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Hydrogenolysis of a wood extractive to an anticarcinogenic and antioxidative compound

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Abstract

Solvent effects and catalyst stability were studied in the three-phase hydrogenolysis of the natural occurring lignan hydroxymatairesinol to matairesinol. To study the solvent effects, the reaction was carried out over a Pd/C catalyst in a variety of solvents, including ethanol, 2-propanol, *tert*-butanol, 2-pentanol, as well as in a mixture of 2-propanol and water (50:50, v/v). Over 70% of the hydroxymatairesinol was converted in 4 h when ethanol, 2-propanol, and 2-pentanol were used as solvents. The reaction was significantly retarded by mixing 2-propanol with water and the lowest activity was obtained in *tert*-butanol. Alcohols with shorter carbon chains were also interacting with the reactant resulting in lower selectivity; the byproducts 7-ethoxymatairesinol and 7-isopropoxymatairesinol were obtained in ethanol (the lowest selectivity) and in 2-propanol, respectively. Hydrogenolysis in 2-propanol over palladium impregnated activated carbon, and two Beta zeolites (H-Beta-300 and H-Beta-150, SiO_2/Al_2O_3 molar ratio 300 and 150) was also investigated with respect to deactivation; consecutive experiments were performed with the catalysts being filtered, washed, dried, and re-reduced in between the runs. The catalysts were prone to deactivation caused by fouling; long chain alkanes and aromatic components were blocking the active sites. The decrease in activity was the largest for the Pd-H-Beta-300 catalyst.

Keywords: Hydrogenolysis; Palladium; Carbon; Zeolite; Solvent effects; Deactivation

1. Introduction

Recent studies have shown that lignans have a preventive effect against hormone-dependent cancers such as breast, prostate, and colon cancers [1]. Moreover, some lignans also have antioxidative effects [2]. Norway spruce (*Picea abies*) knots, i.e. the part of a branch that is embedded in the stem, contain unusually large quantities of lignans, 6–24 wt.%, where hydroxymatairesinol (HMR) is the most abundant, 65–85 wt.% of the lignans [3]. Matairesinol (MAT), which has shown to be superior to HMR in epidemiological studies [4], can be found in smaller amounts in different plants for example in flaxseed and rye [5]. MAT can also be produced through hydrogenolysis of HMR, extracted from Norway spruce knots. The hydrogenolysis of HMR to MAT was studied in our previous work over palladium supported by activated carbons with different acidities [6]. It was concluded that the activity was directly proportional to the acidity of the carbon support. Acidic zeolites (Y, Beta, Mordenite, ZSM-5, as well as the mesoporous material MCM-41) were then impregnated with palladium and tested in the reaction [7]. As the acidity of the promising Beta zeolite was varied by changing the Si/Al ratio, it was concluded that the activity was inversely dependent on the acidity [7]. Both acidity and metal function are needed in the hydrogenolysis reaction, since support material without palladium was not active in the reaction and palladium impregnated on Al_2O_3 and SiO_2 (having small amounts of Brønsted and high amount of Lewis acid sites) had only low activity [7].

It is known, that solvents can have a great influence on the activity and selectivity in catalytic reactions of fine chemicals [8]. In this work, the effect of solvent was investigated using ethanol, 2-propanol, *tert*-butanol, 2-pentanol, as well as a mixture of 2-propanol and water (50:50, v/v). Earlier

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2-propanol was used as a solvent in the hydrogenolysis of HMR [6,7]. Not only activity and selectivity, but also catalyst stability is important when selecting a catalyst. Therefore, the deactivation behaviour of selected catalysts was investigated.

2. Experimental

2.1. Materials

HMR was isolated from Norway spruce knots as described in [6,7]: the knots were ground and extracted in acetone–water mixture. The extract was concentrated in a rotary evaporator and then purified by flash chromatography. Two diastereomers of HMR exist, (7*R*,8*R*,8′*R*)-(−)-7-allo-hydroxymatairesinol (HMR 1) and (7*S*,8*R*,8′*R*)-(−)-7-hydroxymatairesinol (HMR 2). Both isomers react to MAT (Fig. 1a), moreover isomerization between the two isomers also takes place. MAT reacts further through hydrogenolysis of the functional groups on the benzene rings of MAT to four byproducts [6,7]. Moreover, HMR can react with the solvent (Fig. 1b). The 5 wt.% Pd/C was synthesized as described in [6]. The palladium impregnated Beta zeolites synthesis was explained in [7].

2.2. Hydrogenolysis of hydroxymatairesinol

Experiments were performed under atmospheric pressure in a stirred 200 ml glass reactor. The catalyst was pre-activated *in situ* by hydrogen (AGA, 99.999%) gas flow (100 ml/min) at 100 °C in 1 h (including heating time), after which the reactor was cooled down to the reaction temperature 70 °C under nitrogen (AGA, 99.999%) gas flow (100 ml/min). The reactant solution, consisting of HMR dissolved in 100 ml of solvent, was deoxygenated by nitrogen gas flow (100 ml/min) for 10 min in a glass tube. After pouring the reactant solution into the reactor, the stirring was started at reaction time set to zero, the gas flow was changed to hydrogen (100 ml/min) and the first sample was withdrawn. The stirring rate was 1000 rpm. Samples were taken at different time intervals and analysed by

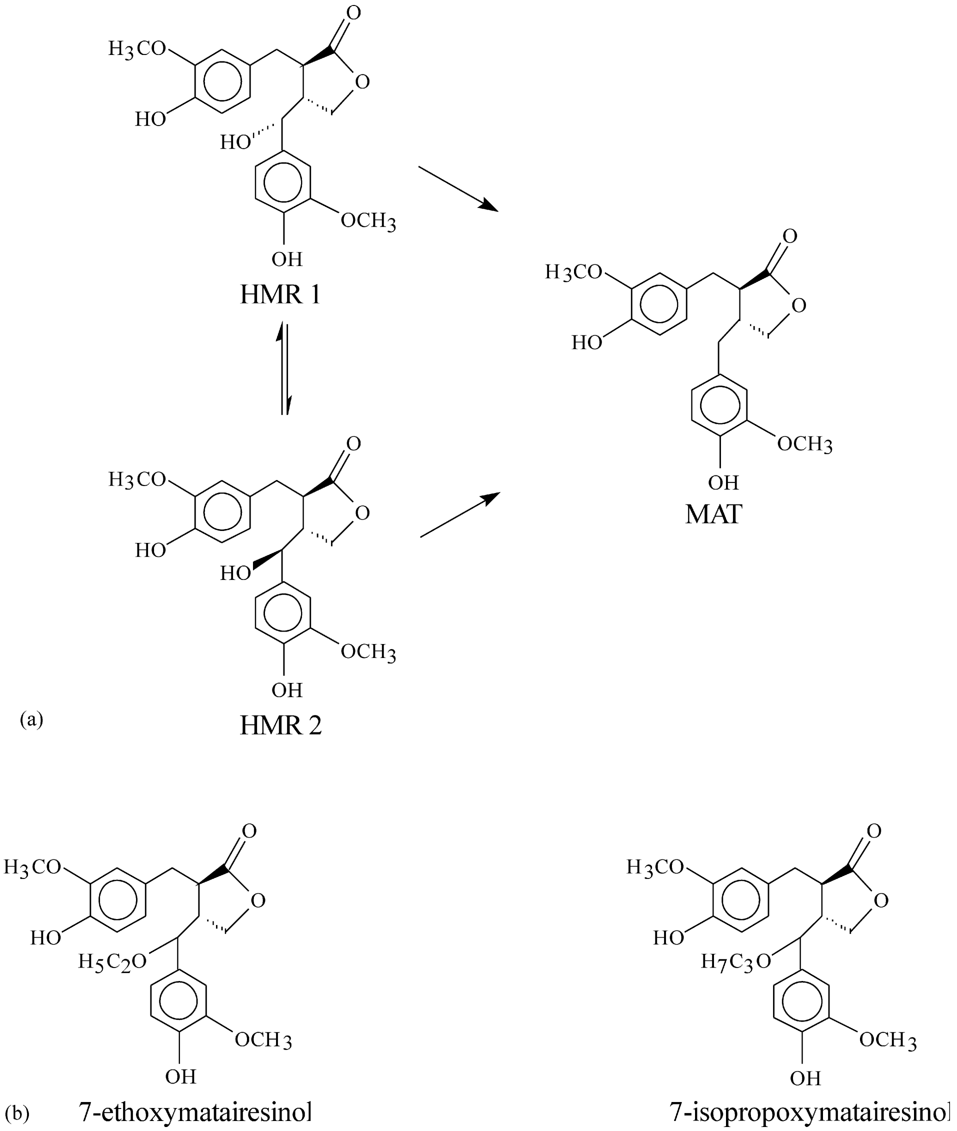

Fig. 1. Hydrogenolysis of hydroxymatairesinol (HMR) to matairesinol (MAT): (a) main reaction, (b) byproducts formed through interactions with the solvent.

a gas chromatograph (GC) as in [6,7]. The samples were silylated prior to analysis as described in [7].

In the experiments with different solvents, 100 mg of HMR and 100 mg of the Pd/C catalyst was used. The solvents ethanol (Altia, 99.5%), 2-propanol (Fluka, 99.8%), *tert*-butanol (Merck, 99.5%), 2-pentanol (Fluka, 98%), as well as a mixture of 2-propanol and de-ionised water (50:50, v/v) were investigated.

In the deactivation study, Pd-H-Beta-300, Pd-H-Beta-150, and Pd/C catalysts were used. The catalyst was filtered, washed, dried, weighed, re-reduced (*in situ* at 100 °C) between the experiments. The filtrate, containing products and reactant, was collected and analysed by direct current plasma atomic emission spectrometry (DCP, ARL Spectra-Span7) to detect any dissolved palladium. 2-Propanol was used as solvent in these experiments. Two different solvents were utilized for catalyst washing; de-ionised water (to keep the catalyst surface intact) and acetone (influence of treatment with an organic solvent). The amount of reactant in the beginning of a new experiment was always the same as the amount of catalyst; 700 mg of catalyst was used in the first experiment with the amount of HMR also being 700 mg. Since the catalyst mass after filtration and drying had decreased, the amount of HMR was also decreased in the subsequent experiment (i.e. the reactant/catalyst ratio was always kept constant). The HMR/Pd molar ratio in experiments with Pd-H-Beta-300 (2 wt.% Pd) was 14.2, with Pd-H-Beta-150 (3.9 wt.% Pd) and Pd/C (5 wt.% Pd) it was 7.3 and 5.7, respectively.

Both fresh and used catalysts were characterized by nitrogen physisorption (surface area) and scanning electron microscopy (SEM). The soluble coke was extracted using dichloromethane and analysed by GC–MS: 10 ml of dichloromethane (Fluka, 99.9%) was added to 200 mg of the catalyst. After 24 h, the solvent containing the external coke was collected and 4 ml of hydrofluoric acid (Merck, 40%) was added to the catalyst and thereafter 10 ml of dichloromethane. After 24 h, the dichloromethane including the internal coke was collected. The coke-containing samples were silylated before they were analysed by GC–MS: 1 ml of the sample (in a glass tube) was dried at room temperature overnight. Then 100 μl *N*,*O*-bis(trimethylsilyl)trifluoro-acetamide (Fluka, 98%), 20 μl trimethylchlorosilane (Acros Organics, 98%), and 20 μl pyridine (J.T. Baker, 99.0%) were added to the residue and the samples were kept in oven at 70 °C for 30 min.

3. Results and discussion

3.1. Solvent effects

HMR is poorly soluble in water and hydrocarbons, but well soluble in alcohols. The hydrogenolysis reaction was carried out in ethanol, 2-propanol, *tert*-butanol, 2-pentanol, as well as a mixture of 2-propanol and water (50:50, v/v). The experimental results and some physical properties for the alcohols are presented in Table 1. The dielectric constant, ε_r, represents the ability of a solvent to separate charge as well as to orient its dipoles and is often used as a measure of solvent polarity [8]. Polar solvents have large dielectric constants. Solvent polarity is a commonly used term related to the capacity of a solvent for solvating dissolved charged or dipolar species. However, in addition to the dielectric constant, other factors are contributing to the polarity of a solvent and therefore a parameter called empirical parameter of solvent polarity (E_T) obtained from spectroscopic measurements has been utilized [8]. The normalised empirical solvent parameter, E_N^T, range from 0.000 for tetramethylsilane to 1.000 for water (the most polar solvent).

Table 1
Hydrogenolysis of HMR in alcohols (70 °C)

Solvent	ε_r[a]	E_N^T[b]	Conversion[c] (4 h)	$Sel_{0.6}$[d]	HMR 2 / HMR 1[e]
Ethanol	24.55	0.654	0.74	0.95	1.27
2-Propanol	19.92	0.546	0.73	0.99	1.26
2-Propanol:water (50:50)	–	–	0.22	–	0.65
tert-Butanol	12.47	0.389	0.06	–	–
2-Pentanol	13.71	0.488	0.74	1.00	1.40

[a] ε_r = relative permittivity (dielectric constant) for the pure liquid at 25 °C (ref. [8]).

[b] E_N^T = the measure of polarity, normalised empirical solvent parameter (ref. [8]).

[c] Conversion $= \frac{c_{HMR,tot,0} - c_{HMR,tot}}{c_{HMR,tot,0}}$.

[d] $Sel_{0.6}$ = selectivity to MAT at conversion = 0.6, selectivity $= \frac{c_{MAT}/c_{HMR,tot,0}}{\text{conversion}}$ $c_{HMR,tot,0}$ is the initial concentration of total HMR, c_{MAT} and $c_{HMR,tot}$ the concentration of MAT and total HMR.

[e] HMR 2/HMR 1 ratio at conversion = 0.2.

Over 70% of the HMR was converted in 4 h as ethanol, 2-propanol, and 2-pentanol were used as solvents (Table 1). When de-ionised water was mixed with 2-propanol, the activity decreased dramatically. The activity was the lowest in *tert*-butanol. Similar results have been observed by Mäki-Arvela et al. [9] for hydrogenation of citral and Kun et al. [10] in the hydrogenation of crotonaldehyde. The bulkiness of the *tert*-butyl group hindering hydrogenation was given as explanation to the lower activity in *tert*-butanol [9,10]. The selectivity was the lowest when ethanol was used as a solvent, the major byproduct being 7-ethoxymatairesinol (see structure in Fig. 1b). The corresponding byproduct 7-isopropoxymatairesinol was obtained in 2-propanol (Fig. 1b). For 2-pentanol no byproduct of this type was formed; as could be expected, an alcohol with longer carbon chain was interacting less with the reactant.

The HMR 2/HMR 1 ratio was 1.9 in the beginning of the reaction, but decreased with the conversion. This ratio, reflecting the isomerization of HMR, is important for the overall reaction as it was observed in our previous work [6,7] that the HMR 1 isomer reacted much slower to MAT than HMR 2. The reaction is retarded when HMR 2 isomerizes to HMR 1 (the HMR 2/HMR 1 ratio is lower). It is visible from Table 1 that the mixture of 2-propanol and water gave a lower HMR 2/HMR 1 ratio, which could explain why the activity was low. Moreover, the hydrogen solubility is lower in water than in the tested alcohols.

3.2. Catalyst deactivation

The deactivation behaviour of three different catalysts, palladium on H-Beta-300, H-Beta-150 (SiO_2/Al_2O_3 molar ratio 300, respectively 150), and activated carbon was studied in 2-propanol, which afforded reasonable activity being also a solvent allowed to be used for food applications. For both Pd-H-Beta-300 and Pd/C three consecutive experiments were performed with water wash and two consecutive experiments with acetone treatment, while for Pd-H-Beta-150 two repeated experiments were performed with acetone wash between. From all the catalysts, Pd-H-Beta-300 had the highest turnover frequency (TOF) in the first experiment. The selectivity to MAT was over 97% for all catalysts and experiments. Fig. 2 illustrates the remaining activity in the second experiment for different catalysts and washing methods and Table 2 displays the surface area and micropore volume of fresh and used catalysts determined by N_2-physisorption. The dispersions of the fresh materials are also included in Table 2; they were measured by CO pulse chemisorption in [6,7].

Pd-H-Beta-150 (acetone wash) had 90% activity left in the second run, which was the lowest activity decrease, followed by acetone treated Pd/C and Pd-H-Beta-300 with 88% and 82% retained activity. Pd-H-Beta-300 had the largest surface area and 82% of the original surface area was left after two experiments, for Pd-H-Beta-150 75%, and for Pd/C 63%.

When Pd-H-Beta-300 was washed with water, 44% of the activity remained in the second experiment and only 19% in the third experiment (64% of the surface area was left after three experiments). For Pd/C washed with water, the remaining activity in the second run was 64% and in the third 49% (45% of the surface area was left after three experiments). In general, it can be concluded that the most severe deactivation occurred on Pd-H-Beta-300 catalyst.

The major categories of deactivation mechanisms are poisoning, coking or fouling, thermal degradation (sintering, evaporation), mechanical damage, and leaching of the metal [11,12]. Sintering generally takes place at high reaction temperatures (e.g. >500 °C) [13] and can therefore be neglected at the mild conditions employed in hydrogenolysis of HMR. No palladium in the liquid-phase was detected by DCP, which excludes leaching as a cause of deactivation. At low reaction temperatures (<200 °C), the coke formation involves mainly condensation and rearrangement steps [14]. Coke is then often referred to as carbonaceous deposits.

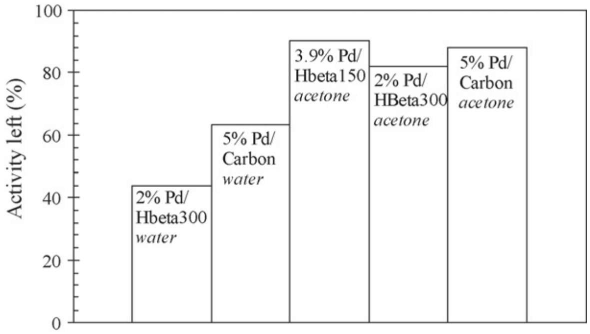

Fig. 2. Activity left (%) in the second experiment for palladium on H-Beta-300, carbon, and H-Beta-150. Two different catalyst treatments were used: washing with water and acetone. Activity left is calculated as TOF 2nd experiment/TOF 1st experiment × 100% and TOF = mol of HMR converted after 240 min/(mol of surface metal × 14,400 s).

Table 2
Surface area, micropore volume, and dispersion

Catalyst	Dubinin surface area (m^2/g)	Micropore volume (ml/g), *t*-plot	Dispersion (%)
2% Pd-H-Beta-300, fresh	862	0.25	9
2% Pd-H-Beta-300, 3 runs, water wash	550	0.16	–
2% Pd-H-Beta-300, 2 runs, acetone wash	706	0.23	–
5% Pd-C, fresh	599	0.19	23
5% Pd-C, 3 runs, water wash	271	0.06	–
5% Pd-C, 2 runs, acetone wash	379	0.11	–
3.9% Pd-H-Beta-150, fresh	724	0.17	9
3.9% Pd-H-Beta-150, 2 runs, acetone wash	543	0.11	–

Hopkins et al. [15] noted that the micropore volume decreased linearly with the coke content. This may suggest that the amount of coke would decrease in the order Pd/C > Pd-H-Beta-150 > Pd-H-Beta-300. Although this is not the same order as the decrease of TOF, we have to take into consideration that the HMR molecule is rather big and may not enter into the small pores. Moreover, most of the palladium particles on the zeolites are larger than the zeolite pores and are therefore located on the outer surface [7].

The soluble coke was studied for the Pd-H-Beta-300 catalyst washed with acetone. Both external and internal coke was analysed. The zeolite structure has to be broken by using hydrofluoric acid before the internal coke can be extracted. To ensure that the acid did not affect the carbonaceous components, one extraction of the external coke was made before the acid was added, in order to compare the results. The same components were present in the two samples: long chain alkanes, such as tetradecane, pentadecane, *iso*-octadecane, cyclopentane, *iso*-docosane, *iso*-tetracosane, *iso*-hexacosane, *iso*-octacosane, *iso*-triacontane, *iso*-dotriacontane, and *iso*-tetratriacontane, as well as aromatic components, for example di-isopropylnaphthalene, di-isobutylphthalate, and di-butylphthalate.

Fresh and used catalysts were analysed by SEM. It is visible from Fig. 3 that the used Pd-H-Beta-300 catalyst treated with acetone (Fig. 3d) did not differ much in appearance from the fresh (Fig. 3a), while the used catalyst cleaned with water (Fig. 3 b–c) had a totally different form. As Fig. 3c reveals, the catalyst is in the form of large spherical clusters. At larger magnification (Fig. 3b) it is visible that these clusters are build from the small catalyst particles shown in Fig. 3a, glued together, and there are also bigger holes present in these spheres. This behaviour is very interesting and must have had an influence on the activity of the catalyst. The parameters that could affect the gluing of the particles are hydrophobicity/hydrophility of the catalyst and

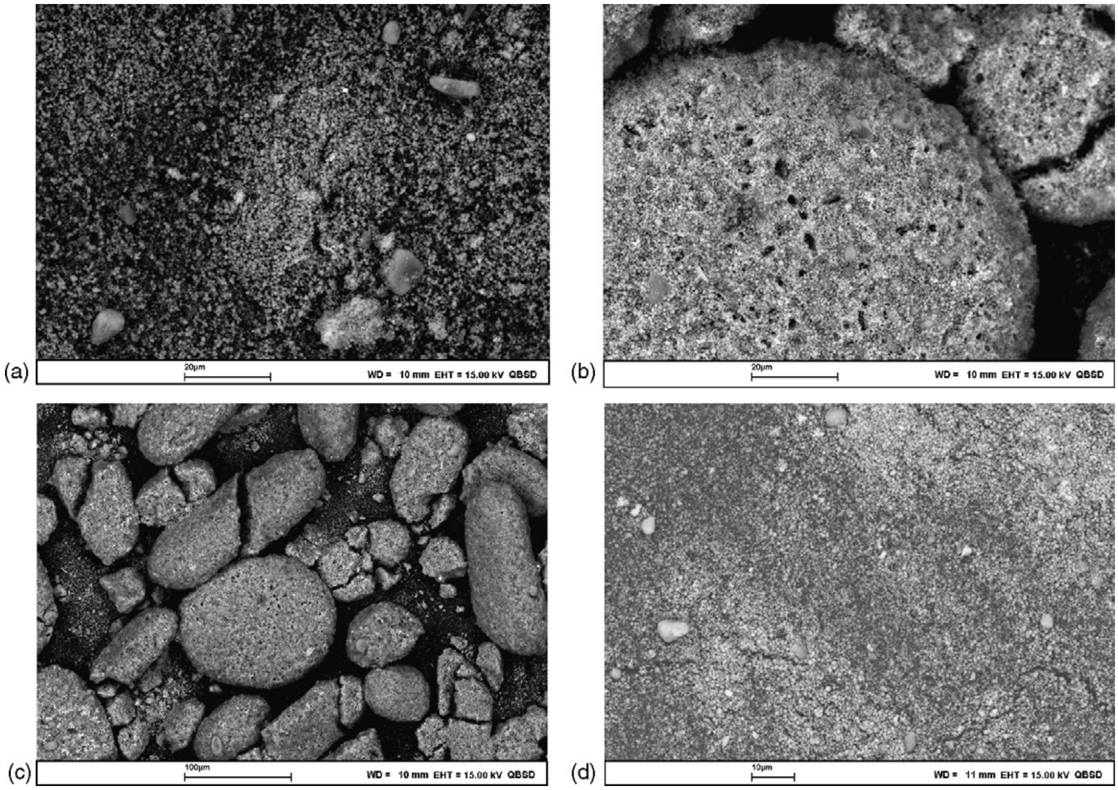

Fig. 3. SEM microgram of Pd-H-Beta-300, (a) fresh catalyst (1000×), (b) catalyst used three times, washed with water (1000×), (c) catalyst used three times, washed with water (250×), and (d) catalyst used two times, washed with acetone (1000×).

the type of solvent used in the washing of the catalyst. When fresh and used Pd/C and Pd-H-Beta-150 catalysts were analysed by SEM, no difference in the appearance between them was visible.

Bjørgen and Kolboe [16] found that dealumination of H-Beta gave catalysts more resistant to deactivation in the conversion of methanol to hydrocarbons. Both de Jong et al. [17] as well as Yoo and Smirniotis [18] studied the alkylation of isobutene with 2-butene over zeolites. It was concluded by de Jong et al. [17] that a zeolite with higher acid site density was deactivating less, while Yoo and Smirniotis [18] observed an acidity optimum. In the present study, the surface area and micropore volume decreased more for Pd-H-Beta-150 compared to Pd-H-Beta-300, which could indicate that a less acidic zeolite was more resistant to coke formation. It was also mentioned in [17] that coke can block the acid sites, meaning that a catalyst with low acid site density could in the worst case have no available acid sites left. In our case, the Pd-H-Beta-300 catalyst has lower acidity than Pd-H-Beta-150. Also, the amount of metal on H-Beta-300 is less than for H-Beta-150. However, some of the coke can be considered to adsorb weakly, since the surface area and TOF decreased less when acetone was used in the washing of the catalyst.

4. Conclusions

Hydrogenolysis of naturally occurring lignan, hydroxymatairesinol was conducted over Pd/C in ethanol, 2-propanol, *tert*-butanol, 2-pentanol, as well as in a mixture of 2-propanol and water (50:50, v/v). High activity was achieved in ethanol, 2-propanol and 2-pentanol. The reaction was markedly retarded when 2-propanol was mixed with water, but the activity was the lowest in *tert*-butanol. Alcohols with shorter carbon chains were also reacting with the substrate resulting in lower selectivity to matairesinol; byproducts 7-ethoxymatairesinol and 7-isopropoxymatairesinol were obtained in ethanol (the lowest selectivity) and in 2-propanol, respectively.

Three different catalysts, Pd-H-Beta-300, Pd-H-Beta-150, and Pd/C, were studied with respect to deactivation in 2-propanol as a solvent. It was concluded, that the activity decreased most for Pd-H-Beta-300, followed by Pd/C and Pd-H-Beta-150. Long chain alkanes and aromatic components constituting coke were blocking the active sites of the catalyst.

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