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Effective Ligandless Pd-containing Catalysts for Triple Bond Hydrogenation and Cross-Coupling in Environmentally Friendly Solvents

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This study is devoted to the investigation of Pd nanoparticle (NP) formation in polymeric environment of hyper-crosslinked polystyrene (HPS) of MN270 type and study of their catalytic properties in several industrially important catalytic reactions such as Suzuki cross-coupling by the example of 4-bromoanisole and phenylboronic acid and triple bond hydrogenation of acetylenic compounds (2-methyl-3-butyne-2-ol, dehydrolinalool and dehydroisophytol). Influence of Pd precursor nature (chlorine containing salt or palladium acetate) and substrate nature was investigated. HPS-based catalysts containing relatively small Pd NPs (about 4 nm in diameter) were shown to be active and selective (selectivity to target products higher than 98 % and 93 % in case of cross-coupling and hydrogenation) in mild reaction conditions 60ºC in environmentally friendly solvents (ethanol and water) at the absence of phase-transfer agents.

1. Introduction

Selective hydrogenation of unsaturated carbon-carbon bond using Pd nanoparticles (NPs) is of great importance as widely applicable in synthesis of fine chemicals, vitamins (Fig. 1) and pharmaceuticals. For example, product of 2-methyl-3-butyne-2-ol (MBY) hydrogenation (2-methyl-3-butene-2-ol (MBE)) can be further used to produce dehydrolinalool (DHL), selective hydrogenation of which results in formation of linalool (LN) – one of the most widely used terpene alcohols.

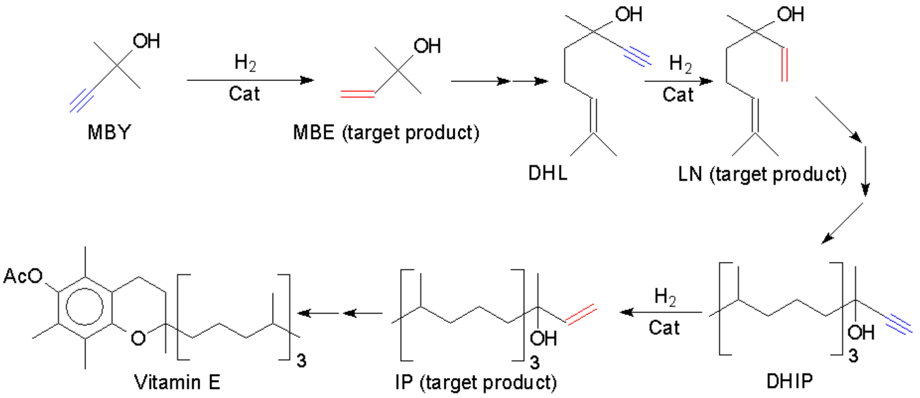

Figure 1: General scheme of synthetic route to vitamin E via "acetylenic process

Most of produced LN is used as a fragrance or flavouring agent. Moreover, LN can be regarded as a basic material for a very large range of other terpenoids. It can be converted to terpineol, geraniol and citral, and used

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in the preparation of citronellol, the ionones, farnesol and sesquiterpenes. Synthesis of fat-soluble vitamins (E and A) usually does not involve LN, but its precursor – DHL. High space-time yields at reasonable selectivities (i.e., avoiding overhydrogenation) are required for the design of an efficient and economic process of obtaining ethylene alcohols (e.g., MBE, LN, isophytol (IP)).

One of the most complicated problems in hydrogenation of alkynols along with achieving high activity, selectivity and stability of catalytic system is control over the Pd NP size, size distribution and morphology (Semagina and Kiwi-Minsker, 2009). To achieve appropriate selectivity, traditional industrial catalysts of alkyne hydrogenation require the addition of modifiers, which are not desirable for environment (Albers et al., 2011). However, in the case of terminal alkynes, neither the control of NP structure (Kiwi-Minsker and Crespo-Quesada, 2012) nor modification (Anderson et al., 2009) yields the benefits (Witte et al., 2012). While analyzing all the possible factors influencing the alkene selectivity (the ability to form a certain hydride phase, the preferential alkyne adsoprtion, definition of small ensembles in order to reduce oligomerization), the size of Pd NPs seems to be the key factor of a triple bond hydrogenation (Nikoshvili et al., 2015). At the same time, another challenge is to provide high stability of catalytically active Pd NPs, as carbonization of palladium surface as well as sintering and leaching of NPs often cause the loss of catalytic activity and selectivity at multiple reuses. Besides the control of Pd NP size, the choice of catalytic support and reaction conditions is important. It is noteworthy that during the development of new effective catalytic systems the use of nanostructured polymers as supports causes increasing interest. Polymers are able to provide control over the particle size and their monodispersion, the main problem of synthesis catalytically active metal NPs.

Suzuki cross-coupling in one of the most widespread method of biaryls formation using aryl halides and aryl boronic acids as substrates (Hajipour et al., 2014). Homogeneous palladium complexes are commonly used as catalysts for the Suzuki reaction providing high reaction rates and excellent yields of target products. However, last decades ligandless catalysts has been considered as an alternative to homogeneous ones, since they can be easily separated from the reaction mixture and reused (Pagliaro et al., 2012). In the case of ligandless catalysts, the peculiarities of catalytic cycle of Suzuki cross-coupling (palladium changes reversibly its oxidation state from (II) to (0) and small palladium clusters, which are likely responsible for observed catalytic activity, can form Pd (0) NPs and vice versa) complicate the kinetic analysis of this reaction. Recently the term of “cocktail”-type catalytic systems was proposed to describe the behavior of majority of ligandless catalysts of Suzuki reaction (Eremin and Ananikov, 2017).

This paper is devoted to the study of Pd-containing catalysts based on non-functionalized hyper-crosslinked polystyrene (HPS) of MN270 type synthesized while using $PdCl_2(CH_3CN)_2$ or $Pd(CH_3COO)_2$ as precursors in selective hydrogenation of industrially important alkynols (MBY, DHL, DHIP) and in Suzuki cross-coupling of 4-bromoanisole (4-BrAn) and phenylboronic acid (PBA) as model compounds at mild conditions in environmentally friendly solvents (ethanol and ethanol-water mixtures).

2. Experimental

2.1 Materials

HPS Macronet MN270 (Purolite Int., UK) was washed with distilled water and acetone and dried under vacuum as described elsewhere (Sulman et al., 2012). 4-Methoxybiphenyl (4-MBP, >99 %), 3-methoxybiphenyl (3-MBP, >96 %) and 2-methoxybiphenyl (2-MBP, >98 %) were purchased from Tokyo Chemical Industry Co. Ltd. 4-BrAn (≥99 %), PBA (95 %), diphenylamine (99 %), biphenyl (99.5 %), MBY (>99 %), MBE (>97 %), 2-methyl-2-butanol (MBA, >96 %), isopropanol (*i*-PrOH, 99.5 %), cyclohexane (>99 %), *n*-hexane (≥97 %), toluene (99.8 %), bis(acetonitrile)palladium(II)chloride ($PdCl_2(CH_3CN)_2$, >99 %), palladium(II) acetate ($Pd(CH_3COO)_2$, >99 %), tetrahydrofuran (THF, ≥99.9 %), ethanol (EtOH, ≥99.8 %), sodium carbonate (Na_2CO_3, ≥99.5 %) and sodium hydroxide (NaOH, ≥98 %) were obtained from Sigma-Aldrich. DHL (98 %) and dehydro-IP (DHIP, 97 %) were purchased from DSM (Switzerland). All chemicals were used as received. Distilled water was purified with an Elsi-Aqua water purification system.

2.2 Catalyst synthesis

Series of Pd-containing HPS-based catalysts was synthesized via wet-impregnation method according to the procedure described elsewhere (Sulman et al., 2012). In a typical experiment, 1 g of pretreated, dried and crushed (<63 μm) granules of MN270 were impregnated with 2.8 mL THF solution of precursor ($PdCl_2(CH_3CN)_2$ or $Pd(CH_3COO)_2$) of a certain concentration. The Pd-containing polymer was dried at 70°C, treated with 2.8 mL of Na_2CO_3 solution (concentration 0.07 mol/L) and dried until the constant weight was achieved. After that the catalyst was washed with distilled water till neutral pH and dried at 70°C.

The following catalysts were synthesized (palladium content was confirmed by the XFA): 0.2 %-Pd/MN270 (0.2 wt.% of Pd, precursor $Pd(CH_3COO)_2$); 1.4 %-Pd/MN270-1 (1.4 wt.% of Pd, precursor $Pd(CH_3COO)_2$); 1.5 %-Pd/MN270-2 (1.5 wt.% of Pd, precursor $PdCl_2(CH_3CN)_2$).

Besides, for all the synthesized catalyst, preliminarily reduction in hydrogen flow at 300ºC for 2 h was carried out (the catalysts were designated as Pd/MN270-1-H_2 and Pd/MN270-2-H_2).

2.3 Procedure of cross-coupling reaction

Testing of HPS-based catalysts in Suzuki cross-coupling was carried out in a 60 mL shaker-type isothermal glass batch reactor at vigorous stirring (800 two-sided shaking per minute) at a temperature of 60ºC. The total volume of liquid phase was 30 mL. EtOH/water mixture at the volumetric ratio of 5 : 1 was used as a solvent. NaOH was used as a base at the quantity of 1.5 mmol (equimolar to PBA). The choice of solvent and alkali metal compound was based on previous studies of HPS-based catalysts of Pd/MN100 series (Nemygina et al., 2016). In each experiment the quantity of aryl halide was equal to 1 mmol, 1.5 molar excess of PBA was used. Catalyst loading in each experiment was 50 mg. Before the catalyst addition in the reactor, in each experiment the blank test (duration of 60 min) was carried out in order to ensure that the reaction did not proceed at the absence of catalyst.

Samples of reaction mixture were periodically taken and analyzed via GC-MS (Shimadzu GCMS-QP2010S) equipped with a capillary column HP-1MS (30 m × 0.25 mm i.d., 0.25 μm film thickness). Helium was used as a carrier gas at pressure of 74.8 kPa and linear velocity of 36.3 cm/s. Oven temperature was programmed: 120ºC (0 min) → 10ºC/min (160ºC) → 25ºC/min (300ºC) → 300ºC (2.4 min). Temperature of injector, interface and ion source was 260ºC, detection range from 10 up to 500 m/z. The concentrations of the reaction mixture components were calculated using the internal standard calibration method (diphenylamine was used as an internal standard).

2.4 Procedure of triple bond hydrogenation

Testing of synthesized Pd/HPS catalysts was carried out in a 60 mL isothermal glass batch reactor installed in a shaker and connected to a gasometrical burette (for hydrogen consumption control). The total volume of liquid phase was 30 mL. At the beginning of each experiment the temperature was set, the reactor was charged with solvent and catalyst and hydrogen was then introduced. Before the MBY addition (time “zero”, $t = 0$ for the reaction), in each experiment the catalysts were preliminarily reduced *in situ* for 60 min in order to ensure Pd(0) oxidation state. Samples of reaction mixture were analyzed via GC-MS (Shimadzu GCMS-QP2010S) equipped with a capillary column HP-1MS (30 m × 0.25 mm i.d., 0.25 μm film thickness). Helium was used as a carrier gas.

Catalytic activity (designated as “*R*”) was defined as $R = N_{MBY} \times N_{Pd}^{-1} \times \tau^{-1} \times X \times 0.01$, where N_{MBY} and N_{Pd} are the numbers of moles of the substrate (MBY) and Pd, taken for the reaction; X is the substrate conversion, %; and τ is the reaction time for achieving of certain conversion of the substrate, s.

2.5 Catalyst characterization

Pd/HPS catalysts were characterized by X-Ray Fluorescence Analysis (XFA), X-Ray Photoelectron Spectroscopy (XPS) and Transmission Electron Microscopy (TEM).

XFA was carried out to determine the Pd content. It was performed with a Zeiss Jena VRA-30 spectrometer (Mo anode, LiF crystal analyzer and SZ detector). Analyses were based on the Co Kα line and a series of standards prepared by mixing 1 g of polystyrene with 10 - 20 mg of standard compounds. The time of data acquisition was constant at 10 s.

XPS data were obtained using Mg Kα (hν = 1253.6 eV) radiation with ES-2403 spectrometer (Institute for Analytic Instrumentation of RAS, St. Petersburg, Russia) equipped with energy analyzer PHOIBOS 100-MCD5 (SPECS, Germany) and X-Ray source XR-50 (SPECS, Germany). All the data were acquired at X-ray power of 250 W. Survey spectra were recorded at an energy step of 0.5 eV with an analyzer pass energy 40 eV, and high resolution spectra were recorded at an energy step of 0.05 eV with an analyzer pass energy 7 eV. Samples were allowed to outgas for 180 min before analysis and were stable during the examination. The data analysis was performed by CasaXPS.

TEM characterization was provided using a JEOL JEM1010 instrument at electron accelerating voltage of 80 kV. Samples were prepared by embedding the catalyst in epoxy resin with following microtomming at ambient temperature. Images of the resulting thin sections (*ca*. 50 nm thick) were collected with the Gatan digital camera and analyzed with the Adobe Photoshop software package and the Scion Image Processing Toolkit.

3. Results and discussion

NP size and structure sensitivity varies depending on the substrate type: in many cases low-molecular weight terminal alkynes (e.g. MBY) remain almost structure insensitive. In this case, the sizes of Pd NPs, which can be controlled varying the peculiarities of catalyst synthesis, are responsible for the ability to form certain Pd hydride phase altering catalytic activity and selectivity. On the other hand, the structure sensitivity of alkynol hydrogenation is a complex phenomenon that originates from the intrinsic structure sensitivity of the reconstruction of Pd carbide phase in response to the reactive environment, which is controlled by the support used. For the low-percentage 0.2 %-Pd/MN270-H_2 catalyst, it was found that one of the main parameters influencing catalytic activity and selectivity is reaction temperature, which influences adsorption-desorption equilibrium of alkynol and hydrogen partial pressure, and also the solvent nature (see Table 1). In the latter case, the activity and selectivity patterns are essentially determined by the strength of the solvent-Pd interactions. The highest MBE selectivity (99.6 %) was achieved in toluene at 60^{o}C. Highest catalytic activity but lowest selectivity was found in the case of *i*-PrOH that is likely due to the ability of *i*-PrOH to be a hydrogen donor rather than EtOH in H-transfer reactions. Among the non-polar non-aromatic solvents, the highest activity was observed for cyclohexane, which likely has the lowest adsorption strength on palladium.

Table 1. Hydrogenation of alkynols over 0.2 %-Pd/MN270-H_2 (precursor $Pd(CH_3COO)_2$) catalyst at variation of solvent nature and type of substrate

Solvent*	Selectivity (MBE) at 95 % of MBY conversion	R, mol(MBY)* mol(Pd)$^{-1}$*s^{-1}	Substrate**	Selectivity at 99 % conversion	R, mol(MBY)* mol(Pd)$^{-1}$*s^{-1}
toluene	>99	35.0	MBY	98	19.0
EtOH	93	85.5	DHL	98	19.2
i-PrOH	86	109.1	DHIP	97	7.8
cyclohexane	82	78.4			
hexane	94	64.2			
Comparison with commercial catalysts of MBY hydrogenation**					
Pd/Al_2O_3 (0.5 % Pd)	94	3.0			
Pd/$CaCO_3$ (2.0 % Pd)	95	2.4			

*Substrate – MBY, partial hydrogen pressure 3 bar, temperature of 60^{o}C
**Toluene was used as a solvent, ambient hydrogen pressure, temperature of 90^{o}C

Precursor nature was investigated by the example of cross-coupling of 4-BrAn and PBA. The results of catalytic testing of both the initial samples and the samples reduced in hydrogen flow are presented in Table 2.

Table 2. Influence Pd precursor nature on activity and selectivity of the catalysts of Pd/MN270 series in Suzuki cross-coupling of 4-BrAn and PBA

Sample designation	Pd precursor	Conversion of 4-BrAn, ± 0.5 %*	Selectivity with respect to 4-MBP, ± 0.5 %*	Yield of 4-MBP, ± 0.5 %*
1.4 %-Pd/MN270-1	$Pd(CH_3COO)_2$	90.0	97.8	88.0
1.4 %-Pd/MN270-1-H_2		79.4	98.1	77.9
1.5 %-Pd/MN270-2	$PdCl_2(CH_3CN)_2$	89.3	98.4	87.9
1.5 %-Pd/MN270-2-H_2		92.4	98.2	90.7

*Calculated for 1 h reaction time

As it can be seen (Table 2), in the case of initial catalysts of Pd/MN270 series the conversion of 4-BrAn reached after 1 h of reaction time slightly depends on the Pd precursor nature. TEM data (Fig. 2) has shown that there is no dependence between the 4-BrAn conversion and the sizes of Pd NPs formed after the Suzuki reaction. In case of the catalysts preliminary reduced in H_2 flow, the best results regarding to the 4-MBP yield were observed for 1.5 %-Pd/MN270-2-H_2 (synthesized while using $PdCl_2(CH_3CN)_2$).

This fact can be explained rather by the incomplete Pd reduction, which takes place in the case of chlorine containing precursors in comparison with palladium acetate, than the differences in sizes of palladium NPs considering that Pd(II) is usually more active in comparison with bulk Pd(0).

XPS data revealed that the surface of freshly prepared catalyst 1.5 %-Pd/MN270-2 contains chlorine, carbon, oxygen, nitrogen and palladium. According to the XPS data, the following values of binding energy (± 0.1 eV) of

Pd $3d_{5/2}$ were found according to the high resolution spectra of Pd 3d: 338.6 eV (binding energy of Pd $3d_{5/2}$ in $PdCl_2(CH_3CN)_2$ was found to be equal to 338.7 eV); 336.3-336.6 eV (small clusters of Pd_n ($n \le 13$)) (Wu et al., 2009); 337.7 eV ($PdCl_2$); 335.0 eV (Pd NPs). The existence of $PdCl_2$ in the catalyst composition can be ascribed to the transformation of initial precursor ($PdCl_2(CH_3CN)_2$) during the catalyst synthesis. It is noteworthy that high percentage of Pd(II) species (about 18 at.%) was found on the surface of reduced catalyst 1.5 %-Pd/MN270-2-H_2 according to the XPS data, which shows the incomplete reduction of palladium during the treatment in hydrogen flow.

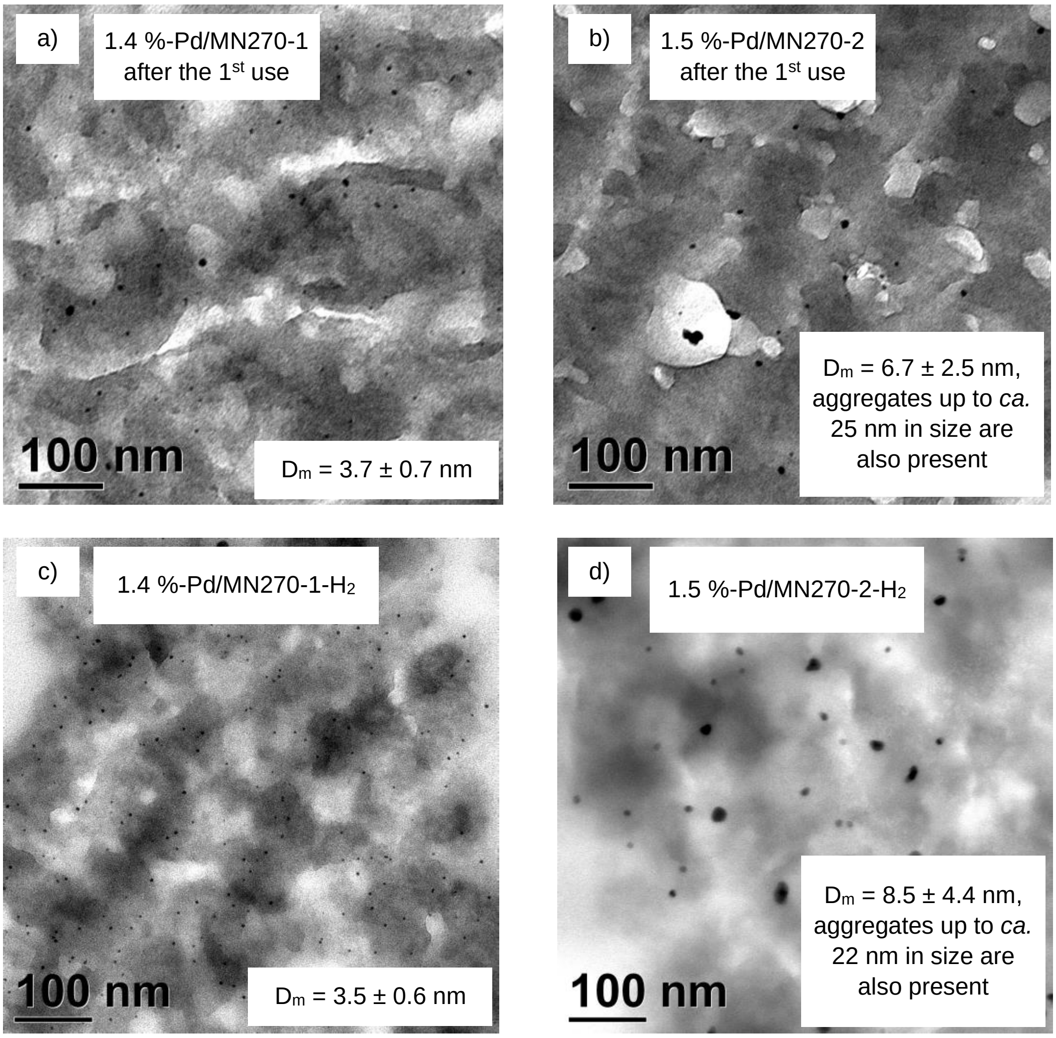

Figure 2: TEM images of Pd/MN270 samples taken after the 1st run in Suzuki cross-coupling of 4-BrAn and PBA (a, b) and preliminarily reduced in H_2 flow (c, d)

The following components were found on the surface of unreduced catalyst 1.4 %-Pd/MN270-1: $Pd(CH_3COO)_2$, PdO, small Pd_n clusters ($n \le 13$) and Pd NPs. The presence of PdO in the catalyst composition is due to the precursor decomposition during the catalyst synthesis and/or to the partial oxidation of the surface of Pd NPs since the catalysts were synthesized and stored in air. In the case of reduced 1.4 %-Pd/MN270-1-H_2 mainly PdO is on the surface that can be ascribed to the partial oxidation of NPs surface after exposition of the catalyst in air. We believe, that since PdO is positioned on the particle surface, it is more accessible for XPS analysis than Pd(0). It can be concluded that the synthesized HPS-based catalysts (both initial and reduced ones) can be considered as “cocktail” type systems containing multiple forms of Pd in the polymeric network, which can simultaneously catalyze the Suzuki reaction.

4. Conclusions

Pd-containing catalysts based on non-functionalized HPS of MN270 type were shown to be active in Suzuki cross-coupling reaction in EtOH/water mixture as a solvent at the absence of phase-transfer agents: about 90 % conversion of 4-BrAn was achieved independent on the palladium precursor nature. In the case of triple bond hydrogenation of alkynols highest selectivity (≥ 99 %) was achieved in toluene for the Pd-containing HPS-based catalyst with low metal loading of 0.2 wt.%, which can be considered as an alternative to the existing industrial catalysts of triple-bond hydrogenation. In EtOH medium, which is environmentally friendly solvent in comparison with toluene, more than two-fold increase of activity in MBY hydrogenation was observed (from 35 mol(MBY)*mol(Pd)$^{-1}$*s^{-1} up to 85.5 mol(MBY)*mol(Pd)$^{-1}$*s^{-1}) that makes EtOH perspective solvent for this process. But selectivity in case of EtOH decreased to 93 %. Such noticeable decrease in selectivity need to be overcame either by the further catalyst search or by the change of reaction conditions.

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