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Enantioselective catalytic hydrogenation of activated ketones using polymer-containing nanocomposites

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ABSTRACT

In this paper formation and stabilization of platinum nanoparticles in the hypercrosslinked polystyrene matrix modified with (−)-cinchonidine and the use of this catalyst in the reaction of ethylpyruvate C=O bond enantioselective hydrogenation are discussed. The series of the catalysts has been synthesized and the influence of the reducing agent nature and the modification method on catalytic properties of nanocomposites have been investigated. All the catalysts developed were characterized by transmission electron microscopy, X-ray photoelectron spectroscopy, X-ray fluorescent analysis, low temperature nitrogen adsorption, and CO adsorption followed by diffuse reflectance infrared Fourier transform spectroscopy.

1. Introduction

Chiral compounds play an increasingly important role in the vital functions of live organisms. Numerous biologically active food supplements, vitamins, hormones, medicines are specific enantiomers. Nowadays the advantages of chiral compounds are well-recognized leading to their increased production and sales [1]. Among others, optically active esters of hydroxycarboxylic acids are considered very promising chiral monomers for synthesis of biodegradable polymers. Their characteristics such as crystallinity, melting temperature, solubility considerably exceed similar characteristics of the corresponding polymers obtained from racemate [2] and thus, optically active esters of hydroxyacids are in great demand.

Optically pure substances can be obtained by their extraction from natural products along with the use of different technological methods such as synthesis, spontaneous crystallization, decomposition of one enantiomer in racemate and asymmetric catalysis. The catalytic approach is becoming increasingly popular as the catalysts can be reusable and the pure chiral products can be obtained with a limited effort [3–5].

To provide highly effective heterogeneous asymmetric catalysis, well-defined catalysts with a specific structure should be used, while the conventional catalysts are unlikely to satisfy this requirement. Specificity of the catalyst structure can be provided by the use of the catalyst, which contains metal nanoparticles (NPs) with a chiral surface created either by adsorption of chiral modifiers or by the use of chiral supports [1,5–9].

Adsorption of chiral modifiers on the surface of metal-containing catalysts leads to the systems which are effective in hydrogenation of ketoester and diketone carbonyl groups [10]. The most studied modified catalysts in the C=O bond hydrogenation are the catalysts on the basis of nickel modified with α-oxy- and α-aminooxyacids. Thus, Ni-tartaric acid catalysts were successfully applied in enantioselective hydrogenation of β-ketoacids, β-ketoesters, β-diketones and β-ketosufonates [11–13]. At the same time, the hydrogenation of methyl esters of α-, γ-, δ-ketoacids by these catalysts occurs with low enantioselectivity, which indicates the major role of the distance between carbonyl groups of the substrate. As other modifiers for nickel Renay, S-alanine, S-valine, S-leucine, S-malic acid, S-2-aminobutyric acid, (*R*,*R*)-tartaric acid, S-glutamic, S-ornithine, and S-lysine were used [11]. Modification of Pt with cinchona or periwinkle alkaloids is also used in asymmetric C=O bond hydrogenation [3,14–16].

The enantio-differentiation in such systems is due to different activation energy of the metal–substrate modified complexes having different configuration. Thus, the reactions with modified

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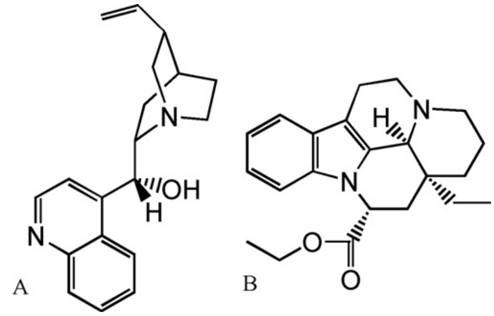

Fig. 1. The examples of the typical modifiers for heterogeneous platinum and palladium catalysts: (A) (−)-cinchonidine (CD); (B) (−)-dihydroapovincaminic acid ethyl ester.

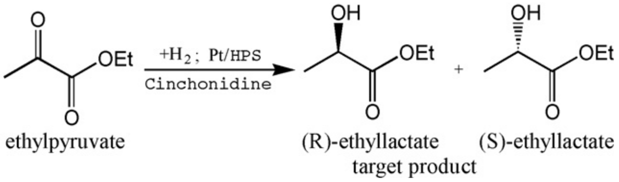

Fig. 2. The scheme of ethylpyruvate hydrogenation.

catalytic systems often depend on the modifier structure and the metal NP size. It is assumed that the modifier and the reagent are co-adsorbed on the surface of the metal NPs and on the larger particles, the adsorption of chiral modifiers is higher [17]. The presence of groups, which are able to coordinate with metal (for example, nitrogen containing group) near the stereogenic center [18], and the bulkiness of substituents [3] are the major features of the alkaloid modifiers (Fig. 1).

Heterogeneous catalysts modified with (−)-cinchonidine (CD) and (−)-10,11-dihydrocinchonidine are frequently used in enantioselective hydrogenation of activated ketones. The hydrogenation of pyruvate derivatives with 70–90% ee leading to the lactate is an example of such a process. Lactate is used as a component of pharmaceuticals and as a preservative in food industry. Alumina is the most frequently used support for the catalyst preparation [4,5,19–22].

As is known, platinum modified with cinchona alkaloids, their derivatives or synthetic optically active substances can be an efficient catalyst of enantioselective reactions [19–21]. If the platinum and modifiers are deposited on the inorganic support, the catalysts are brittle leading to the abrasion and leaching of platinum from the support. Alternatively, we suggest incorporation of Pt NPs in the pores of polymeric network, in particular, in hypercrosslinked polystyrene (HPS) [23]. HPS has several unique properties including high specific surface area and mechanical robustness. Due to presence of well-defined pores, HPS allows one to grow the metal NPs with a narrow particle size distribution, preventing NP aggregation and loss during the catalytic reaction [24,25].

Here we report the synthesis and characterization of Pt NPs in HPS, the catalyst modification with cinchonidine and the study of the heterogeneous Pt/HPS catalysts in a model reaction: enantioselective hydrogenation of ethylpyruvate (Fig. 2) with ee of 75% (R-lactate).

2. Materials and methods

2.1. Materials

The hypercrosslinked polystyrene was purchased from Purolite Int. (UK), as Macronet MN 270/38600 type 2/100 (designated as MN-270). It was washed with acetone and water twice and purified under vacuum. Sodium hydrogen carbonate ($NaHCO_3$), sodium hydroxide (NaOH), hydrochloric acid (HCl) and hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) were obtained from Reakhim (Moscow, Russia) and used without purification. Reagent-grade THF, methanol, toluene, ethyl pyruvate (EtPy), cinchonidine (CD) were purchased from Aldrich and used as received. Distilled water was purified with Elsi-Aqua water purification system.

2.2. Catalyst synthesis

All the catalysts were obtained by the impregnation of hexachloroplatinic acid into the HPS. Some of the Pt-containing catalysts were reduced by hydrazine or sodium borohydride. The five catalysts were synthesized: (i) Pt/HPS (not reduced), (ii) Pt/HPS1 (reduced by hydrazine), (iii) Pt/HPS2 (reduced by sodium borohydride), (iv) Pt/HPS3 (reduced by sodium borohydride and washed with the complex solvent containing THF), (v) Pt(CD)/HPS (Pt/HPS3 impregnated with cinchonidine). The catalysts were tested in the reaction of ethylpyruvate hydrogenation using CD as a modifier.

2.3. Ethylpyruvate hydrogenation methodology

The hydrogenation was conducted batchwise in a PARR 4200 apparatus which provides independent control over parameters such as EtPy and the catalyst concentrations, temperature, hydrogen pressure, and the stirring rate. Required amounts of the catalyst, CD (if it is used) and 20 ml of solvent were loaded into reactor and stirred at 600 rpm for 10 min hydrogen atmosphere (1 bar). Then EtPy was loaded in the reactor.

2.4. GC analysis

Catalysate analysis was conducted by gas chromatography in isothermal regime using Kristallux-4000 equipped by FID and chiral capillary column MACHAREY-NAGEL FS-LIPODEX E.

2.5. X-Ray fluorescence analysis (XRF)

Pt content was estimated by X-ray fluorescence measurements performed with a Spectroscan – Maks – GF1E spectrometer (Spectron, St-Petersburg, Russia) equipped with Mo anode, a LiF crystal analyzer and a SZ detector. The analyses were based on the Co Kα line and a series of HPS/Pt standards prepared by mixing of 1 g of HPS with 10–20 mg of standard Pt compounds. The time of data acquisition (10 s) was constant.

2.6. Liquid nitrogen physisorption

Nitrogen physisorption measurements were conducted at the boiling point of liquid nitrogen using a BECMAN COULTER SA 3100 apparatus (COULTER CORPORATION, Miami, Florida). Samples were degassed in a BECMAN COULTER SA-PREP apparatus for sample preparation (COULTER CORPORATION, Miami, FL), at 120 °C in vacuum for 1 h, prior to the analysis.

2.7. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) was performed with JEOL JEM1010 transmission electron microscope at accelerating voltage of 80 kV. Ground Pt/HPS powders were embedded in epoxy resin. Upon completion of resin cure, the embedded powders were microtomed at ambient temperature, and the resulting thin sections were placed on a carbon-coated copper grids and imaged.

2.8. X-ray photoelectron spectroscopy analysis (XPS)

X-ray photoelectron spectra were obtained using Mg Kα ($h\nu$ = 1253.6 eV) radiation with a ES-2403 spectrometer (provided by the Institute for Analytic Instrumentation of the Russian Academy of Sciences, St. Petersburg, Russia). All data were acquired at an X-ray power of 200 W. Survey spectra were recorded at a step of 1.0 eV, and high resolution spectra were recorded at a step of 0.1 eV. Samples were allowed to outgas for 30 min before analysis and were sufficiently stable during examination.

2.9. CO adsorption followed by diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy

DRIFT spectra were recorded at ambient temperature with a Nicolet 460 Protégé spectrometer equipped with a diffuse reflectance attachment. The samples were placed in a tube supplied with a KBr window and 200 scans were collected from 400 to 6000 cm^{-1} with a 4 cm^{-1} resolution. CO adsorption was performed at ambient temperature at an equilibrium pressure of 20 Torr.

3. Results and discussion

3.1. Characterization of the catalytic systems

Because HPS has high specific surface area, narrow pore size distribution, and ability to swell in any solvent (including non-solvents for initial polymer), it is well-suited as the catalyst support. Specific surface area data based on low temperature nitrogen adsorption are presented in Table 1. Parent HPS has a very high specific surface area which is typical for the systems containing micropores. In fact, this material contains also meso- and macropores. After impregnation with platinic acid, the surface area considerably drops, indicating filling of the significant part of micropores (Table 1, sample Pt/HPS). After platinic acid reduction with hydrazine only marginal increase of the surface area is observed (Table 1, sample Pt/HPS1), while after reduction with $NaBH_4$, the five-fold increase of the specific surface area is observed (Table 1. Pt/HPS2). This demonstrates that in the former case, the Pt NPs or reduction products still block the micropores, while in the latter case, the pores are available for N_2 sorption. The decrease of the specific surface area of the Pt/HPS3 catalyst compared to Pt/HPS2 is likely due to the partial pore blockage when reduction is carried out in the complex solvent, which was applied during the Pt/HPS3 preparation. The decrease of the specific surface area of Pt(CD)/HPS3 is likely due to the sorption of cinchonidine.

To determine the platinum content and its loss compared to a calculated value during the catalyst preparation, the X-ray fluorescence analysis was conducted (see Table 2). These results show that platinic acid is fully adsorbed by a polymeric matrix during formation of Pt/HPS and practically no loss is observed after reduction.

Table 1
Specific surface area of the catalysts from the liquid nitrogen adsorption data

Sample	Surface area (BET model)	
	S_{BET} (m^2/g)	k_{BET}[a]
HPS	1485	0.99949
Pt/HPS	101	0.99945
Pt/HPS1	120	0.99984
Pt/HPS2	506	0.99984
Pt/HPS3	340	0.9999
Pt(CD)/HPS3	311	0.99959

[a] k_{BET} is the correlation coefficient (BET model).

Table 2
Results of the XFA analysis

Sample	Platinum content (%)
Pt/HPS	5.81
Pt/HPS1	5.74
Pt/HPS2	5.75
Pt/HPS3	5.53

Table 3
Results of the XPS analysis

Sample	Binding energy (eV)			
	Pt 4f$_{7/2}$		Pt(0)/Pt(II)	Cl 2p
	I	II		
Pt/HPS	71.3	73.8	8.2	201.2
Pt/HPS1	71.3	–	–	200.6
Pt/HPS2	71.3	–	–	200.6
Pt/HPS3	71.3	–	–	200.0
Pt	71.3			–
H_2PtCl_6	75.6	–	–	

The XPS data (Table 3) demonstrate that platinum in the reduced catalysts is only in the form of Pt(0), while in the Pt/HPS sample we see a mixture of Pt(0) and Pt(II) in the ratio Pt(0)/Pt(II) = 8.2. As was reported earlier [26], incorporation of H_2PtCl_6 in HPS using THF solution in the presence of water leads to the THF oxidation and reduction of Pt(IV) species.

Fig. 3 shows the TEM images and their size histograms of Pt/HPS and Pt/HPS3. Close mean particle sizes (1.9 ± 0.5 nm for Pt/HPS and 2.1 ± 0.8 nm for Pt/HPS3) reveal that platinum compound particles (formed by interaction of platinic acid with the solvent) are the precursors of the Pt NPs formed after reduction. At the same time, some mass transfer takes place during reduction leading to a slight increase of the NP size and size distribution: otherwise, the Pt NPs after reduction would be smaller due to higher density of metallic platinum compared to a platinum compound.

Investigation of the CO adsorption on the catalysts using DRIFT spectroscopy (Fig. 4) shows that for all the reduced samples as well as for the catalyst treated with CD only terminal orientation of the CO molecules is observed (2067–2070 cm^{-1}), which is due to the formation of small platinum NPs. CO adsorption over the unreduced catalyst was not observed. We believe that this is due to the presence of the Pt(II) species and the absence of the continuous Pt(0) surface.

The presence of the only terminal CO adsorption near 2067–2070 cm^{-1} for all catalysts and the similar band location for both non-modified and modified catalysts allow us to assume the presence of the only one type of organometallic centers for the substrate binding.

3.2. Investigation of the catalytic properties of the Pt/HPS systems

In our kinetic studies the influence of the degree of the platinum reduction, solvent nature, a modifier (CD) concentration, a substrate-to-catalyst concentration ratio, a process temperature, hydrogen pressure on enantioselectivity of the process and activity of the catalysts were investigated. For the catalysts Pt/HPS, Pt/HPS1, Pt/HPS2, and Pt/HPS3 the modifier was added in the reaction medium, while for Pt(CD)/HPS, the catalyst was impregnated with CD prior the reaction.

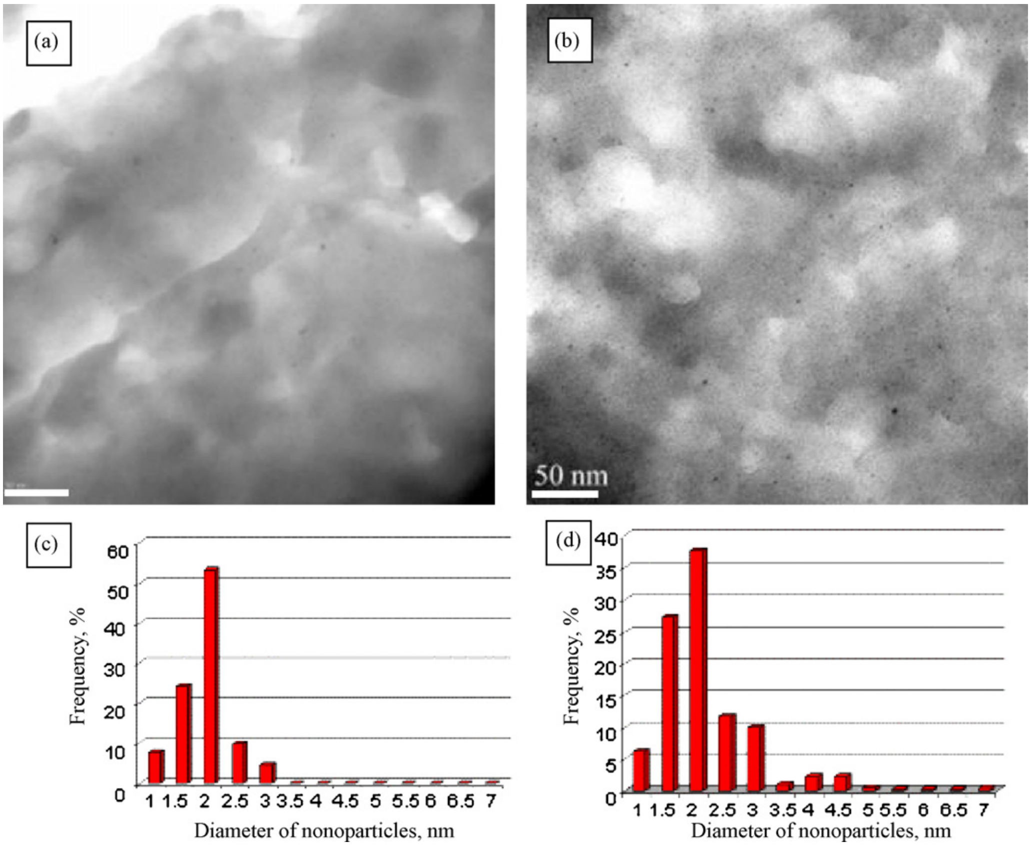

Fig. 3. TEM images of Pt/HPS (a) and Pt/HPS3 (b) and particle size distribution histograms of Pt/HPS (c) and Pt/HPS3 (d).

The results of the enantioselective hydrogenation were characterized using the ee of the product at the 100% conversion according to the following equation:

$$ee = \frac{[R] - [S]}{[R] + [S]} \times 100\%$$

where [R] is the R-ethyllactate concentration; [S] is the S-ethyllactate concentration; ee is the enantiomeric excess.

The enantioselectivity was found to decrease with the increase of the dielectric constant of the solvent in the series: toluene, dichloroethane, tetrahydrofuran, isopropyl alcohol, methanol (Fig. 5). Variations of the modifier concentration and the catalyst loading show no noticeable influence on the enantioselectivity (Fig. 6) up to 800 mol(substrate)/mol(Pt); further increase of this ratio results in the enantioselectivity decrease.

The pressure also shows no noticeable affect on the enantioselectivity of the reaction. For the Pt/HPS, Pt/HPS1 and Pt/HPS2 catalysts, the highest enantioselectivity was observed at the temperature range of 40–50 °C, while for Pt/HPS3 and Pt(CD)/HPS, the optimal temperature was at 20–25 °C.

The activity of the catalytic systems was estimated depending on the relative rate of the reaction at 20% conversion, which remained constant for all the catalysts (0.164 mol(substrate)/(mol(Pt) s). The highest ee values achieved at the optimal conditions for each catalyst are presented in Fig. 7. The use of the reduced catalysts resulted in the higher ee compared to that of the unreduced catalyst. The investigation of the reducing agent nature influence showed that the catalyst obtained after the sodium borohydride reduction is more efficient than that after the hydrazine reduction. It is known that the nature of the reducing agent can strongly influence the metal nanoparticle formation in a polymeric matrix. In our case, we believe that the Pt NPs after the hydrazine reduction block micropores so only a fraction of the NP surface is available for catalysis, while after the $NaBH_4$ reduction the NPs are better available.

The activation energies of ethylpyruvate hydrogenation for all the investigated catalytic systems are presented in Table 4. The apparent activation energy of the Pt/HPS3 catalyst is lower than those of Pt/HPS1 and Pt/HPS2, which can be explained by the modifying influence of complex solvent components on the platinum NP surface.

The influence of the catalyst modification method on the enantioselectivity of hydrogenation has been studied. Normally, modification of the catalysts with cinchona alkaloids occurs *in situ* when the modifier is added in the reaction medium, thus the part of the modifier always remains in the solution and requires additional purification of the final product even at high ee. It can be avoided if the modifier is deposited on the catalyst before the reaction and if the modifier is not washed off during the reaction. We expected that in the case of HPS, such stable adsorption is possible because HPS is an excellent sorbent with the high specific surface (~1500 m^2/g, BET analysis). The Pt/HPS3 catalyst impregnated with the CD solution in a complex solvent (Pt(CD)/HPS3) and dried under vacuum allowed the highest enantiomeric excess of 75%. Such modification of the catalyst allows excluding the modifier from the reaction mixture, which is extremely important for the industrial application.

The comparison of the catalytic systems reported here with the conventional catalyst Pt/Al_2O_3 is presented in Table 5. These data show that the best catalytic systems among studied in this work is Pt(CD)/HPS3, i.e., the catalyst modified with CD prior to the catalytic reaction. It also allows us to carry out the reaction at lower hydrogen pressure and an ambient temperature with high ee (75%).

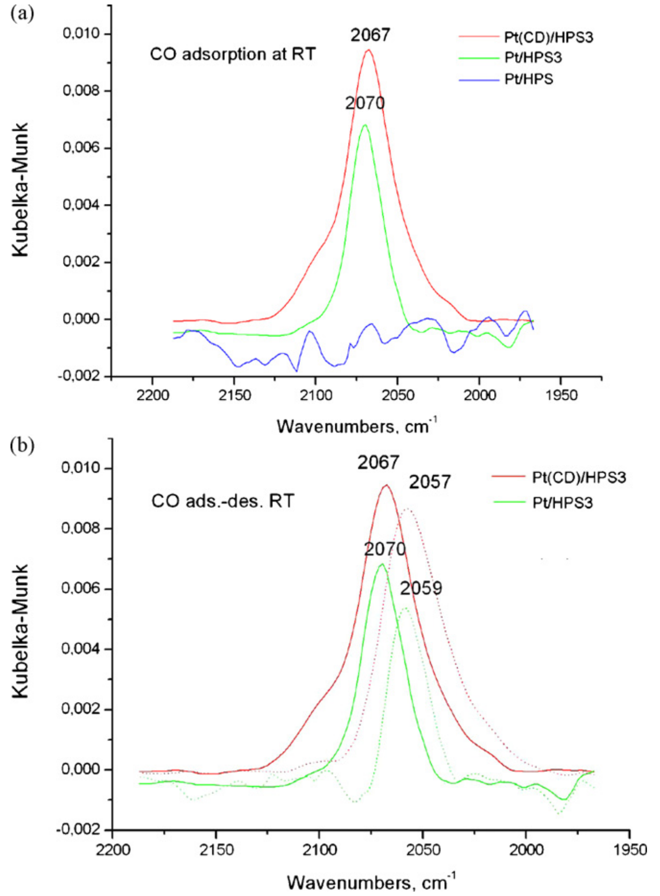

Fig. 4. DRIFT-spectra of CO adsorbed on the platinum nanoparticles in HPS (a) for the unreduced and reduced and (b) non-modified and modified catalytic systems. (Solid line, show adsorption; doted line, show desorption).

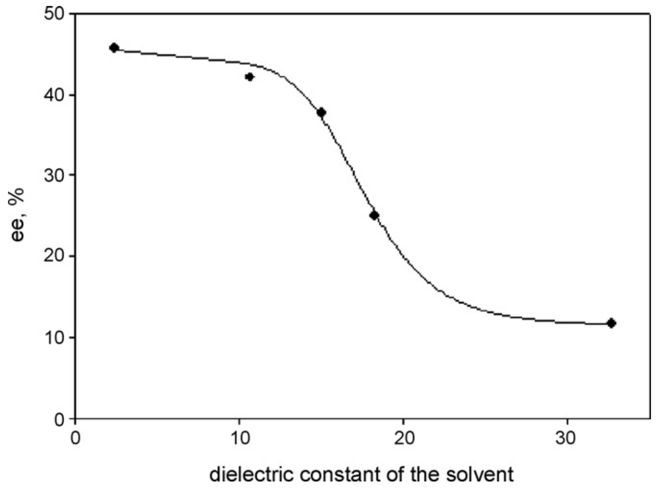

Fig. 5. Dependence of the ethylpyruvate hydrogenation enantioselectivity on the dielectric constant of the solvent (for Pt/HPS2).

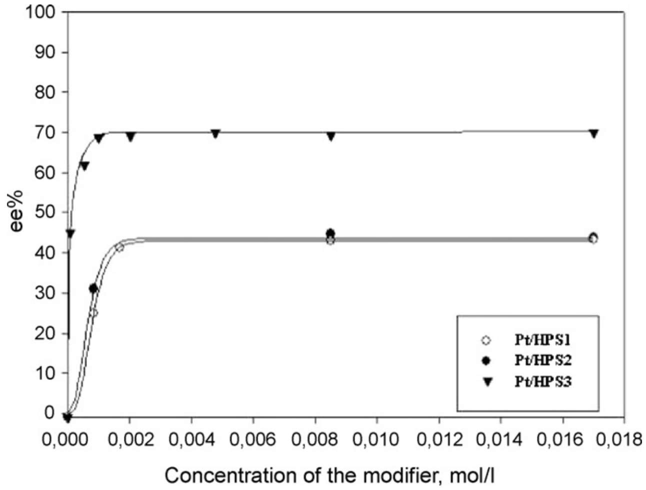

Fig. 6. Influence of the modifier concentration on the enantioselectivity of ethylpyruvate hydrogenation.

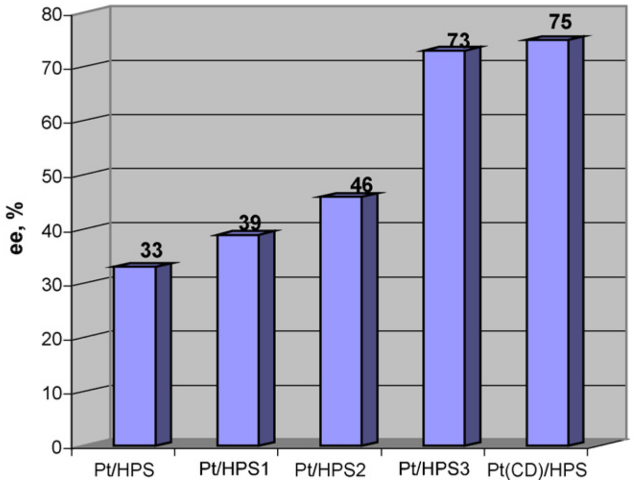

Fig. 7. Enantiomeric excess of the ethylpyruvate hydrogenation product for the Pt/HPS catalysts in toluene at 100% conversion.

The investigation of the Pt/HPS3 stability during the repeated catalytic reactions of the ethylpyruvate hydrogenation showed that the ee remains almost constant and the relative rate only slightly decreases in the repeated use, while the activity of the industrial Pt/Al_2O_3 with the same modifier decreases four-fold after the five uses [27]. The higher stability of the Pt/HPS3 catalyst compared to Pt/Al_2O_3 can be explained by the fact that platinum nanoparticles are stabilized within the small pores of HPS. Moreover, the latter has high mechanical stability. This results in the absence of the catalyst abrasion during the reaction in contrast to the Pt/Al_2O_3 catalyst.

Based on the catalytic and physicochemical studies the hypothesis on the formation of two types of catalyst active centers is proposed: “metallic” and “organometallic” [15]. The modifier adsorbs on the platinum NPs and takes part in the formation of “organometallic” centers. Then the substrate adsorbs on the “organometallic” centers as well (Fig. 8). Molecular hydrogen adsorbs on the “metallic” centers giving chemisorbed hydrogen

Table 4
Activation energies of the ethylpyruvate hydrogenation

Catalyst	Activation energy, E_a (kJ/mol)
Pt/HPS	–
Pt/HPS1	43
Pt/HPS2	43
Pt/HPS3	22
Pt/HPS3	22

Table 5
Comparison of catalytic systems for enantioselective ethylpyruvate hydrogenation

Catalyst	Solvent	*P* (MPa)	*T* (K)	ee (%)
Pt/HPS	Toluene	0.9	328	33
Pt/HPS1	Toluene	0.9	328	39
Pt/HPS2	Toluene	0.9	318	46
Pt/HPS3	Toluene	1.5	298	73
Pt(CD)/HPS3	Toluene	1.5	298	75
	Toluene	5.0	296	76
Pt/Al_2O_3 (5% Pt) cinchonidine Engelhard E 4759	Toluene	4.0	298	73
	Dichlorethane	5.0	293	74
	EtOH	7.0	343	73
	i-PrOH	0.7	283	60

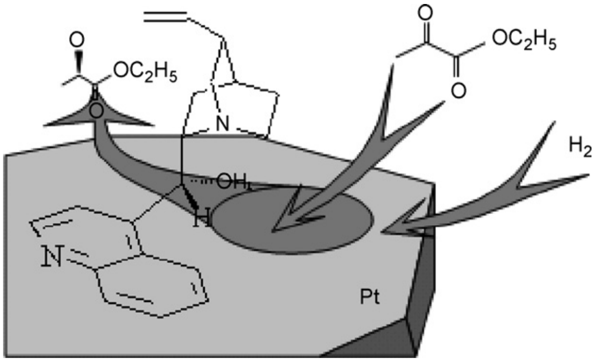

Fig. 8. Cartoon of the substrate adsorption on the "organometallic" site.

atoms, which diffuse over the surface to the substrate adsorbed on the "organometallic" centers.

4. Conclusion

Here the potential of asymmetrical catalysis in C=O bond hydrogenation is briefly reviewed, and the importance of these reactions for modern industry is demonstrated. Catalytic properties of platinum NPs incorporated in HPS are investigated. These catalysts demonstrate high enantioselectivity in ethylpyruvate hydrogenation.

Modification of the reduced Pt/HPS catalyst (in particular, Pt/HPS3) with cinchonidine by impregnation before the catalytic reaction allows us to exclude the additional stage of the product purification from the modifier, when the latter is introduced with the substrate into the reaction medium.

The enantioselectivity of activated ketone hydrogenation with the Pt/HPS catalysts was found to depend on the solvent, reducing agent, temperature, substrate, catalyst and the modifier concentrations.

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