

Acetylene catalytic hydrochlorination over powder catalyst prepared by pre-milling of K_2PtCl_4 salt

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Abstract

Acetylene undergoes hydrochlorination by gaseous HCl in the absence of a solvent on the surface of pre-ground of K_2PtCl_4 powder. In the DCl atmosphere, *trans*-D-vinyl chloride is formed. The catalytic reaction proceeds on the active sites, which are lattice defects in the form of π -acetylene complexes generated by mechanical pre-activation of K_2PtCl_4 salt under acetylene. The limiting step of the reaction is acetylene chloroplatination. It involves a π -acetylene complex and HCl molecule, producing a new π -acetylene platinum(II) complex and intermediate β -chlorovinyl Pt(II) derivative. The protonolysis of the latter species results in vinyl chloride formation.

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1. Introduction

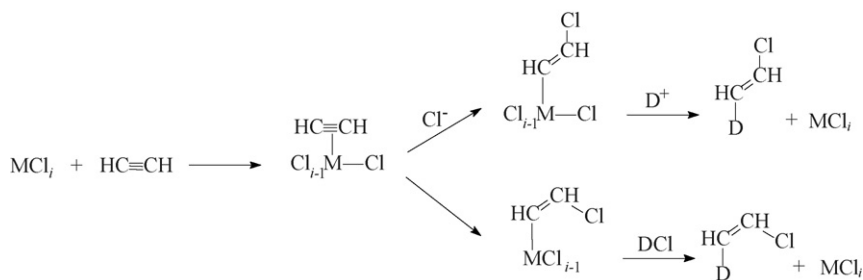
Modern requirements to chemical enterprises assume new process development aimed at lowering chemical pollution in order to decrease toxicity and the volume of waste in chemical industry. Such an approach called green chemistry [1,2] has leapt forward in the last decade. Solid phase mechanochemical synthesis and mechanoactivated reactions can be considered as one of the rapidly developing trends in the framework of green chemistry [2]. Mechanochemical methods open up high possibilities in heterogeneous catalysis: in particular, compounds regarded as catalytically inert could be involved in catalytic reactions in such a way (see, for example [3–5]). Active sites of mechanoactivated catalysts are usually associated [6] with

defects in crystalline solids. Such states are metastable due to retarded diffusive mobility in solids, and their surface concentrations can essentially exceed the equilibrium concentration as well as that which can be obtained by conventional methods of heterogeneous catalysts activation.

However, despite obvious advantages, a progress in this field is strictly restrained by limited data on pathways of mechanical energy transformation into structural defects of different pattern lattice. Most papers dealing with mechanoactivated catalysis are restricted to phenomenological description of the observed effects (see for example [7–11]). In order to clarify the question it is convenient to use relatively clear catalytic systems. For such a model reaction we chose the catalytic acetylene hydrochlorination. It is known [12], that alkyne hydrochlorination catalyzed by metal complexes (Scheme 1) begins with π -coordination of C–C triple bond to a metal center; further attack by external nucleophile on a π -coordinated acetylene yields the product of *trans*-addition of nucleophile and metal complex to the triple bond. The product of *cis*-addition is formed in the case of attack by a coordinated nucleophile. Protonolysis of the mentioned

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Scheme 1.

intermediates gives rise of the final product with the same stereochemistry.

The catalysis of acetylene hydrochlorination on the surface of mechanically pre-activated under acetylene K_2PtCl_6 salt (system 1) was found earlier [5]. A mechanical treatment of K_2PtCl_6 salt in vibration mill under acetylene forms [5] the active sites of catalyst, i.e. topologically bound couple $\{[PtCl_5^*]^- \cdots [PtCl_4]^{2-}\}$, where $[PtCl_5^*]^-$ is a platinum(IV) complex with a coordination vacancy. The reaction mechanism (Scheme 2) involves the acetylene chloroplatination step by coordinatively unsaturated Pt(IV) complexes (step 1) yielding the intermediate β -chlorovinyl Pt(IV) derivative. The role of platinum(II) complexes consists in complementary [13] reduction of β -chlorovinyl Pt(IV) complex into the corresponding Pt(II) derivative. The protonolysis of β -chlorovinyl Pt(II) derivative under the action of HCl (step 3) yields vinyl chloride and recovers the active site of catalyst. The limiting step of the catalytic reaction is the acetylene chloroplatination reaction. The reaction proceeds [5] under the action of HCl molecule in a concert process via six-membered transition state TS1.

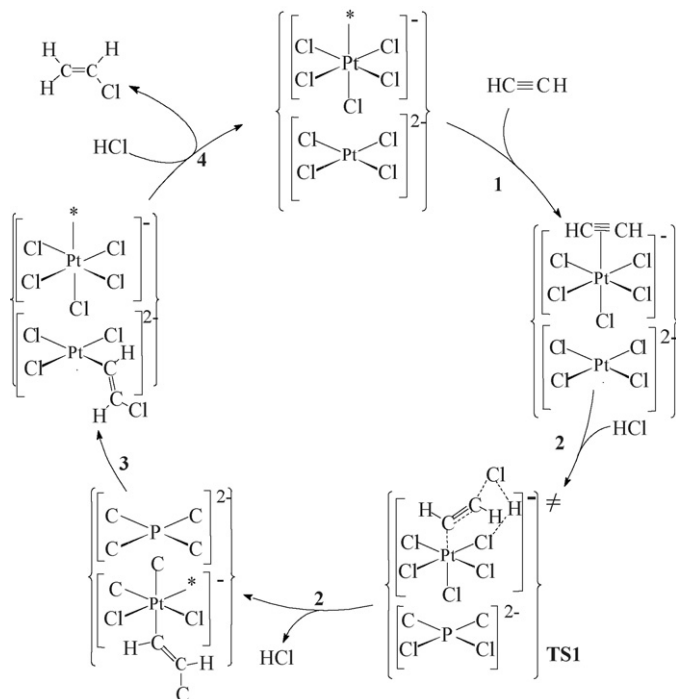
Mechanically pre-activated K_2PtCl_4 salt was inactive under the same conditions [5]. The situation is different in aqueous solutions: Pt(II) chloride complexes catalyze acetylene hydrochlorination, whereas Pt(IV) complexes do not show any catalytic activity [12]. The lack of catalytic activity of mechanically pre-activated chloro platinum(II) complexes was rather unexpected. It is known [14], that mechanical treatment of K_2PtCl_4 powder in vibrational mill generates $[PtCl_3^*]^-$ species with coordination vacancies. Their fraction averages no less than 5% from total amount of surface platinum(II) complexes, and these particles are capable to π -coordinate ethylene forming Zeise's salt. One could assume that acetylene is also capable to get in the coordination sphere of such a particle with coordination vacancy forming π -complex, and following transformations of the latter will finally give vinyl chloride. The aim of the present work is the search for effects of mechanical activation of solid K_2PtCl_4 with respect to heterogeneous catalysis of acetylene hydrochlorination and elucidation of the catalytic reaction mechanism.

2. Experimental

The K_2PtCl_4 (0.3 g) powder was pre-ground for 1.5 h before a run. The increase of the grinding time does not considerably influence the kinetics of the reaction. A vibratory micromill MMVE-0.005 was used with specific power intensity ca. 15 W/kg. The reactions were carried out in a closed vibratory reactor of 10.7 ml capacity containing grinding bodies made of glass. Specific area of the powders was determined by BET procedure from argon desorption.

The reactor containing mechanically pre-activated catalyst was blown through with dry argon, filled with acetylene or gaseous HCl and closed with a rubber seal. Then, ca. 1 ml of acetylene or gaseous HCl was fed into reactor via a rubber seal. All the reactions were carried out at room temperature and continuous shaking providing a kinetic mode of reactions passing. Acetylene consumption and products accumulation were monitored by GLC using an LKhM-8-MD chromatograph with a flame-ionization detector and equipped with data acquisition system MultiChrom Ampersand. The sampling of the gas phase was performed by means of a dozing syringe of the fixed volume through the rubber gasket.

The platinum salt K_2PtCl_4 was prepared according to standard techniques [15] and was recrystallized and preliminary dried for 3 days in a desiccator at 120–140 °C before use. The



Scheme 2.

increase of the drying time did not considerably influence the kinetics of the reaction. All further manipulations with the salt were carried out in a dry glove box.

Acetylene was prepared according to standard techniques [16]. Gaseous HCl (DCl) was received by the reaction of calcinated KCl and H₂SO₄ (D₂SO₄). The gases obtained were dried over P₂O₅ or calcinated CaCl₂ before use. Gaseous HBr was received by anthracene bromination reaction [16]. Receiving of pure isotopomer DCl is difficult because of fast isotope exchange with traces of moisture. The liberated gaseous HCl/DCl mixture was collected in thoroughly dried syringe of 50 ml capacity. Then the IR gas cuvette with windows made from KBr and preliminary cleaned out by blowing of dry argon was filled up with HCl/DCl mixture from the syringe. A gas portion (~1 ml) was carried by a dry syringe from the cuvette into the reactor used for monitoring the acetylene hydrochlorination kinetics. The DCl content in a DCl/HCl mixture was estimated as the ratio of areas under IR bands of DCl and HCl in the IR spectrum taking into account that at the same conditions the intensities of HCl bands are approximately twice higher than for DCl bands [17]. The FTIR Perkin-Elmer Spectrum BX instrument was used for determining of isotope content in the HCl/DCl mixture.

¹H NMR measurements were performed using a Varian GEMINI instrument operating at 200 MHz.

The X-ray diffraction study was performed on a DRON-3 instrument in monochrome Cu K α irradiation using Ni-filter.

The X-ray photoelectron spectroscopy (XPS) measurements were performed using an EC-2402 instrument equipped with energy analyzer PHOIBOS-100_SPECS, ion gun IQE-11/35, and slow electron gun FG-15/40 for compensation of dielectric surface charging. The spectra were excited by Mg K α ($E = 1253.6$ eV, $P = 300$ W) irradiation. The Pt 4f-level spectra were factorized in pairs of components with parameters ΔE_b ($4f_{5/2} - 4f_{7/2}$) = 3.3 eV, $I_{4f_{5/2}}/I_{4f_{7/2}} = 0.75$, full width on the mid-height (FWHM) was equal to 1.1 eV. The factorization was performed by Gauss-Newton method. The component's area were determined after background subtraction by Shirley method [18].

The diffuse reflection of light, IR-spectra for mechanoactivated K₂PtCl₄ powders was registered in the mixture with BaF₂. The Bruker Tensor 27 instrument equipped with diffuse reflection of light device Specac was used.

3. Results

The mechanical pre-activation of dry K₂PtCl₄ salt results in formation of acetylene hydrochlorination catalyst (system 2) as well. The yield of vinyl chloride based on the amount of acetylene consumed in the reaction is close to 100%. No noticeable decrease in catalyst activity is observed after realization of 3 turnover numbers based on bulk catalyst or ~300 based on platinum located on the surface of the catalyst. Addition of water vapor in the reactor causes a significant decrease in the rate of reaction, and in the presence of ca. 1 μ l of water the reaction does not proceed. Apparently, the cause of earlier reported [5] lack of catalytic activity of mechanoactivated chloro platinum(II) complexes lies in suppressive action of water vapor. It is noteworthy,

that in the system 1 so strong suppressive action of water vapor was not observed.

For the most part the non-deuterated vinyl chloride H₂C=CHCl is formed in the atmosphere of HCl/DCl (mole ratio ~ 1:3) with admixture of monodeuterated product which has a *trans* configuration just as in the system 1 (¹H NMR in CDCl₃ solution, δ , ppm: 5.52 (H^a), 6.31 (H^b); $J(\text{H}^a\text{H}^b) = 14.75$, $J(\text{H}^b\text{D}) = 1.03$ Hz):



3.1. The reaction kinetics

The zero-order rate law describes acetylene uptake in the atmosphere of HCl in the system 2 in contrast to the system 1, where the first-order rate law for acetylene consumption was observed [5]. The noticed in the system 2 zero-order rate law for acetylene uptake can be explained by, for example, if the substrate is fast chemisorbed on the surface of mechanically activated salt, and its surface concentration is independent of acetylene partial pressure. Such a chemisorption in a case under consideration could proceed through acetylene bonding in π -complex by platinum(II) species with coordination vacancies.

The first-order rate law describes vinyl chloride accumulation in conditions of large excess of acetylene over HCl (atmosphere of acetylene):

$$v(t)_{\text{VCl}} = v_{\text{VCl}}^{\infty} \cdot (1 - \exp(-k_{\text{ef}}t)), \quad (2)$$

where $v(t)_{\text{VCl}}$ and v_{VCl}^{∞} are amounts of liberated vinyl chloride at the time moment t and at the end of the reaction, respectively, k_{ef} is the observed rate constant for HCl uptake. The k_{ef} value within the limits of experimental error coincides when the reaction is consecutively carried out in the same reactor once charged with acetylene. This can be a consequence of the circumstance when alteration of HCl concentration on the catalyst surface should be neglected. The implementation of the first-order rate law for vinyl chloride accumulation in the heterogeneous reaction (1), obviously, means that HCl is adsorbed according to Henry's equation (cf. [5]):

$$[\text{HCl}]_{\text{ads}} = K \times P(\text{HCl}), \quad (3)$$

where $[\text{HCl}]_{\text{ads}}$ is the surface concentration of HCl, K is the constant of adsorption equilibrium, and $P(\text{HCl})$ is the partial pressure of HCl. In this case the k value for pseudofirst order rate constant for HCl uptake in the absence of gaseous phase has to be associated [5] with experimentally determined value k_{ef} by the ratio:

$$k_{\text{ef}} = \frac{k}{1 + \alpha\lambda}, \quad (4)$$

where $\alpha = (RT \times K)^{-1}$, $\lambda = V_{\text{g}}/S_{\text{sp}} \times m$, V_{g} is the volume of gaseous phase of the reactor, S_{sp} and m are, respectively, the specific surface and mass of the catalyst, R is the absolute gas constant, and T is a temperature.

Eq. (4) satisfies experimental dependency of k_{ef} on the catalyst mass at $k = (1.3 \pm 0.4) \times 10^{-3} \text{ s}^{-1}$ and

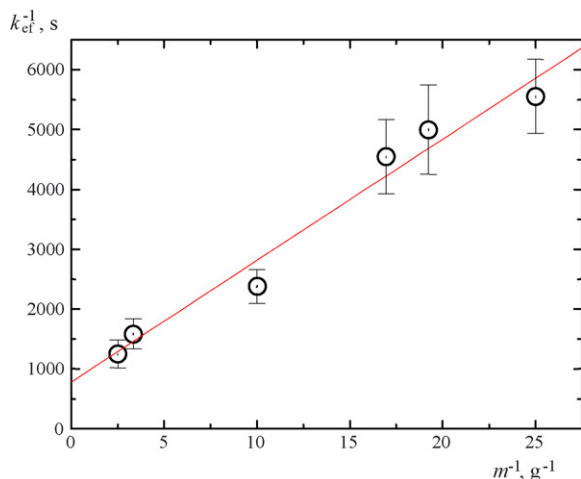


Fig. 1. The dependence of k_{ef} on the mass of the catalyst. The linear anamorphosis of Eq. (5).

$K = (1.0 \pm 0.4) \times 10^{-8} \text{ mol m}^{-2} \text{ Pa}^{-1}$ (Fig. 1). Let us use k and K values obtained above for the TOF magnitude estimation. The rate of vinyl chloride accumulation on 1 m^2 of catalyst surface in the case when the surface is to the limit covered by acetylene molecules (see above) and the partial pressure of HCl is 1 atm comes to $\sim 1.3 \times 10^{-6} \text{ mol/m}^2 \text{ s}$. The catalyst specific surface is $4.2 \text{ m}^2/\text{g}$, hence, the TOF value is equal to $\sim 5.5 \times 10^{-6} \text{ mol/g s}$.

The kinetic data obtained allow us to determine the value of kinetic isotope effect in the system 2. The kinetic data processing for vinyl chloride accumulation liberating at acetylene excess and in the presence of HCl/DCl mixture according to Eq. (5)

$$v(t)_{\text{VCl}} = v_{\text{VCl}}^{\infty} \cdot [1 - x \cdot \exp(-k_{ef} \cdot t) - (1 - x) \cdot \exp(-k_{ef}^{\text{D}} \cdot t)], \quad (5)$$

where x is a mole fraction of HCl in the starting HCl/DCl mixture, k_{ef}^{D} is effective rate constant for DCl uptake, using the determined earlier $k_{ef} = (6.4 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$ value for 0.3 g catalyst gives (Fig. 2) the value $k_{ef}^{\text{D}} = (1.6 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$.

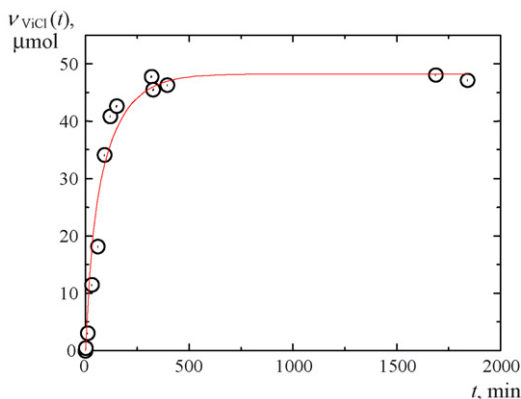


Fig. 2. Typical curve for vinyl chloride accumulation in the presence of HCl/DCl isotopomer mixture. The mole fraction of HCl in the starting mixture $x = 0.2$, the catalyst mass is 0.3 g; the points correspond to experimental data, the enveloping curve is calculated according to Eq. (5) at $k_{ef} = 6.4 \times 10^{-4} \text{ s}^{-1}$ and $k_{ef}^{\text{D}} = (1.6 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$.

Hence the KIE magnitude for the system 2 equals to (4.0 ± 0.9) and actually appreciably exceeds the value of 1.9 for KIE determined [5] in the system 1.

Thus, the mechanical pre-activation of the dry K_2PtCl_4 salt under acetylene forms the heterogeneous catalyst for acetylene hydrochlorination. The different character for kinetic dependencies and sharp distinction in the KIE values for the systems 1 and 2 indicate different reaction mechanisms in these systems.

3.2. The nature of the catalytic active sites

The reaction proceeds very slowly on the surface of mechanically pre-activated in air K_2PtCl_4 salt. The preliminary treatment of K_2PtCl_4 under acetylene, ethylene or propylene is necessary to get the active catalyst. From comparison of X-ray diffraction patterns for K_2PtCl_4 samples mechanically activated in air and acetylene (Fig. 3) it follows that the dispersed medium content does not influence the sample texture: pretreatment under acetylene leads merely to the decrease of the granule's size and partial amorphization of near-surface layers. Such a decrease of crystallite size for the platinum salt sample milled under acetylene in comparison with the sample treated in air is also confirmed by approximately twofold increase in the catalyst specific surface magnitude S_{sp} : (4.2 ± 0.8) against $(2.7 \pm 0.5) \text{ m}^2/\text{g}$.

The X-ray photoelectron spectra and peak synthesis for Pt 4f-level of platinum atoms for K_2PtCl_4 samples mechanically activated in air (sample 1) and acetylene (sample 2) are presented in Fig. 4. The maxima of couple components in Fig. 4 correspond to Pt 4f_{7/2}- and Pt 4f_{5/2}-levels of platinum atoms. The Pt 4f-level of platinum atoms XPS spectra were factorized in three couple of components denoted as a , b and c . The a component (E_p Pt 4f_{7/2} = 71.9 eV) corresponds to the $\text{Pt}(\text{OH})_2$ phase [19], which could originate due to hydrolysis of near-surface layer K_2PtCl_4 complexes by residual water vapor under conditions of mechanical treatment. The a component intensity for the sample 2 is less in comparison with sample 1 (Table 1). The main component in Pt 4f-spectra of samples 1 and 2 is component b (E_p Pt 4f_{7/2} = 72.8 eV), corresponding to the Pt^{2+} -states of K_2PtCl_4 [19]. The component c (E_p Pt 4f_{7/2} = 73.4 eV) can be attributed to Pt^{2+} -states of the species with coordination vacancies $\text{K}_2\text{PtCl}_3^+$ formed [14] under mechanical treatment of the starting material. The appearance for the sample 1 of $\text{K}_2\text{PtCl}_3(\text{H}_2\text{O})^+$ or $\text{K}_2\text{PtCl}_3\text{OH}$ complexes besides K_2PtCl_3 is possible, but further increase of their contribution could be limited by hydrolysis. A noticeable increase in the intensity of component c for the sample 2 is observed. It could result from a stabilization of $\text{K}_2\text{PtCl}_3^+$ species owing to acetylene π -coordination. An increase of the ratio $I(\text{Pt } 4f)/I(\text{Cl } 2p)$ observed for the sample 2 also agrees with increase of $\text{K}_2\text{PtCl}_3^+$ species contribution. The mechanical pretreatment of K_2PtCl_4 in propylene atmosphere leads to the same effects.

It is noteworthy, that a considerable increase in the portion of the species characterized with a high E_p value on the surface of catalyst which are presumably positively charged defects of the lattice $\text{K}_2\text{PtCl}_3^+$ occurs. This increase correlates with an appre-

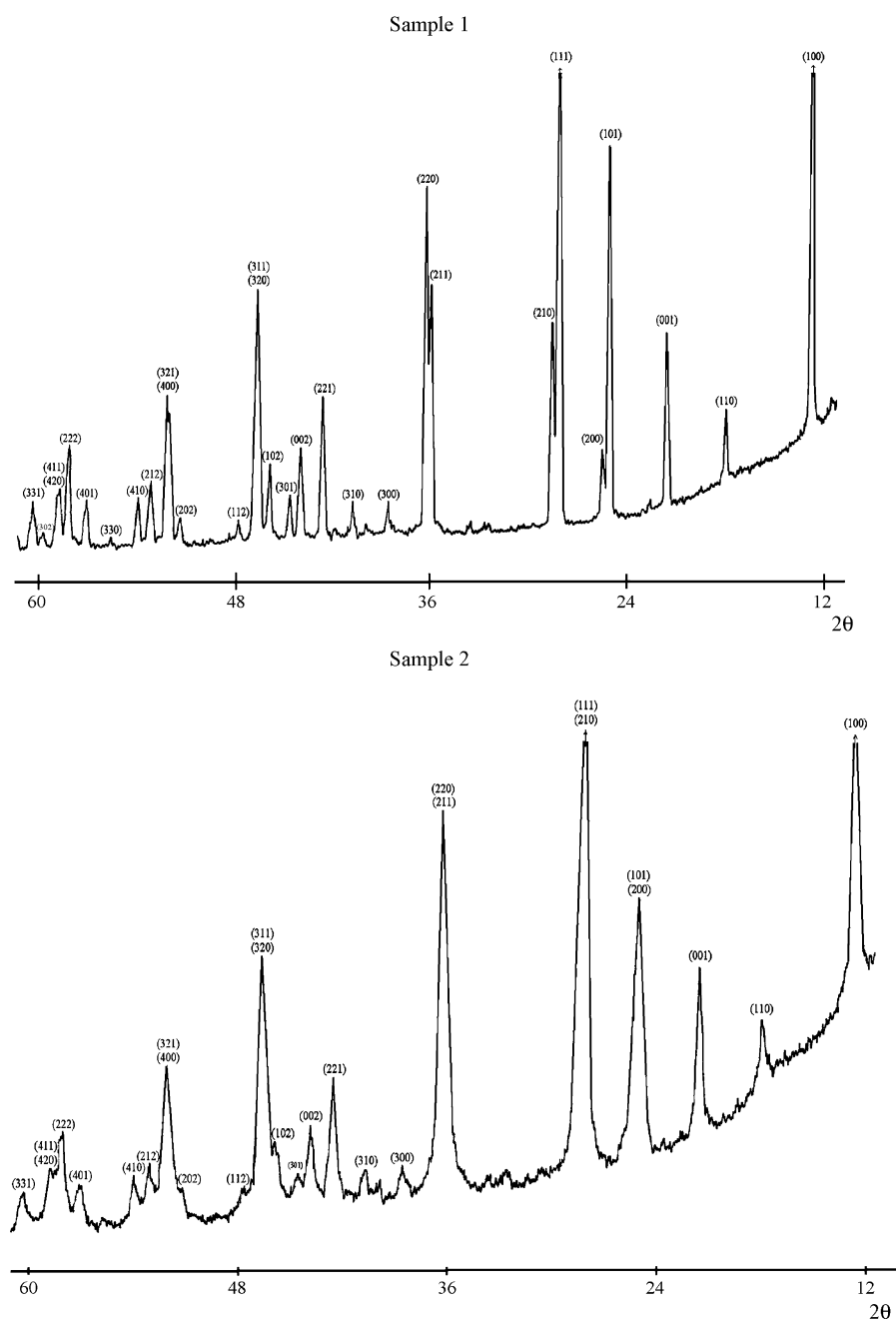


Fig. 3. Diffraction pattern for polycrystalline K_2PtCl_4 samples mechanically pre-treated in air (sample 1) and acetylene (sample 2).

Table 1

Components, peak energies (E_p , eV), relative intensities of the peaks (I , %) and intensities ratio $I(Pt\ 4f)/I(Cl\ 2p)$ for samples 1 and 2 after mechanochemical treatment of K_2PtCl_4 salt in air (sample 1) and acetylene atmosphere (sample 2)

Component	<i>a</i>	<i>b</i>	<i>c</i>	$I(Pt\ 4f)/I(Cl\ 2p)$
Assignment	Pt^{2+} , $Pt(OH)_2$	Pt^{2+} , K_2PtCl_4	Pt^{2+} , $K_2PtCl_3^+$	–
E_p Pt 4f _{7/2} (eV)	71.9	72.8	73.4	–
<i>I</i> (%)				
Sample 1	14 ± 2	74 ± 2	12 ± 2	1.55
Sample 2	9 ± 2	47 ± 2	44 ± 2	1.63

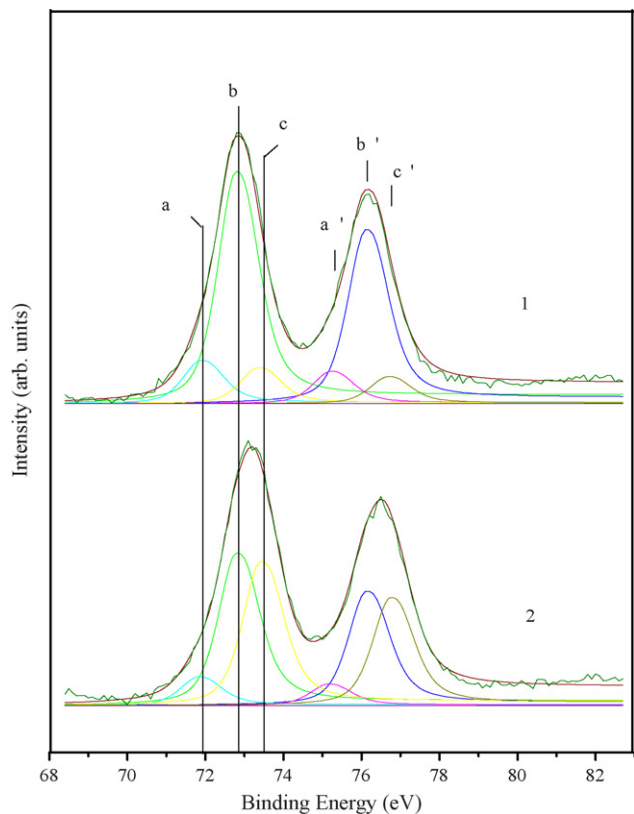


Fig. 4. Peak synthesis for Pt 4f-level XPS-spectrum of platinum atoms for K_2PtCl_4 samples mechanically activated in air (sample 1) and acetylene (sample 2).

ciable growth in activity of the catalyst.¹ Apparently, there is an observed increase in the catalytic activity of the platinum salt pre-ground in the unsaturated compounds when compared to the catalyst pre-activated in air. This can be explained by two factors. The first one is the extension of a specific surface of catalyst. The second factor consists in the π -complexes formation on the surface of the catalyst, which serves as a catalytic active site. From the XPS data (Table 1) and specific surface values one could expect that catalytic activity of the sample 2 would be approximately six times more than for sample 1.

Independently this suggestion is confirmed by the following observations:

- The reactor containing 0.3 g K_2PtCl_4 salt pretreated in air (sample 1) was filled by propylene for a few minutes, after that propylene was removed from the reactor by flow of dry argon. Then the reactor was filled with acetylene, which is capable [20] of replacing the olefins from π -complexes. Next it was closed with a rubber seal, so propylene accumulation in the gas phase of the closed reactor was controlled. The rate for propylene accumulation consisted of two portions. A small amount, $(0.9 \pm 0.1) \mu\text{mol}$, of propylene was liber-

¹ The mentioned above twofold increase in specific surface of the catalyst pre-activated in acetylene, propylene or ethylene in comparison with one pre-ground in air, cannot be a reason for the noticeable increase in the activity of the catalyst.

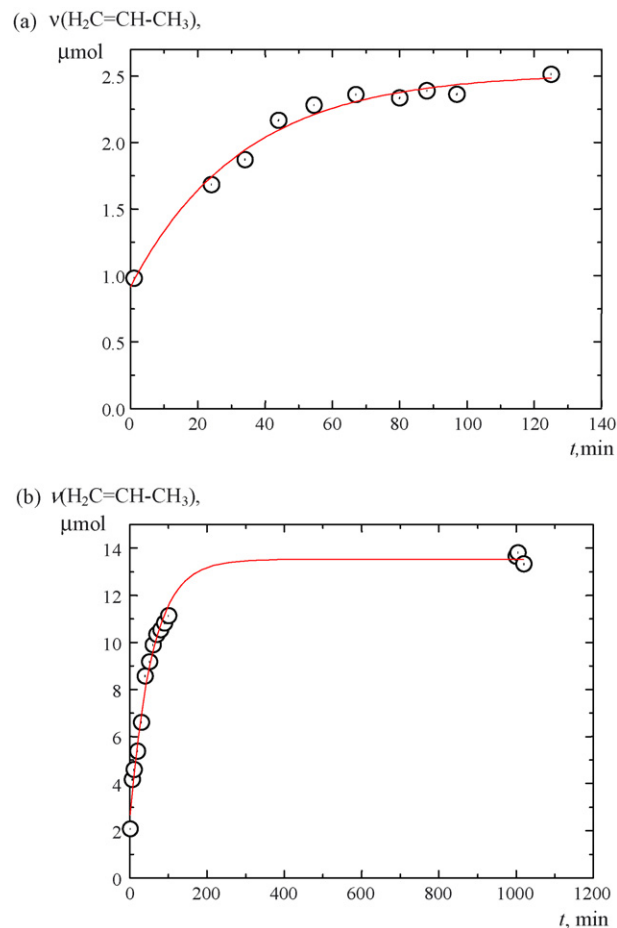


Fig. 5. Typical curve for propylene accumulation in the displacement reaction by acetylene; propylene was preliminary sorbed on the surface of K_2PtCl_4 salt pre-activated in air (a) and in propylene atmosphere (b).

ated immediately, and the rest amount, $(1.6 \pm 0.1) \mu\text{mol}$, of propylene evolved slowly. This follows the first-order rate law (Fig. 5a). One could assume that the portion of propylene liberated immediately was originally physically adsorbed on the catalyst surface and the other portion was chemisorbed in the form of π -complexes with coordinatively unsaturated species $K_2PtCl_3^+$, formed under conditions of the starting material pre-activation.

- The same procedure with 0.3 g of the catalyst pre-activated in propylene atmosphere (sample 2) led to the immediate release of $(2.5 \pm 0.3) \mu\text{mol}$ of initially adsorbed propylene followed by slow evolving of $(11.0 \pm 0.3) \mu\text{mol}$ of chemisorbed propylene (Fig. 5b). The ratio of chemisorbed propylene amounts in the samples is equal to (6.8 ± 0.5) and is in agreement with the estimated ratio of active sites quantities from the XPS data.

The direct evidence for π -acetylene complexes formation in the near-surface layers of the catalyst was acquired through the IR-spectroscopy method of diffuse reflection of light. While the C–C bond stretching vibration of acetylene is generally inactive in IR-spectrum it can occur if acetylene is π -coordinated to a transition metal [21]. This peculiarity allows us to detect of

acetylene π -complexes formation. The reactor containing 0.3 g K_2PtCl_4 salt pre-ground in air was filled by acetylene for a few minutes, after that acetylene was removed from the reactor by flow of dry argon. The weak band at 2095 cm^{-1} corresponding to acetylene C–C bond stretching vibration was found in the diffuse reflection of light IR-spectrum for the treated in such a way platinum complex. The intensity of this band is in order of magnitude greater for the sample obtained in the same way, but if K_2PtCl_4 salt was pre-activated in acetylene atmosphere.

Conclusively, mechanoactivation of the platinum salt in the unsaturated compounds atmosphere results in increase practically in order of magnitude of π -complexes amount, which serve as catalytically active sites of the acetylene hydrochlorination catalyst. It is noteworthy that π -ethylene platinum complex, Zeise's salt $KPt(\eta^2-C_2H_4)Cl_3$, possesses a rhombic lattice in contrast to tetragonal lattice of the starting platinum salt [22]. Therefore, such a π -coordination of unsaturated compounds to the formed on the surface species with coordination vacancies should result in additional stresses in the K_2PtCl_4 matrix and as a consequence should lead to the crystallites downsizing in an agreement with the experimental observations.

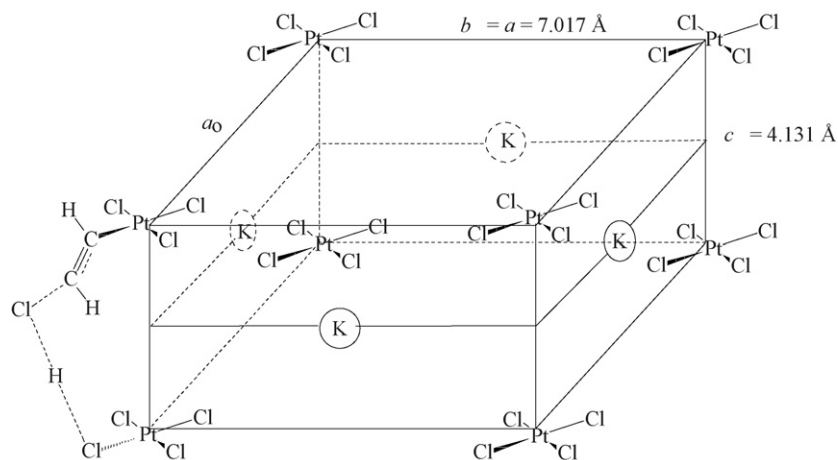
4. Discussion

To comprehend the reaction (1) mechanism it is essential to know the origin of the chlorine atom, which is a part of vinyl chloride formed. The sources of chlorine atoms could be HCl molecules, ligands of the chloro platinum complexes and interstitial chloride ions, arising [14] under mechanical treatment of K_2PtCl_4 salt. Reasoning from the hydrochlorination stereochemistry, the inner sphere chloride ligands participation should be excluded [12]. Relatively small amounts of the interstitial chloride ions formed under K_2PtCl_4 mechanical treatment could not provide the catalytic reaction run. The last conceivable possibility is left: chlorine atom, which is a part of vinyl chloride formed, originates from HCl molecule. This is true because mainly vinyl bromide is formed in the reaction of acetylene with HBr catalyzed by pre-activated K_2PtCl_4 salt, and vinyl chloride is generated merely as traces.

Thus, in the system 2 as well as in the system 1, the hydrochloride molecules are involved in the two reaction steps. The first one is acetylene chloroplatination step leading to the intermediate β -chlorovinyl Pt(II) derivative formation and the second one is the protonolysis of the latter species. Taking into account, that the KIE value in the system 2 at comparable rates of acetylene hydrochlorination is essentially differ from the KIE value in the system 1, one could conclude that in the both systems the limiting stage is acetylene chloroplatination step.

Let us consider the probable mechanism for acetylene chloroplatination step. A sufficiently great KIE value in the system 2 argues in favor of a transition state close to linear and symmetric one [23]. We may assume that the reaction proceeds via HCl molecule attack onto π -acetylene complex, located on the (1 0 0) crystal plane. A local positive charge of the crystal lattice defect in the form of monoanion $[Pt(\eta^2-C_2H_2)Cl_3]^-$ is favorable to a chlorine atom of polar HCl molecule attack onto π -acetylene complex. The reaction proceeds as a concert process in which concurrently with the rupture of H–Cl bond and Pt–Cl bond in the platinum complex neighboring with π -acetylene complex the new Pt–C, C–Cl and H–Cl bonds are formed (Scheme 3).

The distance between platinum complexes on the (1 0 0) crystal plane 4.131 \AA , in a contrast to 7.017 \AA on the (0 0 1) crystal plane [22], and bonds lengths of H–Cl (1.274 \AA) C–Cl (1.719 \AA) and C=C (1.332 \AA) [24] geometrically permit to accomplish almost linear transition state. The reaction should be practically thermoneutral because the H–Cl bond rupture is compensated by formation of the same new bond, and Pt–Cl bond rupture is almost compensated by C–Cl bond formation, so the transition state should be nearly symmetric as well. The stoichiometric consequence of such a reaction must be the formation of a coordinatively unsaturated $[PtCl_3]^*$ complex on the same crystal plane in addition to σ -vinyl platinum(II) derivative. The $[PtCl_3]^*$ complex forms with acetylene π -complex regenerating in that way the active site of catalyst, and the protonolysis of β -chlorovinyl Pt(II) derivative under the action of HCl yields vinyl chloride and the starting $[PtCl_4]^{2-}$ complex. Such a mechanism explains the high stereoselectivity of the catalytic reaction and excludes extremely unfavorable heterolysis of H–Cl bond with H^+ formation in the absence of solvation.



Scheme 3.

Acknowledgements

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