Selective Hydrogenation of Alkynols in Ethanol Medium in a Batch Mode using Polyamine-Supported Pd Catalysts

Ekaterina A. Kholkina[a], Linda Z. Nikoshvili[a,*], Alexey V. Bykov[a], Alexey S. Morozov[b], Ivan V. Bessonov[b], Lioubov Kiwi-Minsker[c,d], Esther M. Sulman[a]

[a]Tver Technical University, A.Nikitina str. 22, 170026, Tver, Russian Federation
[b]JSC «Advanced medical technologies», Lukov lane 4, 107045, Moscow, Russian Federation
[c]Tver State University, Regional Technological Centre, Zhelyabova 33, 170100, Tver, Russian Federation
[d]Ecole Polytechnique Fédérale de Lausanne, GGRC-ISIC-EPFL, CH-1015, Lausanne, Switzlerand
 nlinda@science.tver.ru

Hydrogenation of triple carbon-carbon bond is of high importance and one of the main issues is the development of highly active and selective catalytic systems. Polymeric palladium-containing catalysts can serve as an alternative to traditional catalysts based on inorganic supports. In this work, the series of Pd catalysts based on highly branched polyamines were synthesized at variation of polyamine type and metal precursor nature. It was shown that the developed polyamine-based catalysts allowed achieving 99 % selectivity (at 98 % of substrate conversion) in hydrogenation of dimethylethynylcarbinol.

1. Introduction

Catalytic hydrogenation of triple carbon-carbon bond of alkynols is one of the most widely used reaction in production of fragrances, biologically active compounds and fat-soluble vitamins (Bonrath et al., 2007). Palladium is well known to be the most selective catalyst for hydrogenation of alkynols. Historically, Lindlar catalyst (Pd/CaCO$_3$) was the first commercial catalyst of triple bond hydrogenation (Tschan et al., 2001), providing selectivity of about 96 % at nearly 100 % of substrate conversion, e.g. in hydrogenation of alkynol C$_5$ (Witte et al., 2012). However, the use of environmentally unfriendly modifiers such as lead acetate and quinoline, which contaminate target products, is necessary in order to achieve high selectivity.

Polymeric matrices can be considered as an alternative to inorganic supports while developing palladium-containing catalysts (Stepacheva et al., 2016). Their application allows avoiding the necessity to use modifiers due to the increase of selectivity (Valetsky et al., 2009). It is noteworthy that the nature of polymer is able to influence the catalyst reactivity, as it was shown for reactions of different types including triple bond hydrogenation (Corain and Kralik, 2000). The use of functionalized polymers contributes to dispersion of active metal catalyst, facilitates the diffusion of reactants into the polymer pores and the interaction between reagents and metal nanoparticles. The presence of amino groups, which are able to coordinate metals with formation of complexes, makes nitrogen-containing polymeric matrices one of the most perspective catalytic supports (Nemygina et al., 2016).

In this work, the series of polyamine-supported Pd-containing catalysts intended for selective hydrogenation of triple carbon-carbon bond of alkynol C$_5$ (dimethylethynylcarbinol, DMEC) was synthesized via wet-impregnation method at variation of polyamine (PA) type and palladium precursor nature.

2. Experimental

2.1 Materials

Highly branched polyethyleneimine (PEI) with Mw 50-100 kDa (50 % w/w aqueous solution) was purchased from MP Biomedicals (USA). (±)-Epichlorohydrin (ECH, ≥99 %), diethylene glycol (DEG, 99 %), dichloromethane (≥ 99.8 %), sodium dodecyl sulfate (SDS, 92.5 - 100.5 % based on total alkyl sulfate content basis), hexamethylene diisocyanate (HDI, ≥98.0 %), palladium(II) chloride (PdCl$_2$, ≥ 99.9 %),

bis(acetonitrile)palladium(II)chloride (PdCl$_2$(CH$_3$CN)$_2$, 99 %), palladium(II) acetate (Pd(CH$_3$COO)$_2$, 99.98 %) were purchased from Sigma-Aldrich (USA). Sodium hydroxide (purum p.a., ≥97.0 %), sodium bicarbonate (purum p.a., ≥ 99.0 %) and dimethylethynylcarbinol (DMEC, 99 %) were purchased from Fluka (Czech Republic). Ethanol (95 vol.%) was purchased from JSC "Medkhimprom" (Russian Federation). Acetonitrile (HPLC grade, ≥99.99 %) was purchased from "Criokhrom" Company (Russian Federation). Hydrochloric acid (35 - 38 %) and toluene (99.85 %) were purchased from "Component-Reaktiv" Company (Russian Federation). All chemicals were used as received. Distilled water was purified with an Elsi-Aqua water purification system.

2.2 Synthesis of PAs

Three PAs (M33C, M37A and M50C) were synthesized as described below. The difference between these PAs was mainly in molecular weight, cross-linking degree and types of functional groups.

PA of M33C type was prepared according to the procedure described elsewhere (Chen et al., 2012) with minor modifications. In a typical experiment, 60 g of PEI, 100 mg of SDS and 250 mL of toluene were placed into two-neck round-bottom flask. Then 10 mL of distilled water and 14.2 mL of HCl were added and the mixture was warmed up to 70 °C. After that ECH (7.6 mL in 10 mL of toluene) was added drop-wise to the reaction mixture by dropping funnel over 2 h at continuous stirring. The reaction was carried out under reflux and water was separated using Dean stark apparatus. The reaction was stopped after *ca.* 4 h, when all water was removed. After cooling to ambient temperature, resin was filtered using a Büchner funnel and washed sequentially with ethanol (2 x 200 mL), 10 % sodium hydroxide solution (1 x 100 mL) and distilled water until pH reached 8-9. Reaction product M33C was obtained as off-white powder (34.5 g, 99 %) after freeze-drying.

M37A was prepared according to the following procedure: 27 g of PEI and 1.5 g of SDS were placed into two-neck round-bottom flask and were dissolved in 125 mL of distilled water. Than solution of HDI (4.2 mL) in dichloromethane (12.5 mL) was added drop-wise to the reaction mixture by dropping funnel over 1 h at continuous stirring. After 4 h of stirring at ambient temperature, the reaction mixture was filtered using a Büchner funnel and washed sequentially with ethanol (1x50 mL), petroleum ether/toluene mixture 1:1 (3 x 50 mL), ethanol (2 x 50 mL), 0.5 M HCl (1 x 50 mL), 1 M NaOH (1 x 50 mL) and distilled water until pH reached 8-9. Reaction product M37A was obtained as off-white powder (2.3 g, 13 %) after freeze-drying.

M50C was prepared according to the following procedure: 40 mL of aqueous PEI solution (10 % w/w) and 4.1 mL of DEG were placed into plastic tube (50 mL) with screw cap. The mixture was agitated using shaker during 2 min and placed in freezer at -18 °C overnight. After defrosting, resin was filtered on a Büchner funnel and washed several times with ethanol. Then it was placed in 100 mL round-bottom flask and 40 mL of ethanol was added. The mixture was refluxed for 2-3 h to eliminate the excess of DEG. After cooling to ambient temperature, resin was filtered using a Büchner funnel, washed sequentially with ethanol (2 x 30 mL), 10 % sodium hydroxide solution (1 x 100 mL) and distilled water (5 x 30 mL). Reaction product M50C was obtained as off-white powder (5.0 g, 57 %) after freeze-drying.

2.3 Catalyst synthesis

PA-based catalysts were synthesized via conventional wet-impregnation method at variation of PA type and Pd precursor (PdCl$_2$, PdCl$_2$(CH$_3$CN)$_2$ or Pd(CH$_3$COO)$_2$).

In a typical experiment, 0.3 g of PA was impregnated with 3 mL of solution of palladium precursor. Depending on the Pd compound different solvents were used: ethanol with the addition of HCl (0.1 mL) in the case of palladium chloride, and mixture of ethanol and acetonitrile (1:1) for both PdCl$_2$(CH$_3$CN)$_2$ and Pd(CH$_3$COO)$_2$. After vigorous stirring during 10 min, all the Pd-containing PAs were dried at 75 °C for 1 h until the constant weight was achieved.

The following catalysts were synthesized: PdCl$_2$/M33C (designated as Pd/M33C-1), PdCl$_2$(CH$_3$CN)$_2$/M33C (designated as Pd/M33C-2), Pd(CH$_3$COO)$_2$/M33C (designated as Pd/M33C-3), Pd(CH$_3$COO)$_2$/M37A (designated as Pd/M37A) and Pd(CH$_3$COO)$_2$/M50C (designated as Pd/M50C).

2.4 Testing procedure

Synthesized catalysts were tested in hydrogenation of DMEC to dimethylvinylcarbinol (DMVC) (see Figure 1). The reaction 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) at a temperature of 65 °C at vigorous stirring. The total volume of liquid phase was 30 mL. Ethanol was used as a solvent. Before the DMEC addition (1.5 g), in each experiment the catalysts were preliminarily reduced with hydrogen in situ during 60 min.

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 flow rate 1 mL/min. Analysis conditions: oven temperature 60 °C (isothermal), injector and interface temperature 280 °C, ion source temperature 260 °C, range from 10 up to 200 m/z.

Catalytic activity (designated as "R") was calculated at 50 % of DMEC conversion: $R_{50} = q \times t^{-1} \times 0.50$, where q is DMEC-to-Pd molar ratio, and t is the reaction time for achieving of 50 % of DMEC conversion.

Figure 1: Scheme of DMEC transformation to DMVC

2.5 Methods

Synthesized PAs and PA-based catalysts were characterized by thermogravimetric analysis (TGA), liquid nitrogen physisorption, Fourier transform infrared (FTIR) spectroscopy, X-ray photoelectron spectroscopy (XPS), X-ray fluorescence analysis (XFA) and scanning electron microscopy (SEM).

TGA was carried out using thermoscales TG 209 F1 (NETZSCH, Germany) with increasing temperature from 30 °C up to 200 °C (10 °C/min) and following delay at 200 °C.

Liquid nitrogen physisorption was carried out using Beckman Coulter SA 3100 (Coulter Corporation, USA). Prior to the analysis, samples were degassed in Beckman Coulter SA-PREP at 120 °C in vacuum for 1 h. Weight of each sample was above 0.1 g. The following models were used for calculation of specific surface area (SSA) and pore size distribution: Langmuir, Brunauer-Emmett-Teller (BET), t-plot, Barrett-Joyner-Halenda (BJH). Pore size distribution was measured in the range from 3 nm up to 200 nm.

XPS data were obtained using Mg Kα (hν = 1,253.6 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.

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.

The morphology of PA-based Pd catalysts was evaluated by SEM/EDX analysis using a Phenom ProX instrument at electron accelerating voltage of 17 kV.

3. Results and Discussion

3.1 Catalyst characterization

According to the data of liquid nitrogen physisorption, all the synthesized PAs were found to have very low SSA (23 m^2/g, 19 m^2/g and 38 m^2/g for M33C, M37A and M50C) with predominant meso- and macro-porosity. However, PAs were found to swell very strongly in polar medium, hence the Pd deposition was easily carried out and the access of DMEC to catalytically active sites can be successfully provided.

To find thermal stability of PAs, TGA was carried out. Figure 2 presents the data of TGA for M33C, as an example. It is obvious that M33C is stable in the investigated temperature range. The observed weight loss of about 22 % can be explained by the moisture loss because of high moisture capacity of this kind of polymer and is not due to the thermal destruction of PA structure. This trend is typical for all synthesized PAs. Thus, the reaction of DMEC hydrogenation using PA-based palladium catalysts can proceed at a temperature of 65°C without risk of destruction of polymers.

Figure 3 shows SEM images of (a) Pd/M33C-3, (b) Pd/M37A and (c) Pd/M50C as examples of catalysts based on different PAs and containing the same Pd precursor (Pd(CH$_3$COO)$_2$). It is noteworthy that Figure 3 shows SEM images for freshly prepared (unreduced) catalysts. The presented SEM images demonstrate the presence of palladium-containing particles and their aggregates (as was also confirmed by data of elemental mapping) on the surface of the polymeric supports. It was revealed that PA of M33C type has clearly defined macroporous structure, which is absent in the case of M37A and M50C. It should be also mentioned that morphology of all the synthesized catalysts was revealed to be the same as in the case of initial PA samples.
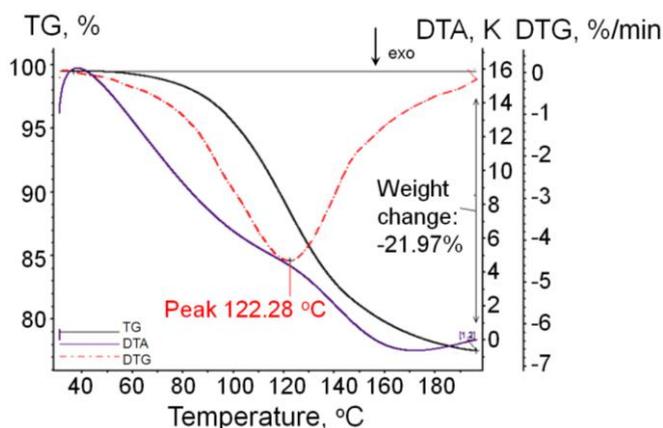
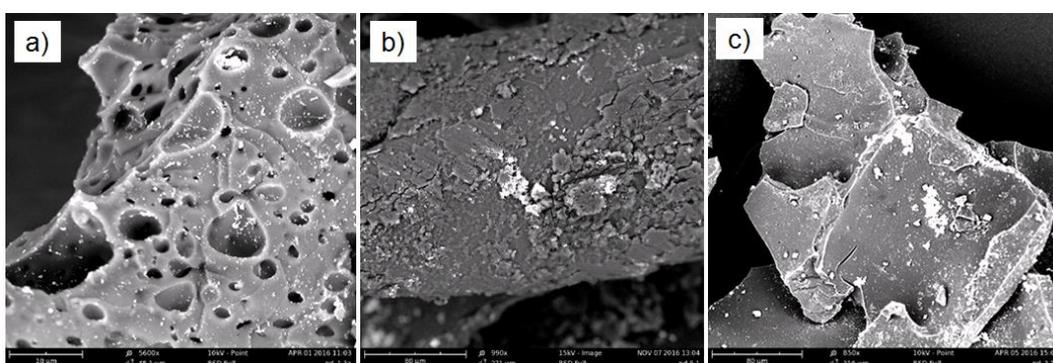*Figure 2: TG curve of PA of M33C type*

Figure 3: SEM images of (a) Pd/M33C-3, scale 10 µm, (b) Pd/M37A, scale 80 µm, and (c) Pd/M50C, scale 80 µm

XPS analysis was performed in order to determine Pd content as well as its oxidation state on the catalyst surface. Surface of all the Pd/PA catalysts was found to contain mainly carbon, oxygen, nitrogen, silicon and palladium (see Figure 4 (a) as an example). Besides, in some cases, other elements such as magnesium, calcium, aluminium, sodium, sulfur and chlorine were found.
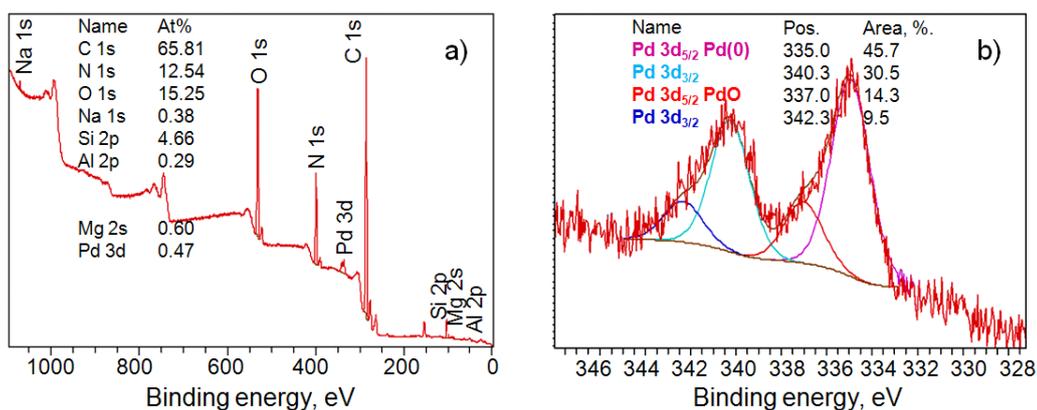

Figure 4: (a) Survey spectrum of Pd/M33C-3 and (b) high-resolution spectrum of Pd 3d of Pd/M33C-3

According to the high resolution spectrum of Pd 3d as shown in Figure 4 (b), the values of the binding energy of Pd $3d_{5/2}$ in the case of catalysts synthesized while using Pd acetate as a precursor were found to be *ca.* 335 eV and 337 eV, which correspond to Pd(0) and PdO (Wagner et al., 1979). The existence of Pd(0) and PdO on the catalyst surface can be ascribed to the transformation of initial precursor during the catalyst

synthesis. Thus, the partial reduction of Pd occurs. This fact can be also confirmed by the absence of induction period on kinetic curves (see Figure 5). It should be emphasized that PdO is easily reducible Pd specie, so it can be completely reduced during the treatment of catalysts with hydrogen in situ before the reaction.

While using $PdCl_2(CH_3CN)_2$ as a precursor for impregnation of PA of M33C type, binding energy of Pd $3d_{5/2}$ was found to be equal to 334.5 eV (corresponds to Pd(0)) and 336.8 eV (presumably corresponds to mixture PdO_x/Pd). In the case of M33C impregnated with $PdCl_2$, the following values of binding energy of Pd $3d_{5/2}$ were found: 337.4 eV (corresponds to PdO) and 335.6 eV (corresponds to Pd(0)).

3.2 Catalytic testing

3.2.1. Influence of Pd precursor nature

PA of M33C type, which is characterized by strongly hydrophilic properties and the presence of free amino groups, was chosen as a support for investigation of the influence of Pd precursor nature. Obtained results are presented in Table 1 and in Figure 5.

Table 1: Influence of Pd precursor nature on DMEC hydrogenation using catalysts based on M33C

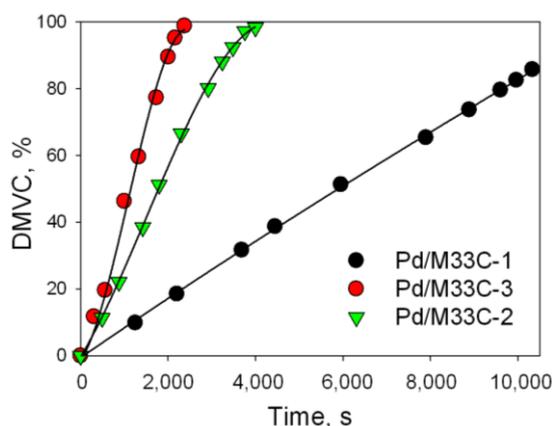| Catalyst	Functional groups of support	Pd content			Conversion of DMEC, %	Selectivity to DMVC, %	Yield of DMVC, %	R_{50}, s^{-1}
		XFA, wt. %	XPS, at. %	SEM/EDX, wt. %				
Pd/M33C-1		1.99	0.08	8.33	88	97	85	0.2
Pd/M33C-2	-NH₂	1.89	0.46	3.29	98	98	96	0.6
Pd/M33C-3		1.88	0.47	10.84	98	99	97	0.9

Figure 5: Kinetic curves of DMVC accumulation at variation of Pd precursor nature for the catalysts of Pd/M33C series

It was found that the nature of Pd precursor noticeably influences the catalyst behaviour. Best results (99 % selectivity at 98 % of substrate conversion) were obtained while using palladium acetate as a precursor. This observation is in good agreement with the data of XPS analysis and SEM/EDX measurements, according to which M33C impregnated with $Pd(CH_3COO)_2$ has highest Pd content on the surface. The use of $PdCl_2(CH_3CN)_2$ as a precursor allowed also achieving high selectivity (99 % at 98 % of substrate conversion), but this catalyst revealed slightly lower activity in comparison with Pd/M33C-3. In case of Pd/M33C-1 ($PdCl_2$), the lowest initial substrate conversion (88 %) was achieved. Figure 5 shows the differences in behaviour of Pd-containing catalysts based on M33C at variation of Pd precursor nature.

$Pd(CH_3COO)_2$ was chosen as optimal metal precursor for further investigation of Pd-containing catalytic systems at variation of PA type.

From the data presented in Figure 5, it is obvious that the induction period is absent, which indicates the presence of reduced form of palladium in all the catalysts of Pd/M33C series.

3.2.2. Influence of PA type

As a second part of this work the investigation of the influence of PA type was carried out using Pd acetate as a precursor. Obtained results are presented in Table 2.

Table 2: Influence of PA type on DMEC hydrogenation over Pd/PA (Pd(CH₃COO)₂) catalysts

Catalyst	Functional groups of support	Pd content, %			Conversion of DMEC, %	Selectivity to DMVC, %	Yield of DMVC, %	R_{50}, s^{-1}
		XFA, wt. %	XPS, at. %	SEM/EDX, wt. %				
Pd/M33C-3	$-NH_2$	1.88	0.47	10.84	98	99	97	0.9
Pd/M37A	$-NH_2$, $-C(O)NH-$	2.10	0.32	9.56	98	98	96	1.0
Pd/M50C	$-NH_2$	1.78	0.64	21.76	98	95	93	0.5
Lindlar catalyst (2 %-Pd/CaCO₃)		2.03	2.58	-	99	95	94	1.2

Based on the data presented in Table 2 it can be concluded that both M33C and M37A allowed synthesizing active and selective catalysts: activity was close to that of commercial Lindlar catalyst, while the selectivity was noticeably higher (98 - 99 % vs. 95 %). The catalyst based on PA of M50C type showed lower of activity and selectivity in spite of the highest Pd content on the surface that is likely due to the relatively poor Pd dispersion in comparison with other two samples and formation of large Pd aggregates (see Figure 3).

4. Conclusions

In the framework of this study the series of PA-based palladium catalysts were synthesized at variation of PA type and metal precursor nature. Developed polymeric Pd-containing catalysts were tested in the reaction of selective hydrogenation of alkynol C_5 – DMEC. The highest value of selectivity with respect to DMVC (99 % at 98 % of DMEC conversion) was achieved while using palladium acetate as a precursor. It was shown that behaviour of the catalysts strongly depends on the PA type. The structure of polymeric support plays an important role: PA of M33C type with highest degree of cross-linking was shown to have best morphology, which allowed formation of highly active Pd aggregates on the catalyst surface.

Acknowledgments

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