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Selective hydrogenation of 2-methyl-3-butyn-2-ol over Pd-nanoparticles stabilized in hypercrosslinked polystyrene: Solvent effect

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ABSTRACT

Selective hydrogenation of 2-methyl-3-butyn-2-ol (MBY) to 2-methyl-3-butene-2-ol (MBE) over Pd supported on hypercrosslinked polystyrene was studied in polar (ethanol, isopropanol, water) and non-polar (cyclohexane, toluene, octane, hexane, heptane and *m*-xylene) solvents. The catalytic activity and selectivity were found to be strongly affected by solvent properties such as dipole moment and dielectric constant, but cannot be explained by solvent polarity only. Hydrogen solubility and solvent–catalyst interaction also influential factors. The catalyst activity decreases in the series: alcohols > cyclohexane > water/ethanol mixture > octane ≥ hexane ≥ xylene > toluene > heptane. The highest values of MBE selectivity of 99.6% and 98.7% at 95% MBY conversion were obtained in toluene and in ethanol, respectively.

1. Introduction

Selective carbon–carbon triple bond alkynol hydrogenation is one of the important reactions in manufacturing of fine chemicals. It is usually carried out in a liquid phase using catalysts containing noble (Pd, Pt, Rh) or transition (Ni) metals [1]. The catalyst activity and selectivity are known to be strongly influenced by a solvent. The choice of a suitable solvent requires understanding of relationships between the solvent nature and the interactions with participation of the solvent that take place in three phase catalytic hydrogenation system [1].

The problem of choosing a suitable solvent for catalytic hydrogenation of various organic compounds has been considered by many researchers. As a result, several factors determining the influence of the solvent on hydrogenation process were identified [2,3].

The first factor is a substrate–solvent–catalyst interaction. For example, Rajadhyaksha and Karwa [3] studied the reaction of selective hydrogenation of 2-nitrotoluene in the presence of the 2 wt% Pd/C catalyst using different alcohols, benzene, *n*-hexane, and cyclohexane as solvents. It was shown that in the case of a positive interaction, the strength of the reagent adsorption on catalytically active centers decreases, while in the case of a negative interaction the increase of adsorption is observed causing the corresponding decrease of selectivity. Augustine et al. [4] investigated hydrogenation of alkenes over Pt- and Pd-containing catalysts in alcohols. MeOH and EtOH were found to compete with hydrogen and to adsorb on the Pd surface, resulting in occupying the catalytic active sites, while *i*-PrOH enters into the reaction as a hydrogen donor. Toukoniitty et al. [5] found that hydrogenation rate depends on the ability of solvent to interact with substrate and to compete with other reagents while present on catalytic surface.

The second factor is a solvent polarity. The attempts were undertaken to explain the differences in catalyst activities considering correlations between the reaction rate and traditional solvent parameters such as a dipole moment (μ) and a dielectric constant (ε) [6]. Drelinkiewicza et al. [7] studied hydrogenation of acetophenone (AP) on polymer supported Pd catalysts using different alcohols and cyclohexane as solvents. The hydrogenation rate was found to be higher in alcohol solutions in comparison to cyclohexane. It was proposed that the catalyst activity is rather influenced by a solvent polarity than H_2 solubility. Enantioselective hydrogenation of AP on chiral Ru-based catalysts using different solvents was investigated by Cheng et al. [8]. Hydrogenation

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was revealed to proceed fast in C_1–C_4 alcohols in a contrast to aprotic polar and non-polar solvents. Mukherjee and Vannice [9] studied hydrogenation of citral on Pt/SiO_2 using eight solvents belonging to different chemical groups in order to find a relationship between the catalyst activity and dielectric constants and dipole moments of the chosen solvents. Hajek et al. [10] used 12 different solvents in hydrogenation of cinnamaldehyde on Ru/Y zeolite and obtained a satisfactory correlation between the solvent polarity and hydrogenation rate, but only in the case of polar solvents. For hydrogenation of benzyl alcohol over Ru/Al_2O_3 and Pt/Al_2O_3 catalysts, the hydrogenation rate was found to be in a good agreement with δ (defined as a difference between the donor and acceptor numbers) [11]. It was determined that both non-polar solvents and polar solvents having negative δ, such as MeOH, EtOH, and acetic acid, had no influence on hydrogenation of benzyl alcohol over Ru/Al_2O_3. However, polar solvents with positive δ, such as acetone, tetrahydrofuran, 1,4-dioxane, and diethyl ether, inhibited the reaction. Besides, alcohols were found to strongly inhibit the activity of the Pt/Al_2O_3 catalyst [11]. The selectivity and reaction rate of Pd catalyzed hydrogenation of ketoisophorone were shown to be strongly dependent on the solvent polarity [12]. Investigated solvents formed a certain series according to their influence on catalytic activity (toluene = acetonitrile ≤ cyclohexane = butanol < *i*-PrOH < EtOH < MeOH) and selectivity (butanol < cyclohexane < toluene = *i*-PrOH < EtOH < MeOH). Masson et al. [13] studied liquid-phase selective hydrogenation of AP on Ni-Raney catalyst using C_1–C_3 alcohols and cyclohexane as solvents. Hydrogenation rate was found to increase linearly with the increase of the dielectric constant of alcohols. At the same time, the reaction rate was higher for cyclohexane (non-polar solvent) than for PrOH (polar solvent), but lower than for *i*-PrOH, which did not allow a complete correlation between the catalytic activity and solvent polarity. Bertero et al. [2] also investigated AP hydrogenation over Ni-containing catalyst (Ni/SiO_2) using a wide range of solvents and found that for protic solvents, the activity pattern was: *i*-PrOH > PrOH > EtOH ≫ MeOH. Besides, the highest selectivity was observed in protic solvents in comparison with aprotic polar and non-polar ones. Hydrogen-bond donor ability (α) as well as solvent–catalyst interaction was suggested to influence the dependence of catalytic activity and selectivity on solvent nature.

The last factor determining the solvent influence on hydrogenation reactions is the solubility of hydrogen. The solvent influence via thermodynamic interactions was proposed by many researchers. Favorable thermodynamic interactions between the solvent and reactants were found to allow reducing the adsorption of reactants on the catalyst [14]. Rautanen et al. [15] revealed that different hydrogenation rates can be achieved depending on the hydrogen solubility: catalytic activity was the same for isooctane and *n*-heptane, while it was lower for cyclohexane, especially at high temperatures [15].

The influence of the solvent nature on hydrogenation of 2-methyl-3-butyn-2-ol (MBY) was studied by Zakumbaeva et al. [16]. It was shown that solvents affect not only the mechanism, but also the enthalpy of hydrogen adsorption on the catalyst surface, which causes a difference in the catalyst activity and selectivity.

Thus, numerous studies showed the influence of solvent on the catalyst performance in selective hydrogenation reactions. However, these studies were mainly carried out on conventional heterogeneous catalysts where noble metals were deposited on carbon or metal oxide supports. As a rule, such catalysts have high metal loading (from 2 up to 10 wt.%) and show rather good correlation between the hydrogenation rate and solvent parameters.

It is noteworthy that heterogeneous catalysts based on inorganic or carbon supports do not usually provide stability of catalytically active phase, i.e., metal nanoparticles are inclined to aggregation and leaching [17–19]. Besides, they often require additional modifiers [17] that results in pollution of target products. The use of nanostructured polymers of different types as supports for catalytic species allows formation of microheterogeneous catalysts, which combine the advantages of both homo- and heterogeneous systems and are suitable for various catalytic applications.

In this paper, we propose hypercrosslinked polystyrene (HPS) as a prospective polymeric support for hydrogenation catalyst. Due to its extremely high surface area and unique porous structure [20,21], HPS allows control over incorporation of various metal-containing compounds and also control nucleation and growth of metal nanoparticles within the polymer matrix. This allows one to prevent metal leaching. However, in spite of numerous studies of HPS as a catalyst support in different oxidation and hydrogenation reactions [21–26], none of them explored the solvent effect. In this paper we are assessing the influence of both polar and non-polar solvents and correlating the solvent characteristics (μ, ε) and catalytic performance (activity/selectivity) of Pd supported on HPS in catalytic hydrogenation of a triple bond in MBY to a double one in 2-methyl-3-butene-2-ol (MBE).

2. Materials and methods

2.1. Materials

Before the use, HPS Macronet MN270 (Purolite Int., United Kingdom) and HPS Optipore, OP, (Sigma-Aldrich, Switzerland) were washed with water and acetone and dried under vacuum [21]. Ethanol (EtOH, >99.5%), *m*-xylene (>98%), hexane (>99%), heptane ((>99%), MBY (>99%), MBE (>97%), 2-methyl-2-butanol (MBA, >96%) were obtained from Fluka (Switzerland). Metal precursor ($Pd(CH_3COO)_2$, >99%), cyclohexane (>99%), acetone (>99.9%) were obtained from Sigma-Aldrich (Switzerland). *n*-Octane (>99%), dodecane (>99%), 1-butanol (>99.5%) were obtained from Acros Organics (Belgium). 2-Propanol (*i*-PrOH, >99%) was obtained from Merck KGaA (Germany). Toluene (>99%) was obtained from AnalaR NORMAPUR (Ireland). All chemicals were used as received. Distilled water was purified with an Elsi-Aqua water purification system.

2.2. Catalysts synthesis

0.2 wt.% Pd/MN270 catalyst was synthesized according to the procedure described elsewhere [21] upon variation of the HPS powdering degree: the granules with the size of <47 μm and <63 μm as well as unpowdered HPS (0.2–1 mm) were investigated [21]. In a typical experiment, 3 g of pretreated, dried and crushed polymer granules were impregnated with 8.5 mL of a $Pd(CH_3COO)_2$ THF solution of a certain concentration. The Pd-containing polymer was dried at 70 °C, treated with Na_2CO_3, washed with distilled water till neutral pH, and dried again. Then the resulting catalyst was reduced by H_2 at 300 °C for 2 h.

The Pd/OP catalyst with 0.5 wt.% of Pd was synthesized using the same impregnation procedure. The resulting Pd-containing polymer was dried at room temperature and reduced by H_2 at 300 °C for 2 h.

The catalyst compositions were confirmed by atomic absorption spectroscopy (AAS) analysis.

2.3. MBY hydrogenation

Hydrogenation experiments were carried out in stainless steel semi-batch reactor (150 mL autoclave, Buchi AG, Uster, Switzerland) equipped with a heating jacket, a hydrogen supply system, a 8-blade disk turbine impeller and a pressure controlled H_2

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supply system. At the beginning of each experiment, an MBY solution (C_{MBY} = 75 g/L, V_{tot} = 80 mL, C_{ST} = 63 g/L (dodecane or 1-butanol (in the case of water/EtOH mixture) were used as a standard for chromatography)) was charged into the reactor and flushed three times with N_2 under stirring. The temperature was set and allowed to stabilize (ca. 30 min). H_2 was then introduced and the system was pressurized (time $t = 0$ for reaction). In a series of blank tests, reactions carried out in the absence of a catalyst did not show any measurable conversion. The consumption of hydrogen was monitored using pressflow gas controller (BPC-6002) (Buchi, Switzerland).

Experiments were carried out at 3 bar of hydrogen partial pressure at various reaction temperatures (313 K or 333 K) and stirring rates (from 500 up to 2000 rpm). Both polar (EtOH, *i*-PrOH, H_2O) and non-polar (alkanes: hexane, cyclohexane, heptane, octane and aromatic hydrocanbons: toluene, xylene) solvents were used. It is noteworthy that the total pressure in the reactor was varied according to the achieved solvent vapor pressure to maintain the equal hydrogen partial pressure in each experiment.

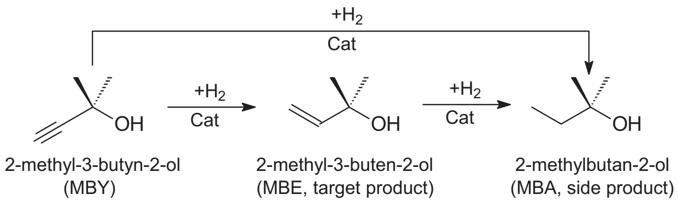
A non-invasive liquid sampling system via syringe allowed a controlled removal of aliquots ($\leq$0.3 cm^3) from the reactor. The samples were analyzed by gas chromatography (GC) using a Perkin-Elmer Auto System XL equipped with a 30-m Stabilwax (Crossbond Carbowax-PEG, Restek) 0.32-mm capillary column with a 0.25-μm coating. The carrier gas (He) pressure was 0.1 MPa. Injector and flame ionization detector temperatures were 473 K and 523 K, respectively. The oven temperature was maintained at 323 K for 4 min, and then increased to 473 K at a ramp rate of 30 K/min. The concentrations of the reaction mixture components Y_i (where i represents MBY, MBE, and MBA) was calculated from the peak areas assuming similar GC response factors. Selectivity to MBE was defined as $S_{MBE} = Y_{MBE} \times X^{-1} \times 100\%$, where X is the MBY conversion. Activity was calculated as $TOF_X = C_{MBY} \times {C_{Pd}}^{-1} \times X \times 0.01 \times \tau^{-1}$, where C_{MBY} and C_{Pd} are the molar amounts of MBY and Pd and τ is the reaction time for achieving the certain MBY conversion X.

2.4. Catalyst characterization

Pd nanoparticle size was evaluated by transmission electron microscopy (TEM) 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 ImageJ software.

BET area was determined using the Sorptomatic 1990 (Carlo Erba). Prior to analysis, the sample was out gassed at 523 K for 2 h under vacuum (#14×19#× 10^{-2} Torr). BET area was obtained by nitrogen adsorption at 77 K according to the method of Dollimore and Heal.

Pd loading was determined by AAS. The sample was dissolved in *aqua regia* at continuous stirring and heating and obtained solution was analyzed using Shimadzu AA-6650 spectrometer with an air–acetylene flame.



Scheme 1. Reaction pathway of MBY hydrogenation.

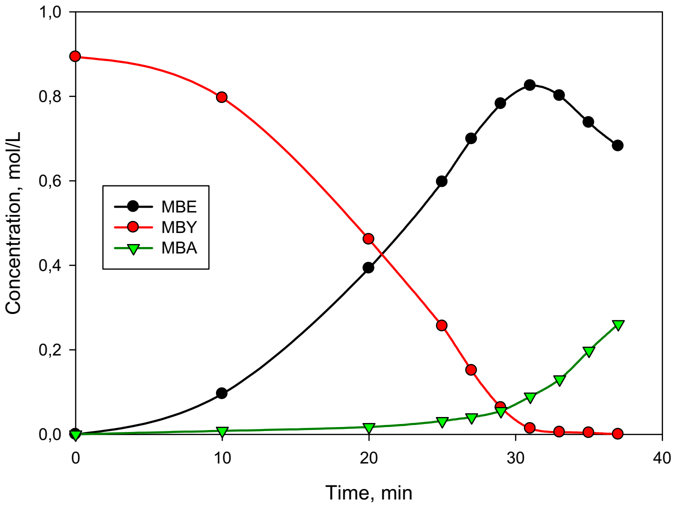


Fig. 1. Kinetic curves of MBY hydrogenation in ethanol over 0.2%Pd/MN270 catalyst (T = 333 K, $P_{H_2} = 3$ bar, stirring–1500 rpm).

3. Results and discussions

Scheme 1 represents the reaction pathway of MBY hydrogenation.

Kinetic curves of MBY hydrogenation obtained in a typical experiment using EtOH as a solvent are shown in Fig. 1. Clearly, the time dependence of the MBE accumulation goes through a maximum at the MBY conversion of about 85%. A further substrate conversion results in over-hydrogenation of MBE to MBA.

3.1. Effect of the support and characterization of the catalysts

A comparative study of the catalysts based on HPS purchased from different suppliers was carried out using EtOH and toluene as solvents (Table 1). From the data presented in Table 1 it is seen that the catalyst based on HPS purchased from Purolite Ltd. (MN270) provides higher activity and selectivity in the MBY selective hydrogenation in comparison with that based on OP. Thus all the further experiments were carried out using 0.2%Pd/MN270 catalyst as the most promising one.

Chosen HPS supports and the HPS-based catalysts synthesized were characterized by the low-temperature nitrogen physisorption and TEM. The BET surface areas (SSA) of both MN270 and OP were very high: 1373 $m^2\ g^{-1}$ and 1065 $m^2\ g^{-1}$, respectively. Besides, the

Table 1
MBY hydrogenation (333 K, $P_{H_2} = 3$ bar, 1500 rpm) over the HPS-based catalysts.

Solvent	Catalyst	D_m, nm	TOF_{50}, mol(MBY)/(mol(Pd)*s)	MBE selectivity, %		Maximum MBE yield, %
				at 50% MBY conversion	at 95% MBY conversion	
EtOH	0.2%Pd/MN270	3.7	85.5	94.8	93.2	88.8
	0.5%Pd/OP	4.2	45.3	91.0	83.0	76.9
Toluenee	0.2%Pd/MN270	3.7	35.0	99.9	99.6	96.4
	0.5%Pd/OP	4.2	36.3	99.5	93.5	86.8

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nitrogen physisorption measurements suggest the presence of both *micro-* (<2 nm) and *meso*-porosity (2–50 nm). The predominant pores measure 4–6 nm allowing control over the Pd nanoparticle formation (see also Refs. [20,21]). For the catalyst 0.2%Pd/MN270, after the first catalytic use, the porosity dramatically changed with an increase of the fraction of mesopores and the appearance of macropores (Fig. 2). The BET SSA dropped to 1070 $m^2 g^{-1}$. According to the *t*-plot the decrease of SSA was mainly caused by the decrease of SSA of micropores (from 1121 $m^2 g^{-1}$ up to 836 $m^2 g^{-1}$), while external SSA changed slightly (from 288 $m^2 g^{-1}$ up to 260 $m^2 g^{-1}$).

The TEM images (Fig. 3) showed that the Pd nanoparticles with a mean diameter of about 4 nm and fairly narrow size distribution were formed in both MN270 and OP.

3.2. *Influence of stirring rate on MBY hydrogenation*

For MN270-based palladium catalyst, the influence of a stirring rate, which was varied from 500 rpm up to 2000 rpm, on MBY hydrogenation rate was investigated to exclude external diffusion limitations (Fig. 4). The catalyst (Pd) concentration was chosen as 7×10^{-6} mol(Pd)/L at the substrate (MBY) concentration of 0.9 mol/L in all the experiments.

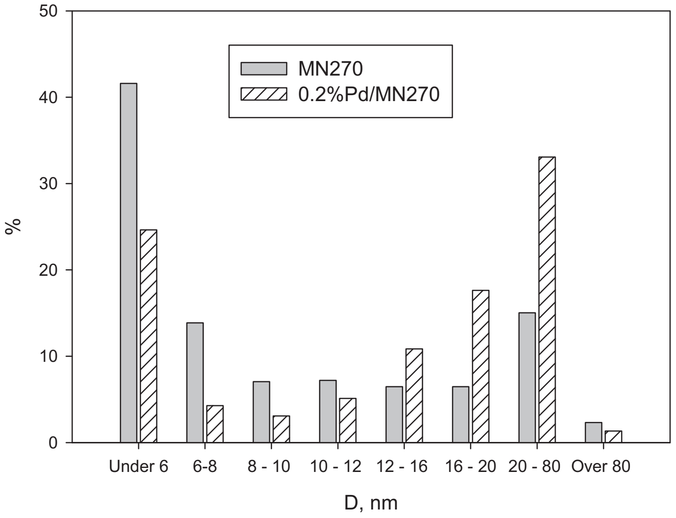

Fig. 2. Pore size distribution for MN270 and Pd-containing sample.

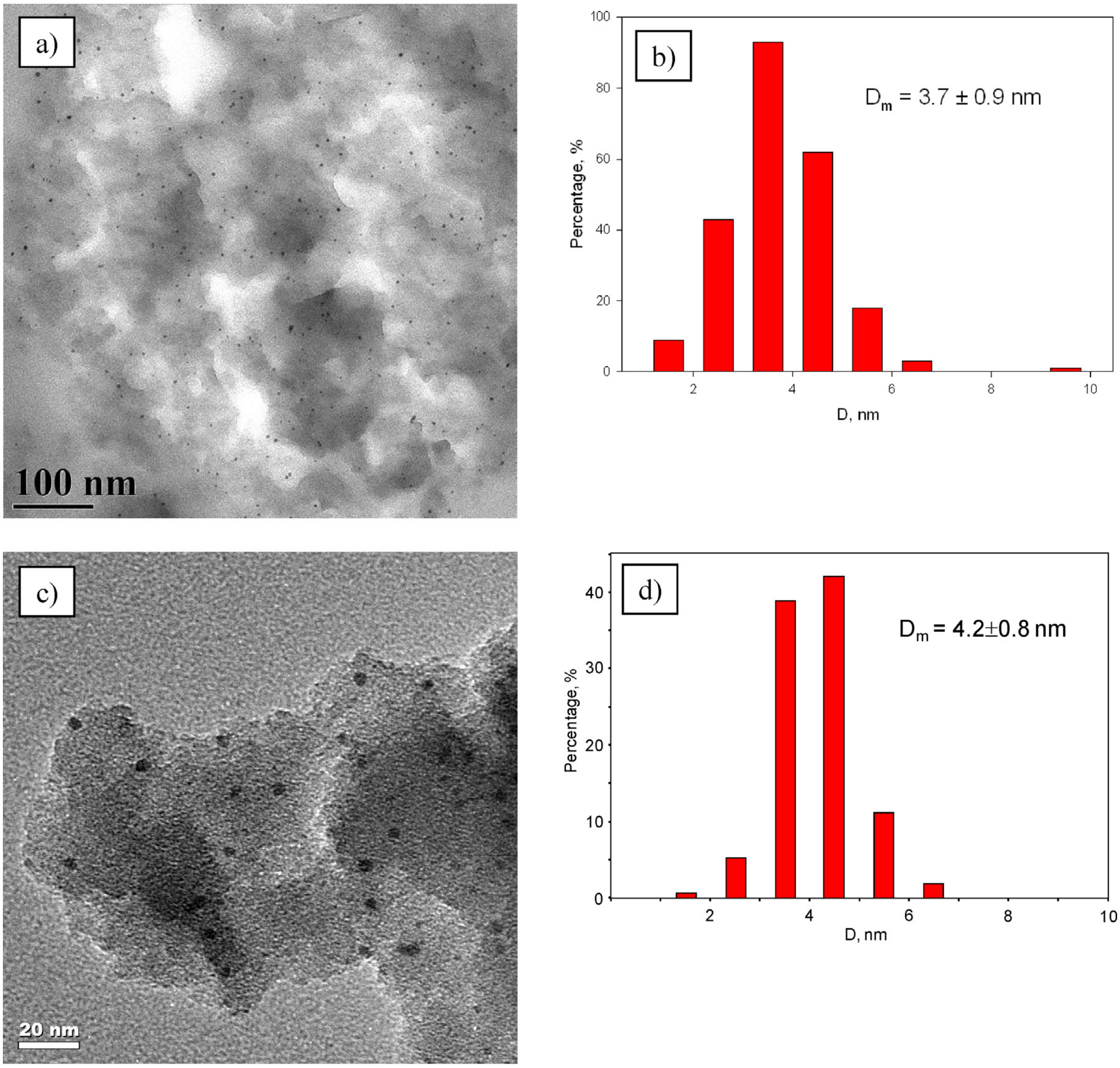

Fig. 3. TEM images and particle size distribution for 0.2%Pd/MN270 (a, b) and 0.5%Pd/OP (c and d) (the samples were taken for TEM analysis after one catalytic use).

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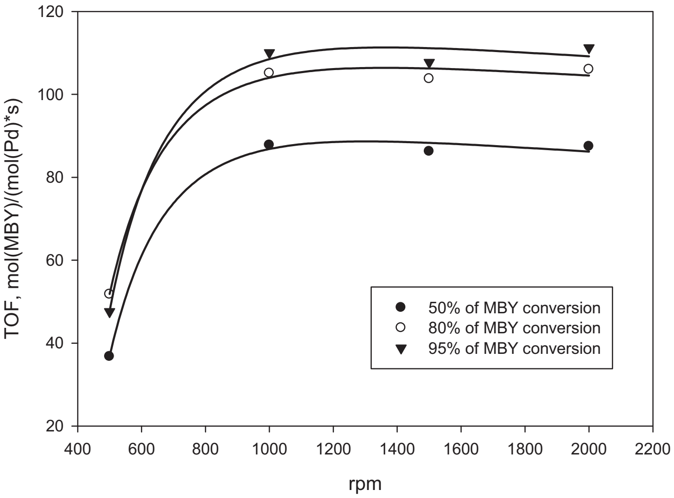

Fig. 4. Dependence of TOF of MBY hydrogenation in EtOH using 0.2%Pd/MN270 on stirring rate (333 K, 3 bar of H_2 pressure).

As it can be seen from Fig. 4, there are no mass transfer limitations above 1000 rpm independently of the degree of MBY conversion. Thus all further experiments were carried out at 1500 rpm.

3.3. *Effect of catalyst and MBY loading*

Before investigation of solvent influence the optimal substrate-to-catalyst ratio should be found. For the catalyst 0.2%Pd/MN270, the MBY loading was varied from 0.3 up to 0.9 mol(MBY)/L at following reaction conditions: 333 K, 3 bar of hydrogen partial pressure, 1500 rpm, catalyst concentration 7×10^{-6} mol(Pd)/L, EtOH was used as a solvent. The dependence of the catalytic activity on the MBY initial concentration is presented in Fig. 5.

An increase of the MBY loading from 0.3 up to 0.6 mol(MBY)/L showed a slight increase of the reaction rate (Fig. 5). Such effect can be observed for rapid reactions when an insufficient amount of substrate may result in incomplete participation of catalytic sites. In this case, the increase of the substrate concentration results in an apparent increase of TOF, which is most likely due to the participation of larger number of catalytic sites in the process. A further increase of the MBY loading up to 0.9 mol(MBY)/L results in the decrease of TOF, which corresponds to the achievement of the kinetic regime for the chosen catalyst, i.e., all the Pd species participate in the reaction (note that external diffusion was excluded at this stage, see Section 3.2). Thus all the further experiments were carried out at the MBY concentration of 0.9 mol(MBY)/L.

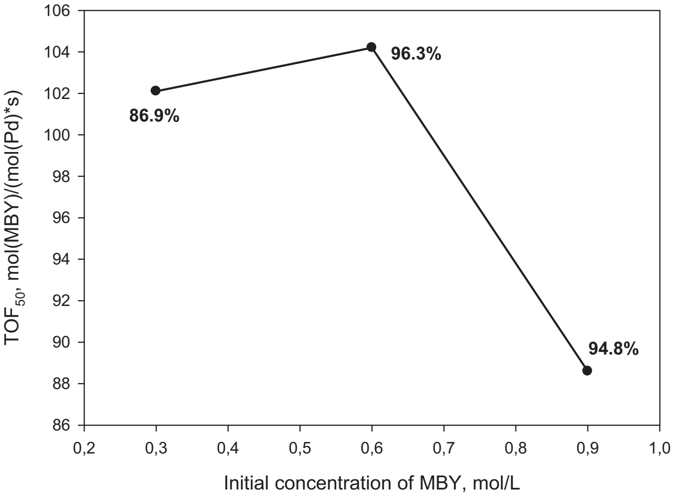

Fig. 5. Dependence of TOF_{50} on MBY loading for 0.2%Pd/MN270 (corresponding values of selectivity are also indicated).

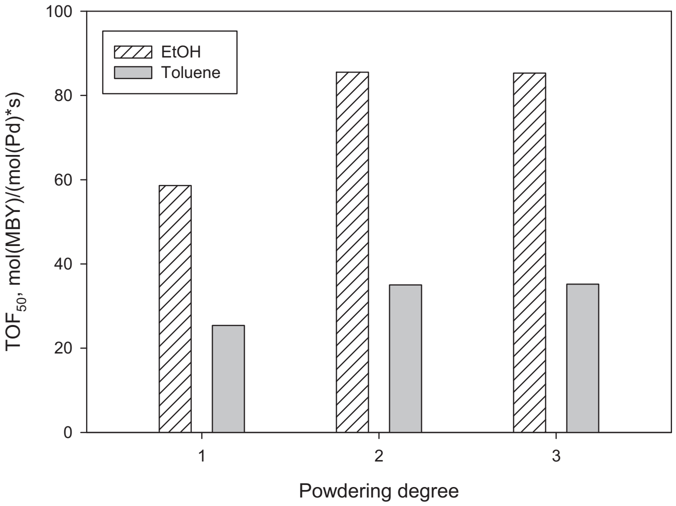

Fig. 6. Dependence of reaction rate (TOF_{50}) on the degree of HPS powdering for 0.2%Pd/MN270: 1–unpowdered MN270 (0.2–1 mm), 2–size of HPS granules less than 63 μm, 3–size of HPS granules less than 47 μm.

3.4. *Influence of powdering degree of the catalyst*

To ensure that for the chosen catalyst (0.2%Pd/MN270) internal diffusion limitations are excluded, we investigated the influence of the HPS particle size, which was varied from unpowdered initial HPS (granules with the diameter of 0.2–1 mm) to < 63 μm and < 47 μm. Although HPS is able to swell in any solvent [27], the swelling may be very different. We tested two solvents, EtOH and toluene, which completely differ in their properties (see Fig. 6) to assess the influence of the HPS powdering degree.

The decrease of the HPS particle size from initial granules to the particles with the size less than 63 μm provides increase of TOF almost by a factor of 1.5 both for EtOH and toluene. Selectivity also increases from 87.3% up to 94.8% (at 50% of MBY conversion). Further powdering of HPS up to < 47 μm has almost no effect on catalytic activity and selectivity in accordance with the data published by Doluda et al. [28] for lactose hydrogenation over Ru/HPS catalysts in water. Thus, all further experiments were carried out using the catalyst based on the HPS granules with the size < 63 μm.

3.5. *Solvent effect*

Fig. 7 shows the solvent effect on MBY conversion. For the reader convenience, we used different designations to curves corresponding to solvents of different groups: dashed lines for polar solvents; dash-dot lines for aromatic non-polar solvents (xylene and toluene) and solid lines for other non-polar solvents.

One can see (Fig. 7) that the rate of the MBY conversion changes with time, e.g., at the high conversion, the conversion rate decreases in many cases. Thus, for a fair comparison, we mainly considered the values of hydrogenation rate and selectivity at the MBY conversion of 50% and also at 95%.

3.5.1. *Influence of solvent polarity*

The data of Fig. 7 show that solvent nature strongly influences the MBY conversion. To find correlations between solvent nature and catalytic activity and selectivity, we considered solvents to

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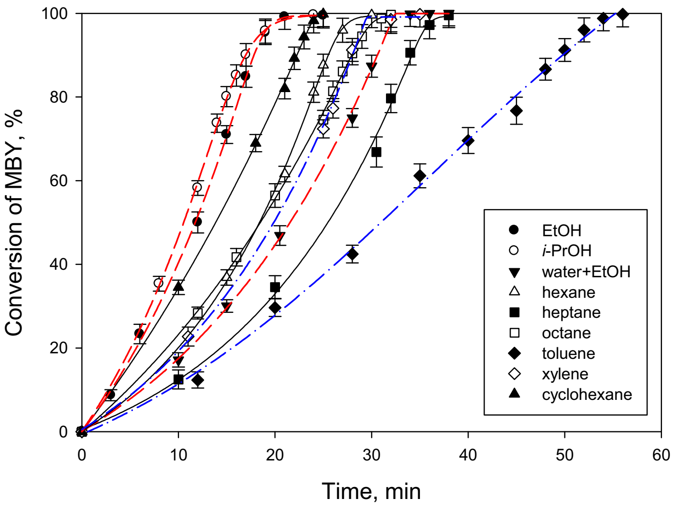

Fig. 7. Solvent effect on MBY conversion over 0.2%Pd/MN270 (333 K, 3 bar of H_2 pressure).

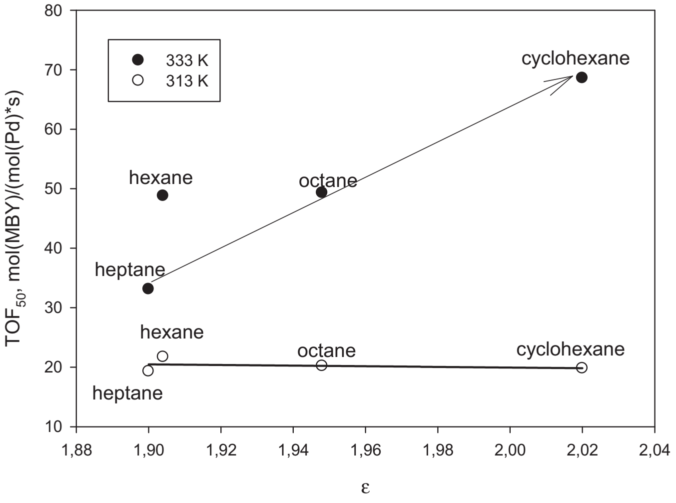

Fig. 9. Dependence of reaction rate (TOF$_{50}$) on dielectric constant of non-polar solvents.

be divided into the three following groups: polar (water, EtOH, *i*-PrOH), non-polar (hexane, heptane, octane and cyclohexane) and aromatic non-polar (*m*-xylene and toluene) solvents.

The results of the MBY hydrogenation in the polar solvents over the 0.2%Pd/MN270 catalyst are presented in Table 2. It is noteworthy that pure water could not be used as a solvent because of the limited solubility of the hydrogenated products and the formation of an emulsion under the reaction conditions.

The temperature increase leads to the increase of the hydrogenation rate (TOF) while the selectivity decreases (Table 2). The decrease of selectivity is likely due to the increase of the over-hydrogenation reaction rate with temperature.

Besides, a clear correlation between the hydrogenation rate (TOF$_{50}$) and the solvent dielectric constant (ε) is observed (Fig. 8). The increase of the solvent polarity was found to result in the appropriate decrease of the reaction rate independently of the reaction temperature. At the same time the selectivity does not seem to be influenced by the solvent polarity. The maximum selectivity was observed for EtOH.

In the case of non-polar solvents (Table 3), the increase of the dielectric constant was found to result in a corresponding increase of TOF at temperature of 333 K (Fig. 9) while selectivity diminished (with the exception of hexane, for which the highest selectivity (100% at 50% of MBY conversion) was observed).

The solvent influence on the catalyst performance was also tested for non-polar aromatic hydrocarbons, such as *m*-xylene and toluene with nonzero dipole moments. The results of the MBY hydrogenation in these solvents are presented in Table 4 and Fig. 10. Similarly, the influence of aromatic non-polar solvents on catalytic activity becomes noticeable only at a higher temperature. It can be seen that at 333 K the higher dipole moment and dielectric constant result in the lower activity but higher selectivity. The highest selectivity (close to 100%) was reached in toluene and the highest TOF$_{50}$ (47.0 mol(MBY)/(mol(Pd)*s)) was observed in *m*-xylene.

However, for all the non-polar solvents, no correlation can be found (see Fig. 11): pairs heptane/toluene and octane/xylene revealed similar TOF$_{50}$ (33.1/35.0 and 49.3/47.0 mol(MBY)/(mol(Pd)*s), respectively) for solvents with dielectric constants. The highest activity (68.6 mol(MBY)/(mol(Pd)*s)) and the lowest selectivity (85.8% at 50% of MBY conversion) were observed for cyclohexane.

At the same time, the increase of the dielectric constant for polar solvents, in contrast to non-polar ones (such as hexane, heptane, octane and cyclohexane), results in the corresponding decrease of TOF$_{50}$. For the water/EtOH mixture, the observed value

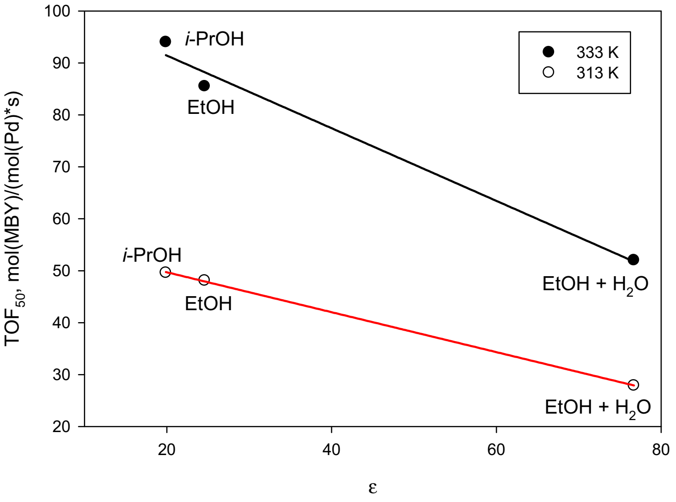

Fig. 8. Dependence of reaction rate (TOF$_{50}$) on dielectric constant of polar solvents.

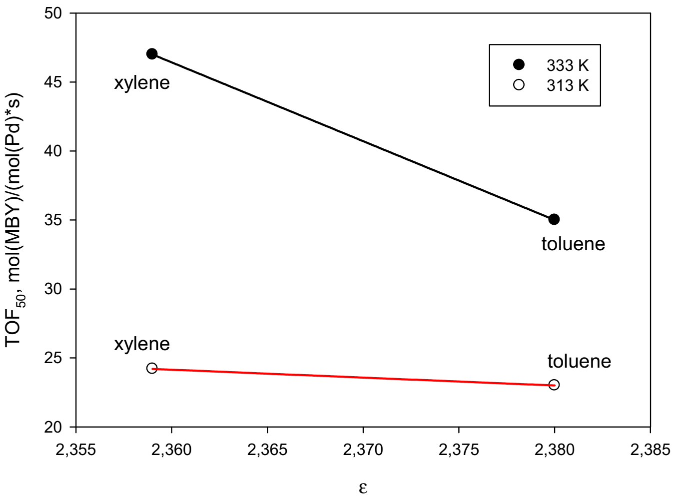

Fig. 10. Dependence of TOF$_{50}$ on dielectric constant of aromatic non-polar solvents.

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Table 2
MBY hydrogenation in polar solvents over 0.2%Pd/MN270 ($P_{H_2} = 3$ bar, 1500 rpm, catalyst concentration 7×10^{-6} mol(Pd)/L, initial concentration of MBY 0.9 mol/L).

Solvent	*T*, K	ε	μ	50% MBY conversion		95% MBY conversion		Maximum MBY yield, %
				TOF$_{50}$, mol(MBY)/(mol(Pd)*s)	MBE selectivity, %	TOF$_{95}$, mol(MBY)/(mol(Pd)*s)	MBE selectivity, %	
i-PrOH	313	19.9	1.66	49.6	97.3	68.2	92.3	89.1
	333			94.0	95.8	109.1	86.0	82.4
EtOH	313	24.6	1.69	48.1	99.5	64.1	98.7	96.4
	333			85.5	94.8	107.7	93.2	88.8
H_2O (70 mL) + EtOH (10 mL)	313	76.7	–	27.9	95.5	34.1	92.4	89.1

Table 3
MBY hydrogenation in non-polar solvents over 0.2%Pd/MN270 ($P_{H_2} = 3$ bar, 1500 rpm, catalyst concentration 7×10^{-6} mol(Pd)/L, initial concentration of MBY 0.9 mol/L).

Solvent	*T*, K	ε	50% MBY conversion		95% MBY conversion		Maximum MBE yield, %
			TOF$_{50}$, mol(MBY)/(mol(Pd)*s)	MBE selectivity, %	TOF$_{95}$, mol(MBY)/(mol(Pd)*s)	MBE selectivity, %	
Heptane	313	1.900	19.3	96.9	27.2	95.9	91.6
	333		33.1	96.3	45.6	92.8	90.4
Hexane	313	1.904	21.7	96.3	25.5	92.7	92.2
	333		48.8	100	64.2	93.9	90.1
Octane	313	1.948	20.2	92.8	22.9	90.4	89.7
	333		49.3	93.6	58.8	92.8	87.8
Cyclohexane	313	2.020	19.8	93.9	23.6	85.4	84.5
	333		68.6	85.8	78.4	81.7	78.5

Table 4
MBY hydrogenation in aromatic non-polar solvents over 0.2%Pd/MN270 ($P_{H_2} = 3$ bar, 1500 rpm, catalyst concentration 7×10^{-6} mol(Pd)/L, initial concentration of MBY 0.9 mol/L).

Solvent	*T*, K	ε	μ	50% MBY conversion		95% MBY conversion		Maximum MBE yield, %
				TOF$_{50}$, mol(MBY)/(mol(Pd)*s)	MBE selectivity, %	TOF$_{95}$, mol(MBY)/(mol(Pd)*s)	MBE selectivity, %	
m-Xylene	313	2.359	0.33	24.2	92.4	33.5	89.3	86.3
	333			47.0	90.6	64.2	89.6	82.4
Toluenee	313	2.380	0.37	23.0	99.7	32.2	99.5	96.0
	333			35.0	100	40.0	99.6	96.4

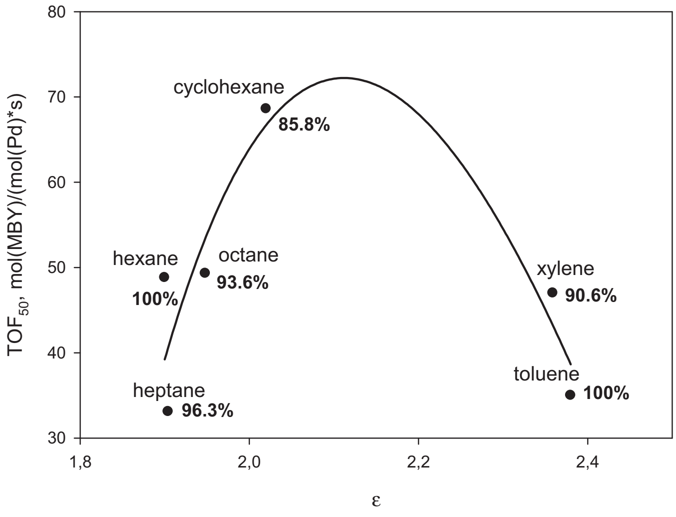
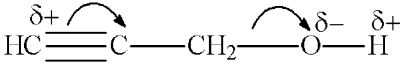


Fig. 11. Dependence of TOF$_{50}$ on dielectric constant for non-polar solvents (corresponding values of selectivity are also indicated).

of TOF$_{50}$ (52.0 mol(MBY)/(mol(Pd)*s) is comparable with the value found in octane (49.3 mol(MBY)/(mol(Pd)*s), though the dielectric constant of octane is about 40 times lower than that of the mixture.

Thus, the difference in TOF cannot be explained simply by the difference in solvent polarity (in contrast to the data reported by Bertero et al. [2] and Drelinkiewicza et al. [7] for AP hydrogenation, when H-bond donor ability and alcohol solvation hindered the substrate adsorption on noble metal).

We suggest that the absence of correlation between the observed activity and solvent polarity can be due to the unusual properties of MBY. The presence of a heteroatom in the alcohol with unpaired electrons in vicinity of triple carbon–carbon bond causes the effect of mesomerism or conjugation. Two atomic orbitals give molecular orbitals (MO) with different energy. The MO with a low binding energy will be the bonding one (π-bond of C–C), and the MO with a high binding energy is the antibonding one (C–OH). A negative charge is localized on oxygen, while carbon and hydrogen of the OH-group are partially positively charged [29]. For example, the energy of the C–O-bond increases in the following order: propargyl alcohol (74.3 kcal/mol) < allylic alcohol (78.9 kcal/mol) < PrOH (91.8 kcal/mol) [30,31], i.e. the mesomeric effect results in the decrease of the C–O binding energy.



In the case of MBY, the C–O binding energy will be also decreased. Besides, due to alkyl groups in MBY, the induction effect (acting in opposite direction of mesomerism) will take place, i.e., the alkyl groups additionally push the electron density in the direction of the triple bond [31].

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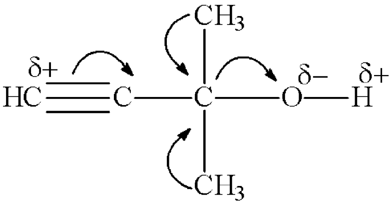

As a result, in the case of MBY, the polarity of OH-group will be decreased (δ- for O will be higher and hence the electron donation from H will be weaker) due to the close proximity of the triple bond as well as two CH_3-groups. For example, a dipole moment of MBY (1.59) is lower than that of propargyl alcohol (1.78) [29]. Thus, we suggest solvent–substrate interactions do not influence the differences in catalytic activity observed.

It is noteworthy that when the reaction was carried out under solvent-free conditions, relatively high values of selectivity were observed (93.8% and 99.8% at 95% and 50% conversions, respectively) at rather low TOF_{50} (33.2 s^{-1} at 333 K, respectively).

3.5.2. *Influence of hydrogen solubility*

According to the investigations carried out by several research groups [2,7,15], hydrogen solubility cannot explain the difference in catalytic activity. The same conclusion can be made also for the MBY selective hydrogenation.

For example, a mole fraction of soluble H_2 in heptane is higher in comparison with that in octane at the same conditions (0.087 vs. 0.091, at 295 K and 13.88 MPa), while in toluene it is higher in comparison with that in *m*-xylene (0.041 vs. 0.045, at 295 K and 13.88 MPa) [32]. However, we observed that catalytic activities in heptane and toluene at 333 K and 3 bar are lower in comparison with those in octane and *m*-xylene, respectively. Hydrogen solubility in cyclohexane almost 1.5 times lower than that in heptane and octane [32], but TOF_{50} of the MBY hydrogenation is by a factor of 1.3–1.4 higher at 333 K and comparable at 313 K (see Table 3). Solubility of hydrogen in hexane is lower than that in octane (0.074 vs. 0.079 at 298 K and 5 MPa [33]), but TOFs at 50% of the MBY conversion are comparable. Although the above mentioned data on the H_2 solubility are presented for relatively low temperatures (295–298 K) and high partial pressures, it is noteworthy that at the certain partial pressure the difference between hydrogen solubilities decreases with the increase of temperature. For example, the difference in mole fraction solubilities of H_2 in octane and hexane at 5 MPa changes in the following order: 0.0049 (298 K) > 0.0025 (323 K) > 0.0016 (373 K) [33]. Thus it can be concluded that the evident increase of the differences in TOFs of the MBY hydrogenation with the temperature for non-polar solvents (see Figs. 8 and 9) is not due to hydrogen solubility and can be explained only by the solvent–catalyst interaction, as all the experiments were carried out at the constant H_2 partial pressure of 3 bar.

Besides, according to the data of Ghavre et al. [34], at a low hydrogen partial pressure of 0.101 MPa and 293 K, the solubility of H_2 in EtOH (2.98×10^{-3} mol/L) is lower than that in toluene (3.50×10^{-3} mol/L) and in cyclohexane (3.63×10^{-3} mol/L), that contradicts to the TOFs values observed. While comparing the catalytic activity observed in EtOH and *i*-PrOH (Table 2) one can see that TOF in *i*-PrOH is higher than that in EtOH, but hydrogen solubility in *i*-PrOH is lower in comparison to the value in EtOH according to the data of Bertero et al. [2].

The effect of hydrogen solubility can only explain the lowest TOF in the water/EtOH mixture, as in water the H_2 solubility by several orders of magnitude lower (0.81×10^{-3} mol/L [34]) than in other polar solvents.

3.5.3. *Influence of solvent–catalyst interactions*

It is known that in many cases the interaction of a solvent with a catalyst is responsible for changes of the reaction rates [2,4,5,35–37].

However, in our case, while dealing with highly porous polymeric network, the measurement of the enthalpy of the solvent desorption from palladium is complicated for several reasons such as capillary effect hindering the solvent evacuation from inner HPS pores and the possible solvent interaction with benzene rings of the polymeric matrix. As the effect of support cannot be excluded, e.g., like it was done by Bertero et al. [2] for SiO_2, we suggested that due to the features of the catalytic support used and low Pd content, there is no possibility to provide quantitative estimation of solvent–catalyst interactions, and for further discussion we only used literature data.

It was reported that in the case of the AP hydrogenation over Ni-containing catalyst, there is a difference in adsorption enthalpy for toluene and benzene. The authors found that weaker adsorption of toluene on Ni in comparison with benzene can explain the lower activity [2 and Refs. therein]. Thus we can also propose that the same kind of the dependence takes place in the case of Pd-HPS. We suggested that *m*-xylene adsorbs weaker on the Pd surface in comparison with toluene due to the existence of an additional methyl group, and hence the TOF observed in *m*-xylene was higher and the selectivity was lower than those in toluene (see Table 4 and Fig. 10). For cyclohexane, which likely has the lowest adsorption strength on palladium among the non-polar solvents, the highest activity was observed (Fig. 11). Moreover, the difference in catalytic activity for solvents belonging to different groups (polar and non-polar), e.g. EtOH and toluene, can be also due to the differences in their adsorption strength.

In the case of polar solvents, higher TOF for *i*-PrOH in comparison with EtOH can be explained by the ability of *i*-PrOH to be a hydrogen donor rather than EtOH in H-transfer reactions, as was reported by different research groups [2,38–40].

3.6. *Activation energy of the reaction*

For the best chosen solvents (EtOH and toluene), the values of apparent activation energy of the MBY hydrogenation over the 0.2%Pd/MN270 catalyst were found to be 26 ± 5 kJ/mol and 40 ± 5 kJ/mol, respectively (see Fig. 12).

The thermodynamic interaction can influence the reaction rate in two ways. Higher activity in the liquid phase can result in an increase of the adsorbed phase concentration at the certain concentration in the liquid phase. This can result in higher rates by a mere mass-transfer effect in the adsorbed phase. While the mass-transfer effect could result in the rate increase without any significant change in the activation energy, the latter would be reflected in the values of the apparent activation energy. As the mass-transfer effects were excluded (Sections 3.2, 3.3 and 3.4), the difference in the values of apparent activation energy is due to the solvent nature.

3.7. *Catalyst reuse*

Stability of the 0.2%Pd/MN270 catalyst was investigated in repeated reaction runs with the same catalyst in EtOH. After each run the catalyst was washed with EtOH and dried in air. The results obtained are presented in Table 5.

According to the AAS analysis, after all runs the Pd loading in the catalyst did not change. One can conclude that there is no metal leaching during the hydrogenation. The HPS-based catalyst demonstrates a combination of stability and selectivity toward the desired product.

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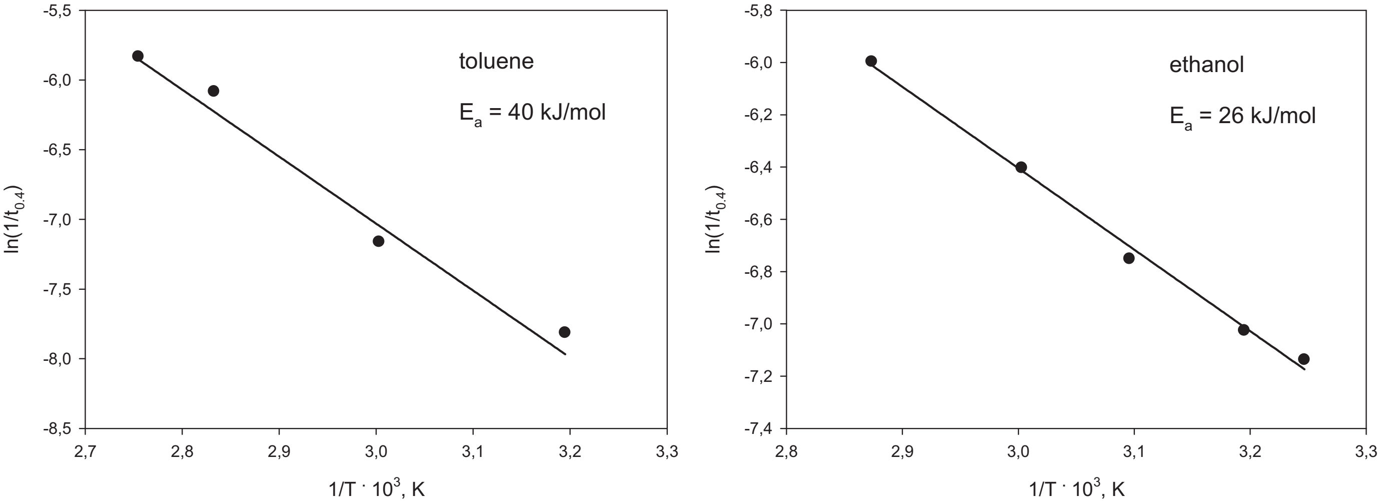

Fig. 12. Arrhenius plots for MBY hydrogenation over the 0.2%Pd/MN270 in toluene (a) and EtOH (b).

Table 5
Reuse of the 0.2%Pd/MN270 (333 K, $P_{H_2} = 3$ bar, 1500 rpm, MBY concentration 0.9 mol(MBY)/L, catalyst concentration 1.2×10^{-5} mol(Pd)/L).

Run	TOF$_{50}$, mol(MBY)/(mol(Pd)*s)	MBE selectivity at 50% MBY conversion, %
1	96.6	99.4
2	96.5	97.2
3	95.9	99.8
4	96.1	99.8

4. Conclusions

This study demonstrated that the activity of the Pd-containing polymer-based catalysts in a selective hydrogenation of MBY is strongly influenced by the solvent nature. The highest TOF values were observed when using polar solvents with the TOF sequence showing as: *i*-PrOH > EtOH > H_2O + EtOH. If the non-polar solvents are used, the activity follows the following pattern: cyclohexane > octane ≥ hexane > heptane; while the selectivity sequence is: hexane > heptane > octane > cyclohexane. Although for each group of the solvents there is a dependence between the dielectric constant (ε) and TOF, the solvent–substrate interactions do not explain the difference in catalytic activity and selectivity. Hydrogen solubility also cannot explain the experimental data, thereby the activity pattern was essentially determined by the strength of the solvent–catalyst interactions.

Among the investigated solvents the highest MBE selectivity (99.6%) was achieved while using the 0.2%Pd/MN270 catalyst in toluene (non-polar aromatic solvent) at 333 K. The results obtained confirm that the choice of solvent is extremely important for the catalyst performance in liquid-phase selective hydrogenation. In addition, the HPS-based catalyst synthesized showed no Pd leaching during the multiple reuses making it promising for various catalytic applications.

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