Applied Catalysis A: General 445–446 (2012) 231–238

Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Application of a cross-linked Pd–chitosan catalyst in liquid-phase-hydrogenation using molecular hydrogen

Stefan Schüßler[a], Nico Blaubach[a], Achim Stolle[a], Giancarlo Cravotto[b], Bernd Ondruschka[a,*]

[a] Institute for Technical Chemistry and Environmental Chemistry (ITUC), Friedrich-Schiller University Jena, Lessingstr. 12, D-07743 Jena, Germany
[b] Dipartimento di Scienza e Tecnologia del Farmaco, University of Torino, Via Pietro Giuria 9, 10125 Torino, Italy

ARTICLE INFO

Article history:
Received 18 June 2012
Received in revised form 17 August 2012
Accepted 18 August 2012
Available online 25 August 2012

Keywords:
Biopolymer
Catalysis
Chitosan
Crosslinking
Hydrogenation
Microwaves
Palladium

ABSTRACT

Chitosan was cross-linked with hexamethylendiisocyanate and loaded with Pd which was subsequently reduced with $NaBH_4$. The prepared catalyst was characterized by FT-IR and elemental analysis. The metal content was determined by ICP-MS measurements. Several substrates (cyclohex-2-enone, benzalacetophenone, 1,2-diphenylacetylene, and *N*-benzylidenaniline) were hydrogenated successfully in ethanol at mild conditions (50 °C, $p(H_2)$ ~6 bar) utilizing a microwave reactor. Reaction parameters like temperature, hydrogen pressure, and the solvent were varied. It was shown that the reduction of the catalyst is crucial for catalytic activity. The catalyst was reused ten times for the hydrogenation of cyclohex-2-enone, without showing a dramatic loss in immobilized metal content. Also the polymeric support material did not show any decomposition.

1. Introduction

Chitosan is a natural occurring linear copolymer, consisting of 2-amino-2-deoxy-D-glucopyranose (glucosamine) and 2-acetamido-2-deoxy-D-glucopyranose (*N*-acetyl glucosamine) with a random distribution (Fig. 1). Moreover, it is non-toxic, biocompatible, and biodegradable.

Chitosan can be produced from chitin, one of the most abundant natural occurring polymers, *via* deacetylation [1,2]. In the case of chitosan most of the monomer units are deacetylated. Since this polymer is soluble in aqueous acid solution, it can be easily processed and a wide range of shapes is known including fibers, spheres, or membranes [3–8]. The most important feature of chitosan is the huge number of free amino groups that it contains making this polymer an attractive, biocompatible sorbant for metal ions [9–18]. In some cases, it is advantageous to modify the polymer by introduction of side groups, cross-linking, or by copolymerization and grafting with other polymers. Reviews on the modification and application of chitosan and its derivatives were published by *Macquarrie* and *Hardy* as well as *Mourya* and *Inamdar* [19,20]. Apart from its application as a sorbent, chitosan was applied in some biological and biomedical applications [21–25]. Taking advantage of its metal sorption capacity, it has been used successfully as a support material in heterogeneous catalysis. For example, there are various reports wherein chitosan or its derivatives were applied as support materials for catalysts in oxidation reactions, Pd-promoted cross-coupling reactions (Suzuki, Heck) and hydrogenation reactions [26–40]. In the case of hydrogenations, most publications dealt with the reduction of aromatic nitro compounds to the corresponding anilines. Only a few publications are known that report the use of chitosan-based catalysts for the hydrogenation of aromatic systems, alkenes, or carbonyl compounds for example [37,39,41–45]. In this work, we will present results on the use of chitosan-derived support materials for the selective microwave-assisted hydrogenation of α,β-unsaturated carbonyl compounds and other functionalities (alkynes, imines) [46]. To the best of our knowledge this is presumable the first report on the hydrogenation of α,β-unsaturated carbonyl compounds using those type of catalysts. To this aim, chitosan which has been cross-linked with hexamethylene diisocyanate (HMDI) will be applied [47]. HMDI cross-linked chitosan has already been successfully applied as a catalyst support by Cravotto and co-workers for the Suzuki reaction as well as for copper-catalyzed cycloaddition reactions between azides and alkynes. This process incorporated both microwave and ultrasound techniques [31,48]. These types of catalysts proved to be highly active. In this paper we have used a similar catalytic system. In addition to the cross-linking treatment of the polymer we also carried out a chemical reduction of the immobilized Pd(II)-species, resulting in a supported Pd(0) catalyst.

---

[*] Corresponding author. Tel.: +49 3641 948400; fax: +49 3641 948402.
E-mail address: Bernd.Ondruschka@uni-jena.de (B. Ondruschka).

0926-860X/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2012.08.021

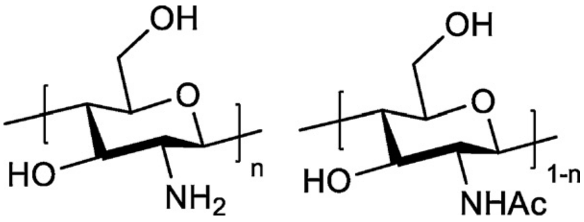


Fig. 1. Chemical structure of the chitosan units: glucosamine and *N*-acetylglucosamine.

2. Experimental

All chemicals were commercially available and used without further purification, if not otherwise noted. The chitosan (medium molecular weight; M_η ~190,000–310,000 g mol^{-1}) was purchased from Sigma Aldrich, deacetylation degree was determined by elemental analysis and found to be 75% [49].

2.1. Catalyst preparation

The catalyst was prepared according to a slightly changed literature protocol [31]. Chitosan (5 g) was dissolved in hydrochloric acid (0.1 N, 350 mL) at 60 °C. $Pd(OAc)_2$ (0.5 mmol, 112.3 mg, 98%) was dissolved in hydrochloric acid (0.1 N, 60 mL) and added to the chitosan solution. The mixture was sonicated for 5 min using an ultrasound-horn (UP200S, 24 kHz, 200 W, 14L2D sonotrode, Hielscher Ultrasonics GmbH, Germany). Hexamethylene diisocyanate (HMDI; 6 mL, 37 mmol) was added to the mixture, which was stirred and sonicated until HMDI was emulsified (about 1 min). The stirring was continued until the mixture turned into a yellowish gel. The gel was left standing for 1 h, cooling to room temperature. The pre-catalyst was crushed and suspended in water and a pH of 10 was adjusted using a 1 N NaOH-solution. The material was washed with water until the filtrate became neutral. The raw product was re-suspended in water and $NaBH_4$ (1.5 g, 40 mmol) was added under vigorous stirring. The solid chitosan material turned dark within seconds. The stirring was continued for 30 min to assure a complete reaction. After this treatment was completed, the raw catalyst was filtered and washed with water until the filtrate was neutral. Then, it was stirred in acetone for 15 min and dried over night at 60 °C in an air atmosphere.

2.2. Catalyst characterization

FT-IR measurements were carried out on a Perkin Elmer Spectrum 100 infrared spectrometer using the ATR-method. The elemental composition of the samples was measured using elemental analysis (Elementaranalysator Vario EL III CHNS; Analysensysteme GmbH, Germany). TGA/DTA measurements were performed on a TA Instrument TGA 2050 (Shimadzu) under nitrogen atmosphere. The analyses were carried out with a constant heating rate of 10 K min^{-1} from 50 to 600 °C. The metal content of the catalyst samples was determined by ICP-MS (Quadrupol-ICP-MS X Series II; ThermoFisher Scientific, Germany).

2.3. General procedure for liquid-phase hydrogenation

Liquid-phase hydrogenations were carried out in a microwave system (Multisynth; MLS, Germany) equipped with a quartz reactor system (QRS) [50–52]. In a typical experiment, 7.5 mmol substrate was dissolved in 30 mL solvent and the catalyst was added. After placing the loaded QRS into the microwave, the mixture was flushed with N_2, and after this the vessel was pressurized with H_2. A flow of hydrogen (0.75 mL min^{-1}) through the QRS was maintained over the whole reaction time. An initial heating ramp of 2 min was given (P_{max} = 400 W) to heat up the reaction mixture, after that the temperature (ATC-CE-sensor) was kept constant for the desired reaction time. After the reaction time was over, the mixture was cooled for 3 min in the microwave system and afterwards the reactor was flushed with nitrogen.

2.4. Analytical methods

Monitoring of the hydrogenation experiments was conducted with gas chromatography (Hewlett Packard G1530A, HP-5 or CarboWAX 30 m, FID). Products were identified by GC–MS or using commercial standard substances. The detailed GC profiles can be found in supporting information. NMR spectra were recorded on a 200 MHz Bruker Avance spectrometer using $CDCl_3$ and TMS (tetramethylsilane) as solvent and internal standard, respectively.

2.5. Synthesis of N-benzylidenaniline

Freshly distilled benzaldehyde (0.042 mol, 4.46 g) and freshly distilled aniline (0.048 mol, 4.5 g) were dissolved in methanol (40 mL) and glacial acetic acid (0.2 mL) was added. The solution was refluxed for 4 h and left standing over night at room temperature (the reaction was monitored *via* gas chromatography until all benzaldehyde was converted). The solution was poured into ice water, wherein a yellowish solid precipitated. The solid was filtered, crushed in a mortar, and washed with water. After washing, the precipitate was dissolved in diethyl ether and the organic phase was washed with dilute hydrochloric acid (pH ~ 4) to remove the excess of aniline. Afterwards, the organic phase was dried over anhydrous $MgSO_4$ and the solvent was evaporated. Yiled = 7.15 g (94%) of a light yellow solid. ^{1}H-NMR ($CDCl_3$; 200 MHz, TMS): 7.20–7.49 (m, 10H); 7.89 (m, 2H); 8.45 (s, 1H) ppm. ^{13}C-NMR ($CDCl_3$; 50 MHz): 120.83; 125.95; 128.74; 128.83; 129.12; 131.42; 136.07; 151.89; 160.38 ppm.

3. Results and discussion

In the following sections, the results of the experimentation are presented. Reaction parameters were investigated and several educts were screened.

3.1. Preparation of the catalyst

The reaction of chitosan with HMDI is supposed to lead to the formation of urea-derivates as well as urethane linkages. Moreover, HMDI can undergo side reactions with the solvent resulting in CO_2 and amines from reaction with H_2O. This means, that the resulting support material should have a large number of polar functionalities. In the literature, the most popular method for cross-linking chitosan is a reaction with glutaraldehyde as a cross-linking agent [53–58]. This substance converts the amine groups of the polymer to Schiff base functions. The Schiff base groups are rather weak and can be cleaved easily, resulting in the decomposition of the material. One advantage of glutaraldehyde is that this substance is soluble in water, whereas HMDI is insoluble. The utilization of ultrasound during the cross-linking reaction was advantageous since the water insoluble HMDI was quickly emulsified [59,60]. According to Cravotto et al. the ultrasound treatment is responsible for breaking interactions within the polymer and supports the formation of the metal complexes [31]. Furthermore, the formation of the emulsion is a very important aspect for this reaction, since this should assure the homogenous distribution of HMDI in the aqueous phase. During the reaction the formation of gases was observed, which indicated the already mentioned HMDI side reaction with the solvent. The mixture got more and more viscous with the ongoing

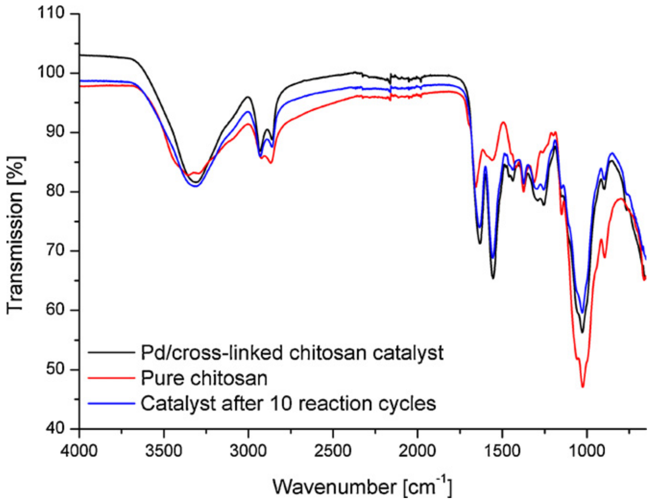


Fig. 2. FT-IR spectra of pure chitosan, the prepared Pd/chitosan-HMDI catalyst and a catalyst that was used in 10 reaction cycles.

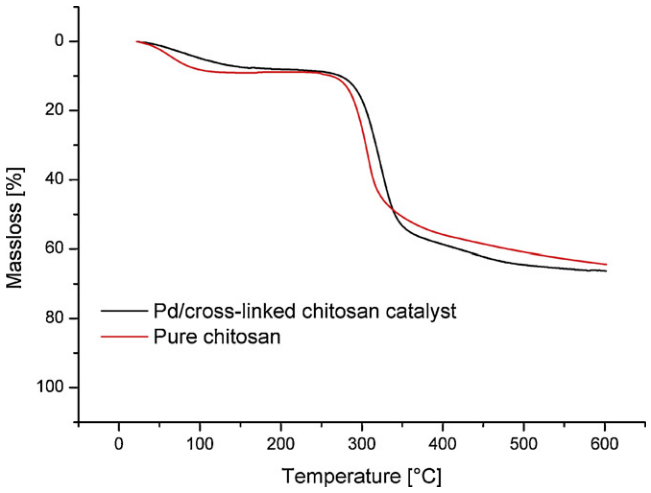


Fig. 3. TGA curves of chitosan and Pd(0)/cross-linked chitosan catalyst.

reaction and suddenly became solid. Due to the gas formation, the material highly increased in its volume.

3.2. *Characterization of the prepared catalyst*

The prepared catalyst was characterized by FT-IR spectroscopy using the ATR method (Fig. 2).

Pure chitosan shows a broad band at around 3320 cm^{-1} which is caused by OH-, NH_2- as well as CONH-vibrations. After cross-linking with HMDI, this band appears less broad. This indicates that these groups underwent reaction with the cross-linking agent. The resulting urea- and urethane-groups also contain the amide-like function which is responsible for the observed band. As was mentioned before, this band can also be an indicator for NH_2 groups which were formed in a side reaction of HMDI with the solvent. The band at 2930 cm^{-1} is caused by CH_2-vibrations. After cross-linking, the number of CH_2 groups in the polymer is higher than in the starting material, resulting in stronger and sharper absorption bands. New bands can be assigned to urea- and urethane-functions (C=O and C—N vibrations) in the polymer as well as the more intensive ones at around 1600 and 1260 cm^{-1}. This demonstrated the successful cross-linking treatment. Absorption at 1026 cm^{-1} is assigned to C—O vibrations, which are typical for carbohydrates. The results are in good agreement with former studies investigating similar systems [31,48]. The catalyst was also characterized by thermo-gravimetric analysis to study its thermal behavior and stability at elevated temperatures (Fig. 3).

We found that the samples show a mass loss at the beginning of the measurement, which can be assigned to sorbed humidity. Interestingly, the cross-linked catalyst shows a slower release of sorbed water. This is caused by the network-like structure of the material, which should hinder the release of adsorbed water or other solvents. In addition, the cross-linking treatment caused a greater number of polar groups which can coordinate water by hydrogen bonding, thus making the release more difficult. Above 250 °C both materials show a dramatic loss of mass which clearly indicates that the materials decompose because of the high temperatures. Elemental analyses were performed to further prove the cross-linking process (Table 1).

Since the hydrogen content can also be affected by humidity, we were mostly interested in the carbon and nitrogen content as well as the C/N-ratio. The cross-linked catalyst showed a lower C/N-ratio than pure chitosan which indicates an increase in nitrogen content during catalyst preparation. Moreover, the elemental analyses revealed that both carbon and nitrogen content increased due to the introduction of the cross-linker units. Since chitosan is a material of natural and mostly marine origin, one should consider that there are trace amounts of catalytic active metals present which could already catalyze the hydrogenation of unsaturated carbonyl compounds [2,61]. Therefore, the ability of commercially available chitosan to promote a hydrogenation reaction was investigated and the metal content was determined with ICP-MS. The hydrogenation of cyclohex-2-enone was performed at 50 °C (0.6 MPa H_2) in the presence of 200 mg chitosan as a test reaction. After 5 h a conversion of only $\leq 3\%$ was detected. To determine the metal content of the prepared catalyst and also to reveal residual Pd traces within the support material, ICP-MS measurements were conducted (Table 1). The ICP-MS analyses revealed that approximately 0.06 mmol g^{-1} Pd was immobilized on the support material. The catalyst was prepared several times according to the same protocol and reproducible results for the metal content (0.057–0.064 mmol Pd g^{-1}) were found. In addition, the unreduced Pd(II)-containing pre-catalysts were investigated by this method and did not differ much from the reduced samples ($\sim$4%). Only trace amounts of Pd were found in pure chitosan, which might explain the catalytic activity of the pure material in the hydrogenation reaction. But in reality, compared to the loaded catalysts, this is negligible.

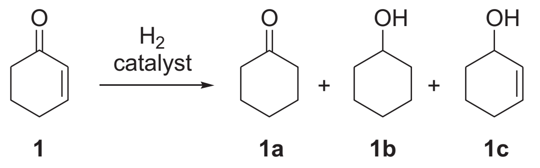
3.3. *Hydrogenation of selected substrates*

To check if the catalyst shows attractive performance for different substrates, hydrogenation reactions with a series of compounds have been carried out. On the one hand a series of α,β-unsaturated carbonyl compounds like cyclohex-2-enone (**1**), benzalacetophenone (**2**), and citral (**3**) were used as model systems. Moreover, the catalytic activity for substrates with different functionalities has been investigated using 1,2-diphenylacetylene (**4**) as an example

Table 1
Elemental analysis and Pd-content of pure chitosan, the as-prepared catalyst, and a catalyst used in 10 reaction cycles.

	Pure chitosan	Fresh catalyst	Used catalyst[a]
C [%]	41.03	46.35	46.03
H [%]	7.23	7.21	7.71
N [%]	7.35	10.47	9.39
C/N-ratio	5.58	4.43	4.90
Pd-loading [mmol g^{-1}][b]	$(2.1 \pm 0.9)\,10^{-7}$	0.0644 ± 0.0014	0.0594 ± 0.0004

[a] After ten cycles or reuse (cyclohex-2-enone, 100 mg catalyst, 30 mL EtOH 0.6 MPa H_2, 50 °C, 30 min per reaction cycle).
[b] Determined by ICP-MS.



Scheme 1. Possible reaction pathways for the hydrogenation of cyclohex-2-enone (**1**).

for C—C triple bonds and *N*-benzylidenaniline (**5**) as an imine model compound.

3.3.1. Cyclohex-2-enone

We applied the catalyst to the hydrogenation of cyclohex-2-enone (**1**). The possible reaction pathways and products are shown in Scheme 1. The reaction was carried out for 4 h (p_{H_2} = 0.6 MPa, 50 °C) in ethanol, using 50 mg of the catalyst. The reaction was monitored by immediate GC-analysis (every 30 min.). As shown in Fig. 4, only cyclohexanonone (**1a**) was found as a product. Only trace amounts of the corresponding alcohol **1b** were observed after **1** was converted. The intermediate **1c** was not detected. It was found that the Pd-catalyst shows a very high selectivity toward the hydrogenation of the α,β-unsaturated carbonyl compound C—C double bonds compared to catalysts that contain Rh or Ru [62,63].

1 also served as model compound for some studies on reaction parameters. Typical reaction parameters like solvent, temperature and hydrogen pressure were investigated. Therefore, the hydrogenation of **1** was performed to look for the influence of these reaction parameters on the conversion of **1** and the selectivity toward the saturated carbonyl compound **1a**. Solvent screening was carried out at 50 °C for 1 h with a hydrogen pressure of about 0.6 MPa using 200 mg of the catalyst. Several solvents, namely ethylacetate (EtOAc), isopropanol (*i*PropOH), ethanol (EtOH), acetonitrile (MeCN), and methanol (MeOH; each 30 mL) were tested. The results of this experimentation are listed in Table 2 (entry 1–5).

The solvent has nearly no influence on the selectivity of the reaction which was always found to be >99%. On the other hand, the conversion showed a great dependence on the solvent. One solvent property that may hold some responsibility is the polarity. As the reaction was carried out in EtOAc, *i*PropOH, EtOH, and MeOH, this theory could be applied nicely. But when MeCN was used as a solvent (which shows a similar polarity as MeOH) the conversion dropped dramatically. Thus, not only is the polarity of the solvents important, but also its ability to build hydrogen bonds. These solvents should show higher interactions with the polymeric support material, since this consists of a high number of polar groups (urea derivatives, urethanes, amines, etc.), which are also able to build hydrogen bonds. Those interactions should result in an increased swelling of the polymeric support. This means that active sites, located on the inside of the polymer are easier to reach for the reactants. This necessarily results in an increased conversion. It should also be noted that the solubility of hydrogen highly depends on the solvent and is higher in polar solvents. Since both EtOH and MeOH showed good results, the first was applied in further experiments due to its lower toxicity. Next, the influence of the hydrogen pressure was investigated *via* the reduction of **1** for 1 h at 50 °C. The catalyst amount was reduced to 50 mg in order to study the effect of pressure (Table 2). The pressure of the applied hydrogen has only a little influence on the conversion (Table 2, entry 6–8). Conversion varies between 60 and 75%, however, increasing hydrogen pressure results in an increase of conversion while selectivity remained constant. Selectivity was always found to be >99%. Since 1.0 MPa is the upper pressure limit of the hydrogenation equipment, the following experiments were carried out at 0.6 MPa. Finally, we investigated the influence that reaction temperature might have and performed the reduction of **1** with 100 mg catalyst for 0.5 h (Table 2, entry 9–11). Temperature showed no influence on selectivity (>99%). The conversion of **1** on the other hand was strongly temperature dependent. At 30 °C conversion of 10–11% was found, whereas at 70 °C **1** was converted quantitatively. The temperature was able to accelerate the reaction itself, but could also cause the polymer to swell more which would mean that more active sites are accessible. Moreover, transport processes could be accelerated by the increased temperatures. Another important aspect is the catalyst itself in respect to the oxidation state of the active site or the support material and its influence to the reaction. In previous experiments, several non-reduced Pd/chitosan catalysts were tested for hydrogenation reactions, but no satisfying results were observed. All these catalysts contained Pd mainly in oxidation state +2, as was shown by XPS analysis [30]. In the present context catalysts were reduced with NaBH$_4$ during their preparation. A comparison of reduced and non-reduced catalysts revealed similar selectivity (>99%) but very different conversions. The non-reduced (Table 2, entry 12) catalyst only achieved a conversion of around 11%, whereas the reduced catalyst showed a conversion that was greater than 99%. This clearly demonstrates that the reduction treatment is essential to obtaining an active hydrogenation catalyst.

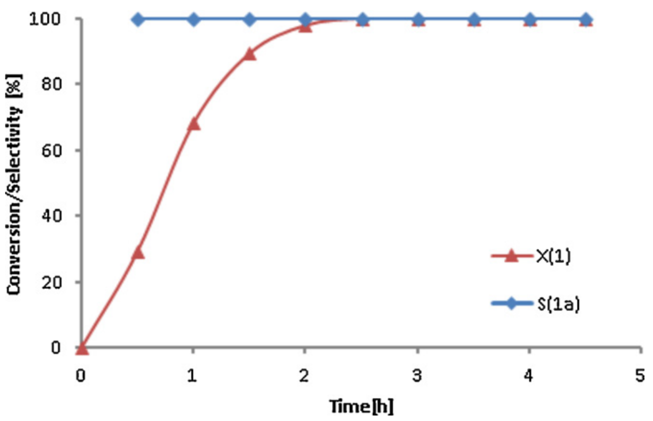
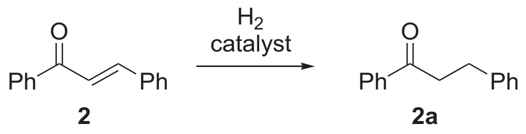


Fig. 4. Time dependence of the conversion (X) and selectivity (S) for the hydrogenation of cyclohex-2-enone (1; $p \approx 0.6$ MPa H_2; 50 °C; 30 mL ethanol, 50 mg catalyst). According to Scheme 1: X(**1**) cyclohex-2-enone; S(**1a**) cyclohexanone.



Scheme 2. Hydrogenation of benzalacetophenone (**2**).

3.3.2. Benzalacetophenone

Benzalacetophenone (**2**) also belongs to the group of α,β-unsaturated carbonyl compounds. A possible reaction is demonstrated in Scheme 2 [52].

In addition to the hydrogenation reaction to form the carbonyl compound **2a**, it is possible to encounter dehydration reactions followed by hydrogenation resulting in 1,3-diphenylpropane. Moreover, it is also possible to obtain byproducts with hydrogenated rings (not displayed here). In this experiment we had to use a greater amount of catalyst (200 mg), whereas the other reaction conditions remained the same as in the hydrogenation of **1**. The results can be found in Fig. 5.

Nearly quantitative conversions of **2** were reached within 2 h furnishing **2a** as the major product, accompanied by small amounts of byproducts (<0.5%). Over the whole time range of this experiment, the selectivity toward **2a** was always >99%. One reason

Table 2
Results of the hydrogenation of cyclohex-2-enone at different reaction conditions.

Entry	Time [h]	Temp. [°C]	Pressure (H_2) [MPa]	m_{Catalyst} [mg]	Solvent	Conversion 1 [%]
1	1	50	0.6	200	EtOAc	17
2	1	50	0.6	200	*i*PropOH	27
3	1	50	0.6	200	MeCN	39
4	1	50	0.6	200	EtOH	>99
5	1	50	0.6	200	MeOH	>99
6	1	50	0.2	50	EtOH	61
7	1	50	0.6	50	EtOH	68
8	1	50	1.0	50	EtOH	75
9	0.5	30	0.6	100	EtOH	11
10	0.5	50	0.6	100	EtOH	69
11	0.5	70	0.6	100	EtOH	99
12[a]	1	50	0.6	200	EtOH	11

Reaction conditions: 30 mL solvent, substrate concentration = 0.25 mol L^{-1}, reduced Pd/cross-linked chitosan.

[a] Non-reduced catalyst was applied.

for the fact that more catalyst was necessary to hydrogenate this compound in the same time than in the hydrogenation of **1** might be the more non-polar nature of this compound, which could make it incompatible with the more polar support material. Also steric factors could play a role with respect to transport processes through the polymer network.

3.3.3. *Citral*

Citral (**3**) and its hydrogenation products citronellal (**3a**) and citronellol are compounds of interest for the production of chemicals and pharmaceuticals but are also used as flavors and fragrances [50,64–67]. Citral (used as a mixture of *E*/*Z* isomers) contains a carbonyl function, a conjugated double bond and an isolated double bond. The catalyst would have three functionalities to react with. Moreover, the intermediates and products can undergo acid-catalyzed cyclization (carbonyl-ene-reaction) or dehydration reactions to form byproducts like menthols or branched hydrocarbons, respectively [68,69]. A simplified reaction network is shown in Scheme 3.

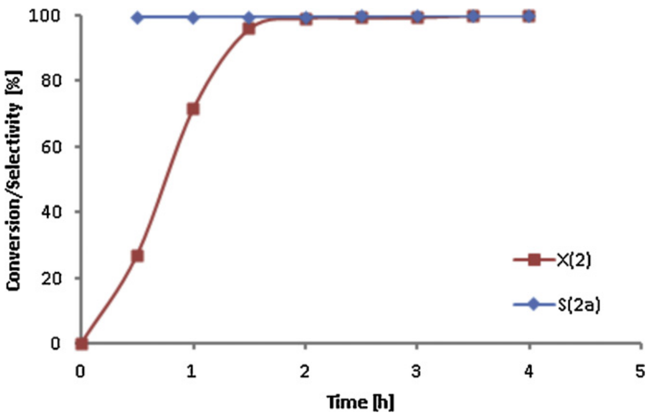
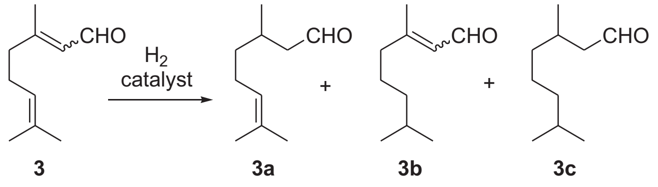


Fig. 5. Time dependence of the conversion (X) and selectivity (S) for the hydrogenation of benzalacetophenone (2; $p \approx 0.6$ MPa; 50 °C; 30 mL ethanol, 200 mg catalyst). According to Scheme 2: X(**2**) benzalacetophenone, S(**2a**) 1,3 diphenylpropan-1-one.



Scheme 3. Possible reaction pathways for the hydrogenation of citral (*E*/*Z*).

Using Pd as active metal component, the reduction of the carbonyl function is effectively suppressed as shown in the previous examples (**1**, **2**). Thus, products from hydrogenation of the C—C double bonds were identified primarily. In this reaction, a broad range of intermediates can occur. The reaction may proceed through the hydrogenation of the conjugated double bond to form **3a**. The other possible path for Pd-catalysts is *via* the hydrogenation of the isolated double bond to form **3b**, which again can occur as a mixture of *E* and *Z* isomers. Both intermediates can be reacted to form the saturated carbonyl compound **3c**. The reaction was carried out at standard conditions (50 °C, 0.6 MPa), using 200 mg of catalyst. The results are presented in Fig. 6.

The hydrogenation of the conjugated double bond is strongly favored, which means, that **3a** is the main reaction product. The isolated double bond is also hydrogenated to form the unsaturated carbonyl compound **3b** with average selectivity of 10%. At nearly complete conversion of **3**, selectivities for **3a** of >50% were found, whereas the selectivity for compound **3b** did not exceeded 10%. The intermediates **3a** and **3b** are reacted to the saturated carbonyl compound **3c** as the reaction proceeded. This experiment showed that the applied catalyst favors unsaturated carbonyl double bonds over isolated double bonds, which reacted much more slowly.

3.3.4. *1,2-Diphenylacetylene*

Another important aspect, if it comes to selective hydrogenation, is the reduction of C—C triple to C—C double bonds. Practical systems for such tasks are Lindlar or Lindlar-type catalysts which

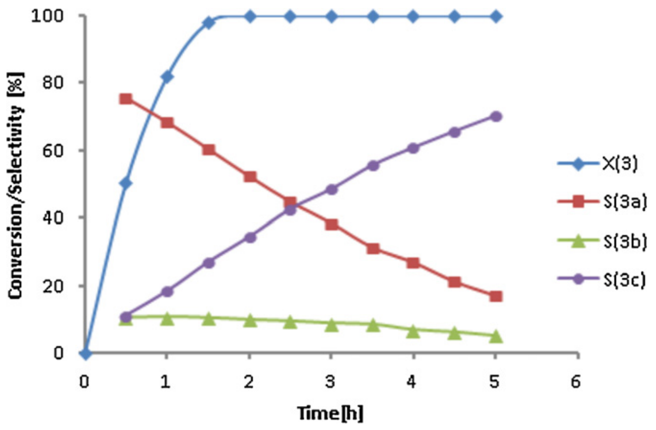
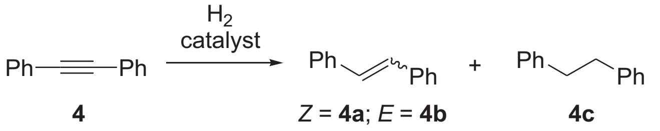
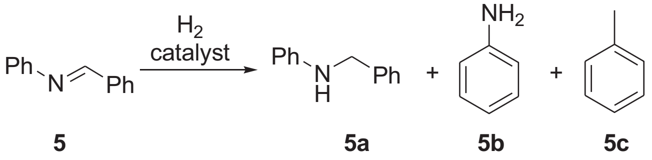


Fig. 6. Time dependence of the conversion (X) and selectivity (S) for the hydrogenation of citral (3; $p \approx 0.6$ MPa H_2; 50 °C; 30 mL ethanol, 200 mg catalyst). According to Scheme 3: X(**3**) citral; S(**3a**) citronellal, S(**3b**) 3,7-dimethyloct-2-enal; S(**3b**) 3,7-dimethyloctanal.



Scheme 4. Possible reaction pathway for the hydrogenation of 1,2-diphenylacetylene.



Scheme 5. Possible reaction pathway for the hydrogenation of *N*-benzylidenaniline (**5**).

also contain Pd as the active metal component. These catalysts have been investigated intensively as they are seen to be very important [70–73]. Other catalyst systems have also been developed and investigated and showed promising results [51,74–76]. To avoid the hydrogenation of the double bond, Lindlar-type catalyst contain $Pb(OAc)_4$ or PbO/PbO_2 and quinoline to decrease the activity of the catalyst. In order to confirm that the Pd containing chitosan catalyst is also suitable for this reaction, we investigated the hydrogenation of 1,2-diphenylacetylene (**4**) according to Scheme 4.

Initially, the triple bond is reduced to a double bond. This intermediate can occur as two isomers, *Z* (**4a**) and *E* (**4b**), however, both are able to further react to 1,2-diphenylethan (**4c**). The reaction was again carried out under standard conditions using 50 mg of the catalyst. Results (Fig. 7) showed that it was not possible to stop the reaction at the double bond state without the use of additives or poisoning the catalyst.

The reaction proceeded quickly, so that the initial amount of **4** was fully converted after around 2 h. It was found that the intermediate is mainly obtained as the *Z*-isomer (**4a**), whereas the *E*-isomer (**4b**) was only observed in low yields. Both isomers were reduced to compound **4c** as the reaction proceeded. It can be seen that at full conversion of **4** (2 h), a selectivity of around 17% for the *Z*-Isomer was obtained. The catalyst was still too active and so higher selectivities could not be obtained.

3.3.5. *N-benzylidenaniline*

N-benzylidenaniline (**5**) was chosen as a model compound to investigate the activity of the catalyst in the reduction of imines to secondary amines (Scheme 5) In case of **5**, imine **5a** can be hydrogenolyed resulting in aniline (**5b**) and toluene (**5c**). This effect was utilized in an interesting approach from Liu and coworkers, where aniline was used as a co-catalyst to reduce benzaldehyde to toluene with a Ni catalyst [77]. The aniline first formed a Schiff base, which was then hydrogenated and hydrogenolyzed to form toluene and aniline. Since previous results in our group revealed a similar behavior, we were now interested to see if the modified Pd/chitosan catalyst also catalyzes this reaction. Results are shown in Fig. 8 and indicate that the initial amount of **5** was converted within 2.5 h and the *N*-Bn-aniline (**5a**) was the major product. However, the formation of aniline (**5b**) and toluene (**5c**) was already detected after 1.5 h. After the full conversion of **5**, the resulting secondary amine **5a** was hydrogenolyzed. Although we observed the hydrogenolysis of **5a**, the total yield of degradation compounds was not higher than 10%. The hydrogenation of the aromatic rings was not observed during this experiment. Thus, the catalyst is suitable for the selective reduction of imines to secondary amines.

3.4. *Recycling*

Another important issue for heterogeneous catalysts is their durability and stability. The known problems of heterogeneous catalysts are the leaching of the active species and the decomposition of the support material. To check if the HMDI-cross-linked Pd/chitosan catalyst is recyclable, the hydrogenation of **1** was repeated ten times with the same catalyst sample, which was recovered after each reaction. The initial amount of catalyst was 100 mg. Reactions were carried out for 30 min (plus 2 min of heating up and 3 min for cooling-down and flushing with nitrogen). After the reaction, the catalyst was filtered off, washed with EtOH and then dried for 3 h at 60 °C. It was then stored at ambient conditions over night and used again. With this experimentation we obtained the results displayed in Fig. 9.

We found a conversion of 69% in the initial reaction with a selectivity of >99%. Interestingly, in the following runs, the catalyst seemed to increase its activity and the conversion was pushed up to around 88%. Increased conversions were found for up to 4 cycles of reuse. In the 5th cycle the conversion started to decrease to a value of 80–81% which then was nearly constant up to the 9th cycle of reuse. For all samples we found a selectivity >99%. Along with the increased conversion, we also found an increase in the mass of the recovered catalyst. After the initial reaction, the mass increased from 100 to 105 mg, which was the value (105–106 mg) that was found for all other cycles. The reason for the increase in the conversion could be found in the architecture of the

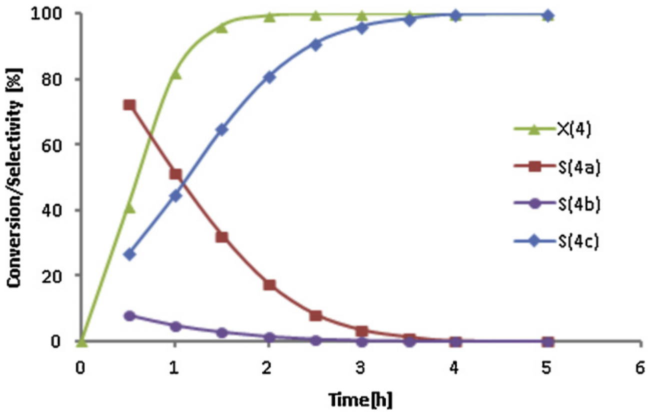


Fig. 7. Time dependence of the conversion (X) and selectivity (S) for the hydrogenation of 1,2-diphenylacetylene (4; $p \approx 0.6$ MPa H_2; 50 °C; 30 mL ethanol, 50 mg catalyst). According to Scheme 4: X(**4**) 1,2-diphenylacetylene; S(**4a**) z-stilbene; S(**4b**) e-stilbene; S(**4c**) 1,2-diphenylethan.

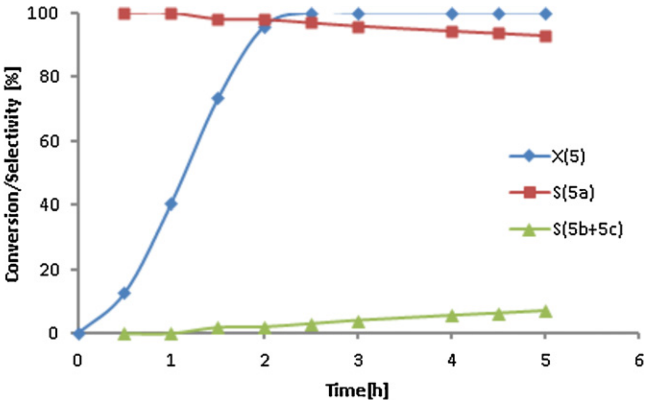


Fig. 8. Time dependence of the conversion (X) and selectivity (S) for the hydrogenation of *N*-benzylidenaniline (5; $p \approx 0.6$ MPa; 50 °C; 30 mL ethanol, 200 mg catalyst). According to Scheme 5: X(**5**) *N*-benzylidenaniline; X(**5a**) *N*-benzylaniline; S(**5b** + **5c**) toluene and aniline.

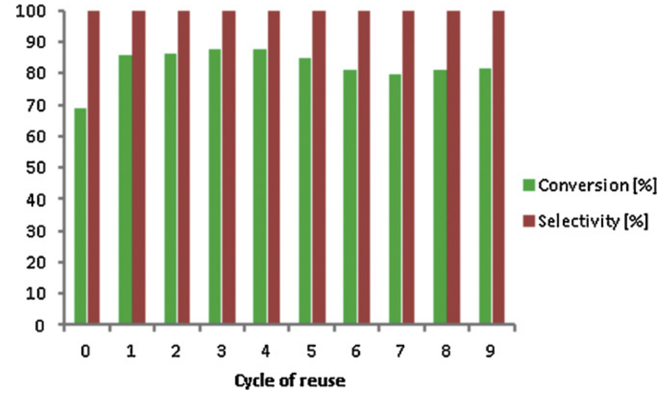


Fig. 9. Results for the recycling study for the hydrogenation of cyclohex-2-enone to cyclohexanone catalyzed by HMDI-cross-linked Pd/chitosan catalyst ($p \approx 0.6$ MPa; 50 °C; 30 mL ethanol, 100 mg catalyst, reaction time = 0.5 h).

catalyst. As already mentioned the support material of the catalyst has a network-like structure and should therefore act as a sponge which can be swollen with solvent. The high number of polar groups within the support could be responsible for solvent hold-up (compare to TGA results, Fig. 3), which is an explanation for the increased mass that was found before each cycle of reuse. It is possible that the swollen catalyst is more active because the interior Pd can be reached more quickly and easily by the educt and the hydrogen than in the dry catalyst which was used for the initial reaction. The constant conversion found in the recycling studies indicates that metal leaching is low. The catalyst was analyzed by ICP-MS to determine the amount of metal-leaching. FT-IR spectroscopy and elemental analyses were also performed to clarify possible structural changes within the support material. Fig. 2 shows the FT-IR spectra of the used (after 10 reaction cycles) and unused catalyst. The spectra are nearly identical, except for some differences in the intensity of the bands. The band for NH_2-, OH- and CONH-groups (~3320 cm^{-1}) appears slightly stronger than in the starting material which might result from residual solvent (EtOH). This allows us to conclude that the support material was not affected during the entire recycling study. The elemental composition of the catalyst was analyzed before and after the recycling study; the content of carbon, hydrogen and nitrogen was determined (Table 1). After 10 reaction cycles, we found a decrease in carbon and nitrogen content and an increase in the hydrogen content. After the application of the catalyst an increase in the C/N-ratio of about 0.5 was noticed which means that the carbon content is higher in the used catalyst compared to the initial catalyst due to presence of residual solvent (in agreement with the FT-IR analysis of the samples). The changes in the elemental composition are not too high, which allows us to conclude that the support material was stable over the entire process. ICP-MS studies revealed that the metal content decreases by up to 8% when the Pd-loading for the fresh catalyst and the loading of the catalyst applied in the recycling study after its 10th application are compared (Table 1).

4. Conclusion

A Pd containing catalyst was successfully prepared by the assistance of ultrasound, using cross-linked chitosan as the support material. After the chemical reduction of the Pd(II) ions, the catalyst showed high activity in several hydrogenation reactions. The selectivity was high, especially for the hydrogenation of α,β-unsaturated carbonyl compounds where only the C=C double bond was reduced. Additionally, the hydrogen addition to internal alkynes and imines was investigated. The reactions were carried out under mild conditions, using microwave heating techniques. The influence of reaction conditions was investigated; the solvent and the temperature showed the greatest influence due to the solubility of hydrogen in the solvent and the architecture of the support material. Moreover, it was found that the catalyst is very stable and easily recyclable lasting ten reaction cycles without any significant loss in activity. ICP-MS analysis demonstrated that most of the initial metal content remained on the support.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata.2012.08.021.

References

[1] S.E.S. Leonhardt, B. Ondruschka, J. Ondruschka, Chem. Eng. Technol. 31 (2008) 917–921.
[2] J. Ondruschka, M. Trutnau, T. Bley, Chem. Ing. Tech. 80 (2008) 811–820.
[3] O.C. Agboh, Y. Qin, Polym. Adv. Technol. 8 (1997) 355–365.
[4] J.Z. Knaul, S.M. Hudson, K.A.M. Creber, J. Appl. Polym. Sci. 72 (1999) 1721–1732.
[5] M. Ravi Kumar, Bull. Mater. Sci. 22 (1999) 905–915.
[6] J.D. Schiffman, C.L. Schauer, Biomacromolecules 8 (2007) 2665–2667.
[7] F. Peirano, T. Vincent, F. Quignard, M. Robitzer, E. Guibal, J. Membr. Sci. 329 (2009) 30–45.
[8] S. Sarkar, E. Guibal, F. Quignard, A.K. SenGupta, J. Nanopart. Res. 14 (2012), http://dx.doi.org/10.1007/s11051-011-0715-2.
[9] Y. Baba, H. Hirakawa, K. Yoshizuka, K. Inuoe, Y. Kawano, Anal. Sci. 10 (1994) 601–605.
[10] E. Guibal, Sep. Purif. Technol. 38 (2004) 43–74.
[11] L. Qi, Z. Xu, Colloids Surf. A251 (2004) 183–190.
[12] A.J. Varma, S.V. Deshpande, J.F. Kennedy, Carbohydr. Polym. 55 (2004) 77–93.
[13] K. Fujiwara, A. Ramesh, T. Maki, H. Hasegawa, K. Ueda, J. Hazard. Mater. 146 (2007) 39–50.
[14] A.M. Donia, A.A. Atia, K.Z. Elwakeel, J. Hazard. Mater. 151 (2008) 372–379.
[15] P. Miretzky, A.F. Cirelli, J. Hazard. Mater. 167 (2009) 10–23.
[16] A. Bhatnagar, M. Sillanpää, Adv. Colloid Interface Sci. 152 (2009) 26–38.
[17] A.C. Zimmermann, A. Mecabô, T. Fagundes, C.A. Rodrigues, J. Hazard. Mater. 179 (2010) 192–196.
[18] W.S.W. Ngah, S. Fatinathan, J. Environ. Sci. 22 (2010) 338–346.
[19] D.J. Macquarrie, J.J.E. Hardy, Ind. Eng. Chem. Res. 44 (2005) 8499–8520.
[20] V.K. Mourya, N.N. Inamdar, React. Funct. Polym. 68 (2008) 1013–1051.
[21] S.N. Chirkov, Appl. Biochem. Microbiol. 38 (2002) 1–8.
[22] I. Aranaz, R. Harris, A. Heras, Curr. Org. Chem. 14 (2010) 308–330.
[23] A. El Hadrami, L.R. Adam, I. El Hadrami, F. Daayf, Marine Drugs 8 (2010) 968–987.
[24] X. Li, P. Wu, G.F. Gao, S. Cheng, Biomacromolecules 12 (2011) 3962–3969.
[25] M. Dash, F. Chiellini, R.M. Ottenbrite, E. Chiellini, Prog. Polym. Sci. 36 (2011) 981–1014.
[26] L. Tang, M. Huang, Y. Jiang, Macromol. Rapid Commun. 15 (1994) 527–529.
[27] G.-L. Yuan, M.-Y. Yin, T.-T. Jiang, M.-Y. Huang, Y.-Y. Jiang, J. Mol. Catal. A: Chem. 159 (2000) 45–50.
[28] H. Zhu, T. Mizugaki, K. Ebitani, K. Kaneda, J. Appl. Polym. Sci. 80 (2001) 447–453.
[29] T. Vincent, S. Spinelli, E. Guibal, Ind. Eng. Chem. Res. 42 (2003) 5968–5976.
[30] T. Vincent, E. Guibal, Environ. Sci. Technol. 38 (2004) 4233–4240.
[31] T. Vincent, F. Peirano, E. Guibal, J. Appl. Polym. Sci. 94 (2004) 1634–1642.
[32] V. Calò, A. Nacci, A. Monopoli, A. Fornaro, L. Sabbatini, N. Cioffi, N. Ditaranto, Organometallics 23 (2004) 5154–5158.
[33] D.-Q. Zhou, D.-J. Zhou, X.-H. Cui, F.-M. Wang, M.-Y. Huang, Y.-Y. Jiang, Polym. Adv. Technol. 15 (2004) 350–354.
[34] E. Guibal, T. Vincent, E. Touraud, S. Colombo, A. Ferguson, J. Appl. Polym. Sci. 100 (2006) 3034–3043.
[35] I.U. Castro, F. Stüber, A. Fabregat, J. Font, A. Fortuny, C. Bengoa, J. Hazard. Mater. 163 (2009) 809–815.
[36] T.C.O. Mac Leod, V. Palaretti, V.P. Barros, A.L. Faria, T.A. Silva, M.D. Assis, Appl. Catal. A361 (2009) 152–159.
[37] A.D. Giuseppe, M. Crucianelli, M. Passacantando, S. Nisi, R. Saladino, J. Catal. 276 (2010) 412–422.
[38] S.E.S. Leonhardt, A. Stolle, B. Ondruschka, G. Cravotto, C.D. Leo, K.D. Jandt, T.F. Keller, Appl. Catal. A379 (2010) 30–37.
[39] K. Martina, S.E.S. Leonhardt, B. Ondruschka, M. Curini, A. Binello, G. Cravotto, J. Mol. Catal. A: Chem. 334 (2011) 60–64.
[40] M. Bradshaw, J. Zou, L. Byrne, K.S. Iyer, S.G. Stewart, C.L. Raston, Chem. Commun. 47 (2011) 12292–12294.
[41] D. Zhou, M. He, Y. Zhang, M. Huang, Y. Jiang, Polym. Adv. Technol. 14 (2003) 287–291.
[42] M. Adlim, M. Abu Bakar, K.Y. Liew, J. Ismail, J. Mol. Catal. A: Chem. 212 (2004) 141–149.
[43] W.-L. Wei, S.-J. Hao, J. Zhou, M.-Y. Huang, Y.-Y. Jiang, Polym. Adv. Technol. 15 (2004) 287–290.

[44] Y. Sun, Y. Guo, Q. Lu, X. Meng, W. Xiaohua, Y. Guo, Y. Wang, X. Liu, Z. Zhang, Catal. Lett. 100 (2005) 213–217.
[45] H. Zhai, A. Zhang, L. Li, S. Long, J. Appl. Polym. Sci. (2011) 2140–2146.
[46] C. Schmöger, A. Stolle, W. Bonrath, B. Ondruschka, Curr. Org. Chem. 15 (2011) 151–167.
[47] E.R. Welsh, C.L. Schauer, S.B. Qadri, R.R. Price, Biomacromolecules 3 (2002) 1370–1374.
[48] G. Cravotto, D. Garella, S. Tagliapietra, A. Stolle, S. Schüßler, S.E.S. Leonhardt, B. Ondruschka, New J. Chem. (2012) 1304–1307.
[49] Z.M. dos Santos, A.L.P.F. Caroni, M.R. Pereira, D.R. da Silva, J.L.C. Fonseca, Carbohydr. Res. 344 (2009) 2591–2595.
[50] T. Gallert, M. Hahn, M. Sellin, C. Schmöger, A. Stolle, B. Ondruschka, T.F. Keller, K.D. Jandt, ChemSusChem. 4 (2011) 1654–1661.
[51] C. Schmöger, T. Gallert, A. Stolle, B. Ondruschka, W. Bonrath, Chem. Eng. Technol. 34 (2011) 445–451.
[52] A. Stolle, C. Schmöger, B. Ondruschka, W. Bonrath, T.F. Keller, K.D. Jandt, Chin. J. Catal. 32 (2011) 1312–1322.
[53] T. Vincent, E. Guibal, Ind. Eng. Chem. Res. 41 (2002) 5158–5164.
[54] D.R. Rohindra, A.V. Nand, J.R. Khurma, South Pacific J. Nat. Sci. 22 (2004) 32–35.
[55] S.-S. Yi, D.-H. Lee, E. Sin, Y.-S. Lee, Tetrahedron Lett. 48 (2007) 6771–6775.
[56] N. Kildeeva, P. Perminov, L. Vladimirov, V. Novikov, S. Mikhailov, Russ. J. Bioorg. Chem. 35 (2009) 360–369.
[57] B. Hoffmann, D. Seitz, A. Mencke, A. Kokott, G. Ziegler, J. Mater. Sci. Mater. Med. 20 (2009) 1495–1503.
[58] M. Zeng, X. Zhang, L. Shao, C. Qi, X.-M. Zhang, J. Organomet. Chem. 704 (2012) 29–37.
[59] B. Abismail, J.P. Canselier, A.M. Wilhelm, H. Bajaj, C. Gourdon, Ultrason. Sonochem. 6 (1999) 75–83.
[60] T.S.H. Leong, T.J. Wooster, S.E. Kentish, M. Ashokkumar, Ultrason. Sonochem. 16 (2009) 721–727.
[61] K. Kurita, Mar. Biotechnol. 8 (2006) 203–226.
[62] E. Ronzón, G. Del Angel, J. Mol. Catal. A: Chem. 148 (1999) 105–115.
[63] J.-M. Andanson, S. Marx, A. Baiker, Catal. Sci. Technol. 2 (2012) 1403–1409.
[64] U.K. Singh, M. Albert Vannice, J. Catal. 191 (2000) 165–180.
[65] S. Yilmaz, S. Ucar, L. Artok, H. Gulec, Appl. Catal. A287 (2005) 261–266.
[66] M. Steffan, M. Lucas, A. Brandner, P. Claus, M. Wollny, N. Oldenburg, Chem. Ing. Tech. 78 (2006) 923–929.
[67] M. Steffan, F. Klasovsky, J. Arras, C. Roth, J. Radnik, H. Hofmeister, P. Claus, Adv. Synth. Catal. 350 (2008) 1337–1348.
[68] P. Claus, Top. Catal. 5 (1998) 51–62.
[69] P. Reyes, H. Rojas, G. Pecchi, J.L.G. Fierro, J. Mol. Catal. A: Chem. 179 (2002) 293–299.
[70] H. Lindlar, Helv. Chim. Acta 35 (1952) 446–450.
[71] J. Rajaram, A.P.S. Narula, H.P.S. Chawla, S. Dev, Tetrahedron 39 (1983) 2315–2322.
[72] J.G. Ulan, E. Kuo, W.F. Maier, R.S. Rai, G. Thomas, J. Org. Chem. 52 (1987) 3126–3132.
[73] J. Stachurski, J.M. Thomas, Catal. Lett. 1 (1988) 67–72.
[74] J.F. Daeuble, C. McGettigan, J.M. Stryker, Tetrahedron Lett. 31 (1990) 2397–2400.
[75] R. Tschan, M.M. Schubert, A. Baiker, W. Bonrath, H. Lansink-Rotgerink, Catal. Lett. 75 (2001) 31–36.
[76] F. Alonso, I. Osante, M. Yus, Tetrahedron 63 (2007) 93–102.
[77] S. Liu, X. Fan, X. Yan, X. Du, L. Chen, Appl. Catal. A400 (2011) 99–103.