions was observed over the palladium complexes with copolymer styrene and divinylbenzene (DVB) modified with iminodithiol groups (PdCl$_2$-CoP-SH). Palladium complexes with linear poly(2-vinylpyridine) (PdCl$_2$-PVP) and aminocellulose (PdCl$_2$-Cell-NH) were active for 2-propen-1-ol hydrogenation. XPS study of the initial catalysts as well as pre-treated with hydrogen and spent catalysts showed that Pd in active hydrogenation catalysts is reduced to Pd(0). Isomerisation catalyst PdCl$_2$-CoP-SH includes mainly Pd(II). Catalytic activity and selectivity of the obtained polymer-metal complexes depend on the structure of polymer matrix and the functional groups. The mechanism of hydrogenation is discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Polymer-palladium catalysts; 2-Propen-1-ol; Hydrogenation; Isomerisation

1. Introduction

Development of catalytic, macromolecule and coordination chemistry has led to the appearance of a new direction — catalysis on polymer-metal complexes. Preparation methods, properties of these types of catalysts are discussed in a number of reviews [1–3].

Palladium polymer catalysts are widely used in different organic synthesis [4–7]. Their behaviour depends on polymer composition and structure, conditions of catalyst preparation. It is important to investigate comparatively palladium complexes with various types of macromolecule ligands in one-model catalytic reaction.

In this paper we have studied hydrogenation of 2-propen-1-ol on palladium complexes with the following polymer ligands: poly(2-vinylpyridine), cellulose and copolymer styrene and divinylbenzene (DVB), modified with amino- or iminodithiol groups. The effect of polymer structure and nature of functional groups on the route of catalytic reaction has been studied.

2. Experimental

2.1. Catalysts

Industrial poly(2-vinylpyridine) ($M = 350,000$) and cellulose as well as synthesised macroporous beaded copolymers of styrene and DVB with amino-

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(4.0 meq/g) or iminodithiol groups [8] were used as ligands to polymer-metal catalysts.

Swelled precipitate of $PdCl_2$–poly(2-vinylpyridine) (PVP) complex is formed by interaction of the ethanol solutions of $PdCl_2$ and PVP [9]. This precipitate was kept in mother liquor for 3 days and then washed with ethanol and dried in air. Pd content in $PdCl_2$-PVP complexes was 26.5 wt.%. Pd active centres were located both on the surface and in the bulk of PMC.

Palladium complexes with cellulose and copolymer styrene with DVB, containing amino- (CoP-NH) and iminodithiol groups (CoP-SH), were prepared by sorption of $PdCl_2$ from ethanol solution on polymers. After complete binding of the Pd(II) with polymer matrices, the PMCs were washed with ethanol and dried in air. Pd content in the complexes was 5 wt.%.

Five percent Pd/Al_2O_3 was prepared by sorption of $PdCl_2$ from ethanol solution [10]. After 2 h of stirring the obtained catalyst was washed with ethanol, dried in air and used in catalytic hydrogenation.

$Pd(PyCl)_2$ *cis*-dichlorodipyridine palladium was prepared as referred in [11] by interaction of water solutions of potassium chloropalladate with pyridinium acetate. After 1 h of stirring, yellow precipitate was washed with water and dried in air.

2.2. Catalytic process

Hydrogenation and isomerisation of 2-propen-1-ol were carried out in thermostatic glass vessel with permanent shaking. The reactions were carried out in water (25 ml) at 25°C and atmospheric pressure of hydrogen. Catalysts were treated with hydrogen for 0.5 h before injection of 2-propen-1-ol into the reactor.

The stability of the catalysts was studied by hydrogenation of successive portions of 2-propen-1-ol on the same sample of the catalyst. Concentration of palladium [Pd] was 11×10^{-4} mol l^{-1}, concentration of 2-propen-1-ol was 0.18 mol l^{-1}. The Arrhenius plot was obtained for 15–55°C temperature range.

Reaction orders were determined at the following concentrations:

$$[Pd] = (1.1–5.0) \times 10^{-3} \text{ g-atom l}^{-1}$$

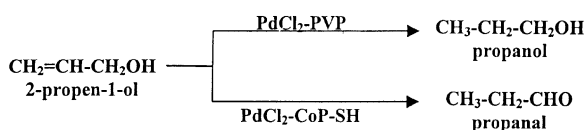$$[\text{2-propen-1-ol}] = 0.18–0.85 \text{ mol l}^{-1}$$

The reaction order for hydrogen was determined at 0.1–6.0 MPa pressure range in special steel reactor.

The analysis of hydrogenation and isomerisation products was carried out by GLC with flame ionisation detector. The conditions of the analysis were described in Ref. [10]. Based on the chromatographic analysis, the selectivity of hydrogenation ($S_{hydr.}$) and isomerisation ($S_{isom.}$) of 2-propen-1-ol were determined by the ratios of the yield of target product to the sum of all the reaction products.

The initial, treated with hydrogen and spent complexes have been studied by XPS method. XPS spectra were recorded using the ES-200B spectrometer (England) with Al Kα irradiation ($E = 1486.6$ eV). Calibration of the spectra was carried out according to the binding energy of C 1s electrons of hydrocarbons on the surface of samples [12]. (BE of C 1s was taken to be equal to 285.0 eV.) The contact time of the reduced and used samples of PMC with air in catalytic process was not more than 5 min.

3. Results and discussion

We found out that the reaction of 2-propen-1-ol hydrogenation is accompanied with the migration of the double bond of 2-propen-1-ol and formation of propanal as reaction product. The reaction route in the same conditions depends on the catalyst.

$$CH_2=CH\text{-}CH_2OH \xrightarrow{\begin{array}{c} PdCl_2\text{-}PVP \\ PdCl_2\text{-}CoP\text{-}SH \end{array}} \begin{array}{c} CH_3\text{-}CH_2\text{-}CH_2OH \text{ propanol} \\ CH_3\text{-}CH_2\text{-}CHO \text{ propanal} \end{array}$$

Carbonyl group of propanal as well as α,β-unsaturated aldehydes [13] are not hydrogenated on Pd catalysts under mild conditions.

The $PdCl_2$-PVP catalyst is highly active and stable in hydrogenation of successful portions of 2-propen-1-ol (Fig. 1a). Each subsequent portion of the four initial runs was hydrogenated at a higher rate than the previous one (Fig. 1b). It can be explained by the swelling of the $PdCl_2$-PVP and increasing the accessibility of Pd active centres located inside the polymer matrix. Selectivity of the process is about 98% (Table 1). Higher activity but lower selectivity was observed on Pd fixed on hydrophilic linear cellulose with amino- and iminodithiol groups ($PdCl_2$-Cell-NH and Pd-Cell-SH). The homogeneous $Pd(PyCl)_2$ and
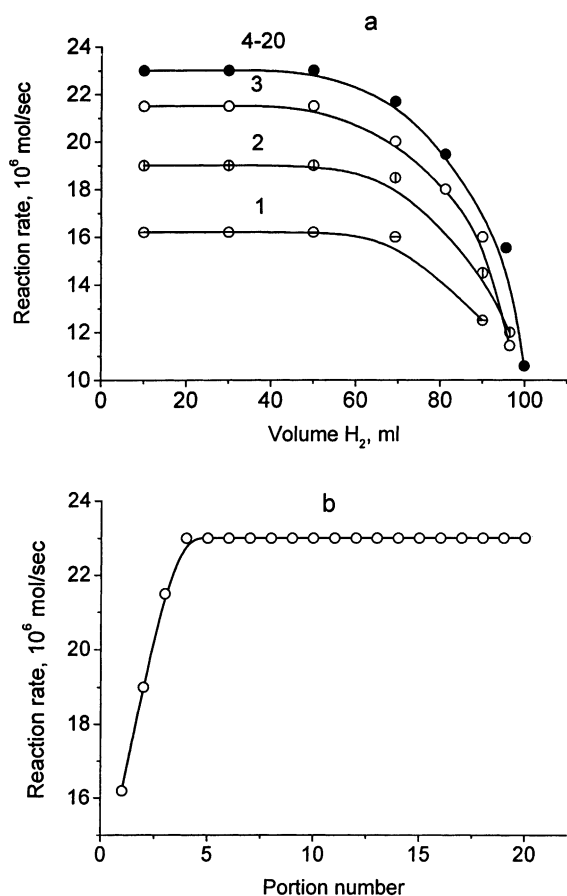
Fig. 1. Dependence of reaction rate on: (a) quantity of hydrogen uptake in hydrogenation of 20 successive portions of 2-propen-1-ol (0.3 ml each) in water (25 ml) on PdCl$_2$-PVP (0.03 g) at 25°C; (b) number of hydrogenated portions of 2-propen-1-ol.

heterogeneous 5%Pd/Al$_2$O$_3$ catalysts showed lower activity and selectivity (Table 1). The hydrogenation rate is sharply decreased (Table 1) over PdCl$_2$ bonded with hydrophobic macroprous copolymer styrene and DVB with both amino- and iminodithiol groups. The yield of propanal is high (about 80%) only on the PdCl$_2$-CoP-SH catalyst (Fig. 2a). Selectivity of the isomerisation is 74%.

In the first three isomerisation runs on the PdCl$_2$-CoP-SH, the selectivity of the process is increased from 74 to 90% and remained the same for the next 3–5 runs (Fig. 2b, curve 2). No Pd leaching from the catalyst was observed. This was confirmed by reuse of the washed spent Pd-CoP-SH catalyst

in 2-propen-1-ol isomerisation. The catalyst showed slightly worse catalytic activity and selectivity as compared to that for the freshly prepared catalyst.

Thus, palladium complexes with linear PVP and hydrophobic aminocellulose are good catalysts for 2-propen-1-ol hydrogenation. PdCl$_2$-PVP complex is the most selective one for this process (Table 1). PdCl$_2$-CoP-SH possesses the best isomerisation ability. The highest yield of propanal (90%) is obtained on this complex under the same conditions.

According to XPS, palladium in the spectrum of the initial PdCl$_2$-PVP complex showed a peak with binding energy (BE) of 338.2 eV (Table 2). Three energy states at 335.3, 336.5 and 338.2 eV were registered in the spectrum of the complex reduced by hydrogen. These peaks were assigned to Pd(0), Pd(I) and Pd(II), respectively [13,14]. Signals of Pd(II) and Pd(0) remain in the XPS spectrum of the spent catalyst.

The Pd in the spectrum of initial PdCl$_2$-CoP-NH complex is presented by a peak of Pd(II) with BE $3d_{5/2}$ equal to 337.4 eV (Table 2) [15]. For the H$_2$ treated complex, this peak is transformed into a wide band with a maximum at 335.9 eV, responding to Pd(II) and Pd(0) valence states. The spectrum of the spent catalyst consist of two separate peaks with BE of 335.6 and 339.3 eV that correspond to Pd(0) and Pd(II), respectively. Treatment of the Pd-cellulose complex with H$_2$ leads to complete reduction of Pd(II) to Pd(0) which is also seen in the spectrum of the spent catalyst (Table 2).

In the initial PdCl$_2$-CoP-SH complex as well as in the hydrogen-treated one, palladium remains in the same Pd(II) valence state. Only small amount of Pd(0) appeared in the spent catalyst which is testified by the shoulder at 335.3 eV in the XPS spectrum. Somewhat lower values for Pd(II) BE in this complex and the initial PdCl$_2$-Cell-SH (336.1–336.2 eV) can be explained by donor properties of the dithiol groups. Similar values of BE Pd $3d_{5/2}$ is usually assigned to Pd(I). We have studied Pd-polymer complexes modified with iminodithiol groups by ESP method. No signal of Pd(I) was registered in any of the tested samples.

The obtained XPS data can be explained by the effect of polymer ligands. It is proposed that Pd(II) forms stronger bonds with iminodithiol groups than with pyridine or aminogroups due to the chelate effect of the former groups [16]. Electron donor properties of

Table 1

Results of hydrogenation and isomerisation of 2-propen-1-ol (0.18 mol/l) on Pd-polymer complexes in water at 25°C and valence state of Pd (XPS data)

Complex	Functional group	H_2 uptake rate $\times$ 10^{-3} mol/s (g Pd)	$S_{hydr.}$ (%)	$S_{isom.}$ (%)	Pd valence state after H_2 treatment (XPS data)
Pd(PyCl)$_2$	–	0.05	67	33	Pd(II)
Pd/Al$_2$O$_3$	–	0.32	75	25	Pd(0)
PdCl$_2$-PVP	[-CH$_2$-CH-CH$_2$-]$_n$	1.06	98	2	Pd(II) 70%, Pd(I) 1%, Pd(0) 30%
PdCl$_2$-Cell-NH	Cel-O-CH$_2$-CH- OH / H$_2$N-CH$_2$	1.00	77	23	Pd(0), mainly
PdCl$_2$-CoP-NH	P─⟨O⟩─NH$_2$	0.01	68	32	Pd(0), mainly
PdCl$_2$-Cell-SH	Cel-O-CH$_2$-CH-OH / HC – HC - H$_2$C -HN-CH$_2$ / SH / SH	1.04	52	48	Pd(0)
PdCl$_2$-CoP-SH	P─⟨O⟩─NH CH$_2$ - CH - CH / SH / SH	0.005	26	74	Pd(II)

sulphur ligands are higher than those for N-containing groups [17]. This confirms formation of more stable complexes with iminodithiol groups. However, Pd in complexes with iminodithiol-cellulose matrix is easily reduced to Pd(0). Hydrophilic nature of cellulose seems to provide higher mobility of complex components and, therefore, weakening metal–chelate bonds as compared to the hydrophobic rigid-chain copolymer styrene and DVB.

In accordance with the results, active hydrogenation catalysts can be prepared by interaction of ethanol solution of PdCl$_2$ with PVP or hydrophilic aminocel-
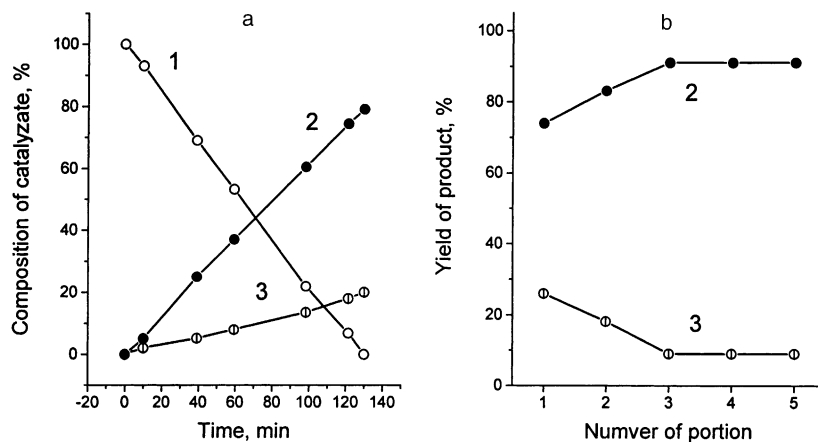

Fig. 2. Composition of reaction products (a) and yield of the products (b) of hydrogenation of the five successive portions of 2-propen-1-ol in water (25 ml) on the PdCl$_2$-CoP-SH (0.1 g) at 25°C. 1 — 2-propen-1-ol; 2 — propanal; 3 — propanol.

Table 2
XPS study of Pd valence state in palladium complexes with different polymer ligands

Catalyst	Pd $3d_{5/2}$ binding energy (eV)		
	Initial	Treated with H_2	After hydrogenation
PdCl$_2$-PVP	338.2	335.3	335.6
		336.5	
		338.2	338.0
PdCl$_2$-CoP-NH	337.4	335.9	335.6
		337.4	339.3
PdCl$_2$-Cell-SH	336.1	335.1	335.1
PdCl$_2$-CoP-SH	336.2	336.1	335.3
			336.9

lulose. Palladium in these catalysts is easily reduced to Pd(0) during pre-treatment with hydrogen.

Selective isomerisation catalyst is obtained by sorption of PdCl$_2$ on hydrophobic copolymer of styrene and DVB modified with iminodithiol groups. It is known [18] that isomerisation occurs easily in hydrogen medium. This proposal is confirmed by the fact that the reaction of isomerisation on this catalyst is not observed in argon atmosphere without hydrogen, and it is proposed that the first step of the process is metal hydride formation [19] with breaking off the NH–Pd bond of PdCl$_2$-CoP-SH.

To determine the mechanism of hydrogenation reaction on PMC and to compare it with mechanism on homogeneous catalysts, kinetics of 2-propen-1-ol hydrogenation has been studied on the most selective PdCl$_2$-PVP catalyst.

Reaction order for alcohol was found close to zero. Dependence of the initial rate on hydrogen pressure (0.1–2.0 MPa) is linear and emerges from the origin of coordinates. So the reaction order for hydrogen is equal to 1. The reaction order for catalyst is also 1. Hence, the empirical kinetic equation for hydrogenation of 2-propen-1-ol over PdCl$_2$-PVP is

$$W = \frac{dH_2}{dt} = k_{eff.} P_{H_2}[Pd] \tag{1}$$

In the first approximation, the reaction scheme may be presented by the equations:

$$Pd + H_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} PdH_2 \tag{2}$$

$$PdH_2 + C \overset{k_2}{\rightarrow} Pd + CH_2 \tag{3}$$

where C is 2-propen-1-ol. Thus steady-state reaction rate is

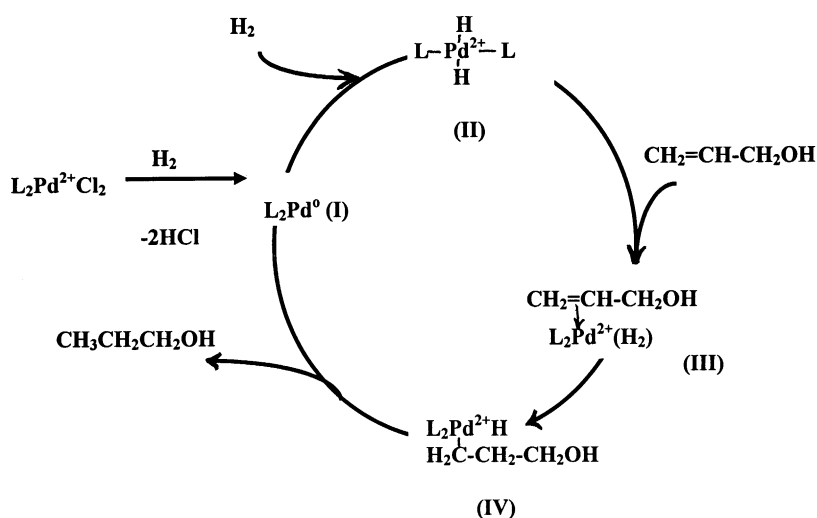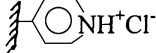$$-\frac{dH_2}{dt} = \frac{k_1 k_2[Pd][H_2][C]}{k_1 + k_2[C]} \tag{4}$$

Fig. 3. Scheme of catalytic cycle of 2-propen-1-ol hydrogenation catalysed by PdCl$_2$-PVP complex.

When the reaction (3) is fast, i.e. $k_2[C] \gg k_{-1}$, then the obtained equation (4) conforms to the empirical one (1). Thus, $k_{\text{eff.}} = k_1$.

Taking into account the hydrogen solubility in water, the rate constant of the second order is $3.8 \times 10^3 \, \text{l mol}^{-1} \, \text{s}^{-1}$ at $25°C$ and $P_H = 0.1 \, \text{MPa}$.

Dependence of the rate constant on the temperature in Arrhenius coordinates is linear. $E_{\text{act.}} = 31.7 \, \text{kJ mol}^{-1}$ ($H^{\#} = E - RT = 29.3 \, \text{kJ mol}^{-1}$; $S^{\#} = -0.077 \, \text{kJ mol}^{-1} \, °C^{-1}$). High negative entropy of activation indicates that the limiting step is formation of hydride complex. Thus, the following scheme of 2-propen-1-ol hydrogenation on $PdCl_2$-PVP complex can be suggested (Fig. 3) taking into account the mechanism of hydrogenation over homogeneous Pd catalysts [18–20]. At the first step, a treatment of the Pd(II) complex with hydrogen leads to formation of Pd(0) complexes (I on the scheme, Fig. 3). Both valence states of palladium have been registered by XPS methods in the samples treated with hydrogen [9]. Apparently, the HCl can react with nitrogen of free pyridine groups of PVP to form salts similar to quaternary ammonium ones: $\text{NH}^{+}\text{Cl}^{-}$. Further interaction of complex with hydrogen leads to the formation of the Pd(II) hydride complex (II on the scheme) by oxidative addition reaction. Interaction of this complex with 2-propen-1-ol leads to formation of π-complex (III), which transformed into Pd(II) alkylhydride σ-complex (IV).

Thus, mechanisms of catalytic reaction on homogeneous catalysts can be used to describe hydrogenation on heterogeneous polymer-metal complexes.

4. Conclusions

The reaction route depends on the Pd valence state and can be varied by changing of the polymer ligands. Swelling polymers (PVP and cellulose) with N-containing functional groups can be used for preparation of active and selective hydrogenation catalysts. Isomerisation of 2-propen-1-ol into propanal under hydrogenation conditions can be carried out over the palladium complexes with copolymer styrene and DVB modified with iminodithiol groups ($PdCl_2$-CoP-SH).

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