Dalton Transactions

Cite this: Dalton Trans., 2012, 41, 2910



Palladium supported on chitosan as a recyclable and selective catalyst for the synthesis of 2-phenyl ethanol[†]

Aasif A. Dabbawala, N. Sudheesh and Hari C. Bajaj*

Received 12th October 2011, Accepted 5th December 2011 DOI: 10.1039/c2dt11924b

Two different chitosan supported palladium based catalysts were prepared, wherein dispersed palladium nanoparticles were obtained *via* chemical reduction supported on chitosan (Pd/CTS) and amine functionalized modified chitosan (Pd/AFCTS). The catalytic activity of the Pd-based catalysts, Pd/CTS and Pd/AFCTS, were assessed in the hydrogenation of styrene oxide to 2-phenyl ethanol. Both Pd-based catalysts enhanced the formation of the desired 2-phenyl ethanol in contrast to a conventional Pd/C catalyst without the assistance of inorganic or organic base. A considerable influence on the conversion and selectivity was observed in the case of Pd/AFCTS, consisting of palladium nanoparticles stabilized and dispersed on amine-functionalized chitosan matrix, affording complete conversion of styrene oxide with 98% selectivity to 2-phenyl ethanol. The catalyst Pd/AFCTS has also been recycled without significant loss of activity and selectivity.

Introduction

2-Phenylethanol (2-PEA), a colorless liquid having a mild but lasting odor of rose petals with bacteriostatic and antifungicidal properties is a valuable fragrance chemical. Due to its pleasing smell, 2-PEA is extensively used in perfumes, deodorants, cosmetics, soaps, detergents and as a food additive.^{1,2} Besides its direct application 2-PEA is also used as an intermediate in the synthesis of industrially important compounds.^{3,4} However, the selective synthesis of 2-PEA by conventional industrial processes such as (i) Friedel-Crafts alkylation of benzene using ethylene oxide with AlCl₃ as catalyst, 2,3 (ii) using Grignard-type reactant and ethylene oxide followed by decomposition of sulphuric acid⁴ and (iii) the ring opening of the epoxide using various hydrogenating agents⁵⁻¹³ are limited due to the generation of large amounts of inorganic salts, multi-step syntheses, need of special reagents and operation complexity by use of either corrosive, toxic or cumbersome reagents. Therefore, a process that produces a high purity of 2-PEA in a more environment friendly manner is highly desirable. A two-step catalytic process has been proposed wherein in the first step, styrene was catalytically oxidized to styrene oxide,^{14,15} followed by its hydrogenation to 2-PEA by molecular hydrogen using a heterogeneous catalyst.

The catalytic hydrogenation of styrene oxide to 2-PEA drew a lot of interest in academia and industry and is considered as an

effective, cleaner and more economical alternative to produce 2-PEA.¹⁶⁻³⁰ The hydrogenation of styrene oxide is usually accompanied with the formation of several side products such as phenyl acetaldehyde, benzaldehyde, 1-phenyl ethanol, styrene and ethyl benzene (Scheme 1). The presence of these by-products may destroy the aroma of the 2-PEA, making it unsuitable for perfumery formulations. Thus, various attempts have made to increase the selectivity for PEA.²³⁻³⁰ Several publications described the use of Pd/C or RANEY® nickel as the hydrogenation catalyst in the presence or absence of a base promoter for the selective preparation of 2-PEA from styrene oxide.²⁴⁻²⁶ The high conversion was obtained with a supported Pd based catalyst; and when alkali is used as a basic promoter, a high selectivity to 2-PEA is achieved. Consequently, a variety of supported palladium catalysts has been developed by immobilizing Pd on various supports. These supported catalysts are mainly based on

In recent years biopolymers have gained a great research attention for their use as a support in catalysis.^{31–36} Chitosan, the second most abundant natural polymer after cellulose, is a natural biopolymer produced by the alkaline N-deacetylation of

inorganic oxides like zeolites, alumina and MgO.²⁷⁻³⁰



Scheme 1 The catalytic hydrogenation of styrene oxide to produce 2-phenylethanol.

Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute, Council of Scientific and Industrial Research (CSIR-CSMCRI), G. B. Marg, Bhavnagar, 364002 Gujarat, India. E-mail: hcbajaj@csmcri.org; Fax: +91-278-2566970; Tel: +91-278-2471793

[†]Electronic supplementary information (ESI) available. See DOI: 10.1039/c2dt11924b



Scheme 2 A schematic approach for the synthesis of chitosan supported Pd nanoparticles.

chitin. Chitin, the naturally occurring polysaccharide, is extracted from the shells of crustacea, such as crabs, lobsters, prawns, and shrimps and the amount of its production is estimated to be several billion tons per year.³⁷ Chitosan, a reactive functional polymer, has a wide range of applications in biomedicine, pharmacology and agriculture.³⁸

Chitosan is characterized as a heteropolymer consisting of D-glucosamine units and *N*-acetyl D-glucosamine. The insolubility of chitosan in the majority of common solvents and good chemo-physical and biological properties (hydrophilic, biode-gradable, non-toxic and biocompatible) make chitosan an excellent candidate as a support for liquid phase catalysis.^{39,40} Moreover, the presence of amine functional groups (Scheme 2) in chitosan leads to interesting chelating properties for metal cations³¹ as well as efficient base catalysts.^{41,42} The use of such a basic support can provide a process having advantages of easy handling of the catalyst, easy separation of the products and avoiding the use of alkali or organic bases.

The present paper describes the use of chitosan supported Pd catalysts for the selective synthesis 2-PEA. The two different Pd catalysts were prepared with chitosan and modified chitosan. The modified chitosan supported Pd catalyst is found to be an efficient catalyst for the hydrogenation of styrene oxide; the selectivity for the desired product is high and is consistent over many catalyst-reuse experiments.

Experimental

Materials

Methanol, ethanol, toluene, tetrahydrofuran (THF), 1,4-dioxane and hexane were purchased from Sigma-Aldrich as anhydrous grade material and used as received. PdCl₂, styrene oxide (99%), catalyst 5% Pd/C, Aminopropyltrimethoxysilane (97%), salicyl-aldehyde and chitosan (low-molecular weight) were purchased from M/s Sigma-Aldrich Chemicals, USA and used as received. The hydrogen gas (99.9%) used was from Hydro Gas India Pvt. Ltd., India.

Instrumentation

All the hydrogenation reactions were performed in a 100 mL stainless steel autoclave reactor (Autoclave Engineers, EZE-Seal Reactor, USA). ¹H NMR spectra of compounds were measured in CDCl₃ solvent and using TMS as an internal reference, on a Bruker Avance 500 MHz FT-NMR. Infrared (IR) spectra were recorded using KBr pellet on a Perkin-Elmer spectrum GX FT-IR system in the range 400–4000 cm^{-1} with a resolution of 4 cm⁻¹. The C, H and N elemental analysis has been done on a Perkin-Elmer, 2400 CHNS/O analyzer. Surface area measurements were carried out using a Micromeritics ASAP 2010 instrument, USA. The samples were activated at 100 °C for 4 h under vacuum (5 \times 10⁻² mmHg) prior to N₂ adsorption measurements. The specific surface areas, pore diameters, and pore volumes of the samples were determined from nitrogen adsorption isotherms measured at -196 °C as per Brunauer, Emmett, Teller (BET) method. The metal contents in the catalysts were determined by inductively coupled plasma emission spectrometry (ICPES; Perkin-Elmer, OES, Optical 2000 DV) under standard conditions by digesting the sample in a minimum amount of concentrated HNO₃.

Scanning electron microscopy images of the support and catalyst were measured on a microscope (Leo Series VP1430, Germany). The samples were coated with gold using sputter coating to avoid charging. Analyses were carried out at an accelerating voltage of 18 kV and a probe current of 102 AMP.

Thermogravimetric analysis (TGA) were carried out using a Mettler TGA/SDTA 851^e equipment in flowing N₂ (flow rate = 50 mL min⁻¹), at a heating rate of 10 °C min⁻¹ and data were processed using Star^e software.

Transmission electron microscopy (TEM) images were obtained with a JEOL JEM-2100 microscope with an acceleration voltage of 200 kV using carbon coated 200 mesh copper grids. The samples were ultrasonically dispersed in ethanol for 5 min and deposited onto carbon film using capillary and dried in air for 30 min.

Products were analyzed with Shimadzu GC-17A gas chromatograph (GC) using flame ionization detector (FID) having 5% diphenyl- and 95% dimethyl siloxane capillary column (60 m length, 0.25 mm diameter). The column temperature was initially kept at 50 °C for 5 min and then raised to 200 °C at 10 °C min⁻¹. Nitrogen was used as a carrier gas (1.2 mL min⁻¹). Furthermore, the reaction mixture was analyzed by GC–MS (Shimadzu, GC-MS QP 2010, Japan) to confirm the products *via* mass fragmentation patterns.

Synthesis of modified chitosan

Generally chitosan is treated with HCl and then the chitosan beads are prepared by adding it into an NaOH solution. Chitosan (CTS) can be used as such as a catalyst support. However, it is better to functionalize the chitosan avoiding the use of acids and alkalis to obtain an active base catalyst. Therefore, the chitosan was modified. Amino functionalization of the chitosan (Scheme 2) was done by treating chitosan with aminopropyltrimethoxysilane (APTMS). In a typical procedure, 1.5 g of chitosan and 1 g of APTMS were taken in 25 mL toluene in a 50 mL round bottom flask (RBF). The RBF was connected with a water condenser and an inert atmosphere was created by nitrogen. The RBF was placed in an oil bath at 110 °C. The refluxing was continued for 24 h with stirring at 450 rpm. After 24 h, the flask was cooled to room temperature. The catalyst was filtered, dried at 100 °C and powdered to get the amino functionalized chitosan (AFCTS).

Synthesis of chitosan supported Pd catalyst

The chitosan supported Pd catalysts were synthesized in two steps; adsorption of Pd salt followed by reduction with NaBH₄ with the modification of reported procedures.^{31,32} Mainly, the two different Pd catalysts were prepared with raw chitosan (CTS) and amino functionalized chitosan (AFCTS). To immobilize Pd on CTS or on AFCTS, 66.4 mg of PdCl₂ salt (2% Pd metal by weight) was placed together with 50 mL ethanol and 2.0 g CTS/ AFCTS support in a 2-necked 100 mL round bottom flask equipped with a mechanical stirrer and a reflux condenser connected to a nitrogen inlet. The resulting mixture was stirred at reflux temperature under an N₂ atmosphere³² for a period of 12 h. The prepared Pd/CTS or AFCTS complex was reduced with excess NaBH₄ with constant stirring for 3 h at room temperature. Finally, the catalyst was separated by filtration, washed with ethanol and dried to give dark grey catalyst CTS-2Pd or AFCTS-2Pd (Scheme 2). The catalyst AFCTS-Pd with different Pd content (such as AFCTS-0.5Pd, AFCTS-1Pd, and AFCTS-3Pd) were also prepared with the method described above by varying the Pd salt amount.

Catalytic hydrogenation reaction

In typical hydrogenation experiment, the required amount of catalyst (CTS-Pd or AFCTS-Pd), substrate styrene oxide and solvent were charged into a stainless steel autoclave 100 mL reactor. The reactor was flushed with H₂ three times at room temperature after which the reactor was brought to the desired reaction temperature and pressurized with H₂ at the desired pressure. The reaction was initiated by stirring (900 rpm); the reaction started immediately as was evidenced by a pressure drop and accompanied by a slight increase of the temperature. The constant pressure of the reactor was maintained by supplying the hydrogen during the reaction. To check conversion, samples were withdrawn via sampling valve from the reactor at different time intervals during the course of the reaction and analysed by gas chromatography. Furthermore, the reaction mixture was analyzed by GC-MS (Shimadzu, GC-MS QP 2010, Japan) to confirm the products via mass fragmentation patterns. After the desired reaction time, the stirring was stopped and the reactor was cooled down to room temperature, depressurized, flushed with N₂, opened and decanted the reaction mixture from the catalyst to collect the final sample for a GC analysis. Finally, the solvent was distilled from the reaction mixture to obtain the final product. To ensure the reproducibility of the results, repeated experiments were carried out under identical reaction conditions and data were found to be reproducible within $\pm 2\%$ variation.

Results and discussion

Characterization of catalysts

The catalysts were characterized thoroughly by various instrumental techniques. The FT-IR spectra of the raw chitosan, AFCTS and catalysts (chitosan supported Pd: CTS-Pd. AFCTS-Pd and recycled AFCTS-Pd-R) in the 4000-400 cm⁻¹ region matched well (Fig. 1) with the reported spectra.⁴³ The FT-IR spectra of raw chitosan and AFCTS gave a band at 1596 cm^{-1} indicating the presence of the -NH₂ group. The slightly higher intensity of the band at 1596 cm⁻¹ in AFCTS than in raw chitosan confirms the functionalization of APTMS in raw chitosan. The absorption bands at 1150 cm^{-1} (anti-symmetric stretching of the C-O-C Bridge), 1081 and 1032 cm⁻¹ (skeletal vibration involving the C-O stretching) are characteristic of saccharide structure. The absorption bands at 3440 and 2921 cm⁻¹ are attributed to the O–H and methylene (-CH₂) group, respectively. The broad peak at 3440 also indicated that the hydroxyl groups are hydrogen-bonded. The FT-IR spectra of the catalysts, CTS-Pd and AFCTS-Pd were identical to the corresponding chitosan support. However, the intensity of the IR band at 1596 cm⁻¹ decreased indicating the stabilization of the palladium nanoparticles in the chitosan matrix through the amine groups. It may also be noted that the reused catalyst (AFCTS-2Pd-R) showed a negligible change in FT-IR pattern (Fig. 1), which is consistent with the catalyst re-use experiments.

The thermal behavior of raw chitosan, AFCTS, CTS-Pd and AFCTS-Pd are shown in Fig. 2. Raw chitosan has two main weight losses with one starting at 60 °C and another starting at around 260 °C. The first weight loss of ~9% was attributed to the removal of adsorbed water molecules. The second stage weight loss of 57% is due to the decomposition of the polysac-charide chain. The AFCTS, CTS-Pd and AFCTS-Pd displayed similar thermal behavior with a two step weight loss. The first weight loss was ~2.5–3.0% in the range of 50–120 °C due to the physically adsorbed water molecule and the second step weight loss was of ~54% for the decomposition the polysaccharide framework. The catalysts are thermally stable up to 250 °C.

The surface morphology of the support (AFCTS) and catalyst (AFCTS-Pd) by SEM images (Fig. 3) clearly depict the layered



Fig. 1 FT-IR spectra of the support and catalysts.



Fig. 2 TGA profile of the support and catalyst.

structure of the support. The catalyst surface has a lower surface area, which is confirmed by the N_2 sorption studies.

The BET surface area of the support and catalyst were found to be ~1.04 m² g⁻¹ with a pore diameter of 128 Å. C, H, and N analysis of CTS and AFCTS were recorded and found to be: CTS (C 39.32, H 6.55, N 8.37); AFCTS (C 41.04, H 6.71, N 10.96). From these results it is clear that the chitosan was functionalized by APTMS.

The percentage of palladium content in the catalysts, CTS-Pd and AFCTS-Pd was determined by chemical analysis using Inductive Coupled Plasma (ICP). No significant difference was observed in the ICP analysis of the catalysts related to the theoretical Pd content and was in accordance with the calculated compositions.

The TEM images of catalyst AFCTS-2Pd (Fig. 4) displayed the well dispersed nature of the Pd nanoparticles with diameters in the range of 8–25 nm situated on the external surface of the support.

The number of accessible amino groups on the catalyst (AFCTS-Pd) was determined by reacting the catalyst with salicylaldehyde.¹⁰ The catalyst (50 mg) was mixed with 3 mL of 0.16 M solution of salicylaldehyde in ethanol with nitrobenzene as GC internal standard. The salicylaldehyde forms salicylidimine Schiff base with the accessible amino group present on the catalyst. The residual salicylaldehyde concentration was determined by GC analysis, from which the accessible amino groups were calculated. The percentage amount of accessible amine groups was ~32%. In the modified chitosan, the grafted APTMS will have most of the amino groups exposed on the surface whereas the amino groups of the raw chitosan itself being in bulk will not have that much exposure.

However, the functionalized APTMS and $-NH_2$ group in chitosan itself are responsible to contribute for the observed 32% of accessible amino groups in the catalyst AFCTS-Pd. The salicylaldehyde adsorption onto $-NH_2$ groups is carried out in the presence of a protic solvent such as ethanol, which leads to the swelling of polysaccharide framework of chitosan^{19,20} and allows salicylaldehyde to enter into the polymer chain to have access to the bulk amino groups. This resulted in the higher accessible basic sites although the catalyst has a lower surface area.

Catalytic activity

The complete conversion of styrene oxide and selective preparation of 2-phenyl ethanol by hydrogenation of styrene oxide is a complex process. Therefore, the studies have been mainly focused on selectivity issues and product distribution using different catalyst systems. The catalytic performances of chitosan supported Pd catalysts are summarized in Table 1. The catalytic results indicated that the chitosan supported Pd catalysts selectively gave 2-phenylethanol at 40 °C and 2.0 MPa hydrogen pressure. The main side products were phenyl acetaldehyde and ethyl benzene. No formation of 1-phenyl ethanol was observed. Under the same reaction conditions, the CTS-2Pd gave 2-PEA selectivity of 90% with 57% conversion of styrene oxide in 1 h



Fig. 3 SEM images of (a) the support AFCTS and (b) the catalyst AFCTS-Pd.



Fig. 4 TEM images of AFCTS-Pd.

wore r childban bapportea ra eatar, Lea n, arogenation or britene onnae	Table 1	Chitosan	supported	Pd	catalyzed	l hydro	genation	of sty	vrene o	xide	ļ
---	---------	----------	-----------	----	-----------	---------	----------	--------	---------	------	---

Entry	Catalyst	Pd (%)	Conv. ^{<i>b</i>} (%)	Selectivity (%)				
				$2-\text{PEA}^c$	$1-\text{PEA}^d$	PAD ^e	ETB ^f	
1	CTS		0					
2	CTS-2Pd	2	57	90		8	2	
3	AFCTS-0.5Pd	0.5	38	91	_	9		
4	AFCTS-1Pd	1	53	94	_	6		
5	AFCTS-2Pd	2	71	97	_	3		
6	AFCTS-3Pd	3	85	97		3		
7	Pd5-C	5	93	84	2	14		
/	1 45-0	5	<i>)))</i>	-	2	14		

^{*a*} Reaction conditions: styrene oxide = 25 mmol, catalyst. = 60 mg, temp. = 40 °C, hydrogen pressure = 2.0 MPa, solvent (methanol) = 30 mL, reaction time = 60 min. ^{*b*} Conversion of styrene oxide, ^{*c*} Selectivity to 2-phenyl ethanol, ^{*d*} Selectivity to 1-phenyl ethanol, ^{*e*} Selectivity to phenyl acetaldehyde (PAD), ^{*f*} Selectivity to ethyl benzene

whereas AFCTS-2Pd gave 71% conversion with 97% selectivity to 2-PEA, indicating that AFCTS-2Pd was more active (Table 1, entry 5). This reveals the crucial role played by the surface amino functional groups in the amino functionalized chitosan and higher activity of AFCTS-Pd compared to the non functionalized chitosan. To ascertain the role of palladium present in the chitosan supported Pd catalysts, one hydrogenation experiment was carried out using bare chitosan (without Pd) as a catalyst at 40 °C and 2.0 MPa partial pressure of hydrogen. No hydrogenation of styrene oxide was observed even after 3 h reaction time (Table 1, entry 1), which indicated that the Pd present in the chitosan supported Pd catalysts is only the active metal centre (or active sites) for hydrogenation of styrene oxide.

In order to check the influence of Pd loading, the palladium content was varied from 0.5 to 3% in the AFCTS-Pd catalyst. As expected, the conversion of styrene oxide hydrogenation was found to increase with an increase in Pd content indicating linear dependency with respect to the palladium content (Table 1). Similar results have been reported for Pd catalyzed hydrogenation of styrene oxide by Chaudhari *et al.*²⁶ The conversion and 2-PEA selectivity were low at low palladium content (0.5%) and improved with an increase in palladium content (3%). These results further corroborate that Pd is the active metal centre as the

conversion and selectivity varied with Pd content. It is of interest to compare the catalytic performance of the AFCTS-3Pd with Pd5-C (5% Pd supported on carbon), the experiment was carried out with catalyst Pd5-C under similar reaction conditions (temp. 40 °C, 2 MPa hydrogen pressure). For the Pd5-C, high conversion (93%) of styrene oxide was obtained as compared to the AFCTS-3Pd catalyst (85%) due to the high surface area and organophilic character of the carbon support. Although, selectivity for 2-PEA was considerably lower for Pd5-C (84%) than that observed for the AFCTS-3Pd catalyst (97%). The AFCTS-3Pd catalyst even at lower Pd loading than Pd5-C displayed comparable catalytic activity and high selectivity of 2-PEA (Table 1, entries 6 and 7). The effect of reaction parameters like temperature, catalyst amount, pressure of hydrogen, solvent and stirring rate on conversion and selectivity of 2-PEA in the hydrogenation experiments using AFCTS-2Pd catalyst were investigated in detail.

Effect of temperature

In order to elucidate the influence of the reaction temperature in the hydrogenation of styrene oxide, the temperature was varied



Fig. 5 Effect of temperature on (a) initial rate and (b) selectivity to 2-PEA using AFCTS-2Pd as a catalyst. Reaction conditions: styrene oxide = 25 mmol, substrate/Pd = 2216, hydrogen partial pressure = 2.0 MPa, solvent (methanol) = 30 mL.

from 30 to 80 °C at constant hydrogen pressure (2.0 MPa). The initial rate (calculated at 30-40% conversion level) for hydrogenation of styrene oxide catalyzed by AFCTS-2Pd increased almost linearly on increasing the reaction temperature (Fig. 5). However, on increasing the temperature from 30 to 80 °C, there was slight decrease in the selectivity (from 97 to 92%) for 2-PEA. Interestingly, 1-phenylethanol was not formed in the studied temperature range. The low reaction temperature (30 °C) resulted in higher selectivity to 2-PEA (97%) but the initial rate of styrene hydrogenation was rather low [21.61 mol/(mol_{Pd}. min)]. While at 80 °C, the initial rate of reaction increased to 44.32 mol/(mol_{Pd}.min) with 2-PEA selectivity decreased to 92%. The decrease in 2-PEA selectivity at high temperature is mainly due to the formation of phenyl acetaldehyde (Scheme 2). The optimum reaction temperature was selected as 40 °C for further study.

Effect of catalyst amount

In hydrogenation, the amount of catalyst can alter the distribution of product and influence the selectivity. The effect of catalyst amount on conversion and selectivity in hydrogenation of styrene oxide was studied at 40 $^{\circ}$ C and 2.0 MPa hydrogen pressure by varying the amount of catalyst from 30 to 120 mg



Fig. 6 Effect of catalyst amount on the AFCTS-2Pd catalyzed hydrogenation of styrene oxide. Reaction conditions: styrene oxide = 25 mmol, Temp. = 40 °C, hydrogen pressure = 2.0 MPa, solvent (methanol) = 30 mL, reaction time = 60 min.

(styrene oxide/catalyst ratio 25 to 100). The results are summarized in Fig. 6. The reaction was very slow at a low amount of catalyst and the conversion as well as selectivity to 2-PEA increased with an increase in the catalyst amount. The 30 mg AFCTS-2Pd catalyst resulted in 29% conversion of styrene oxide with 90% 2-PEA selectivity. The conversion and selectivity to 2-PEA increased to 92% and 98% respectively at 120 mg of catalyst under the employed experimental conditions. The high conversion and selectivity at higher catalyst amount can be attributed to the higher number of active sites present on the surface of the catalyst.

Effect of hydrogen pressure

In the hydrogenation reaction, a minimum pressure of hydrogen is required to dissolve a sufficient amount of hydrogen in the reaction solvent. The hydrogenation of styrene oxide catalyzed by AFCTS-2Pd was studied at 40 °C under different hydrogen pressures (1.0–4.0 MPa). The results of the effect of the hydrogen pressure on conversion and selectivity of styrene oxide hydrogenation are given in Fig. 7.

The conversion of styrene oxide increased on increasing the partial pressure of hydrogen. The hydrogenation of styrene oxide proceeds slowly at low hydrogen pressure due to low concentration of dissolved hydrogen. At 1.0 MPa hydrogen pressure, conversion was found to be 59%. The conversion increased considerably with an increase of hydrogen pressure. For example, on the increase of H₂ pressure from 1.0–4.0 MPa, the conversion was increased from 59 to 90%. In all instances, a high selectivity to 2-PEA was obtained. The higher hydrogen pressure favors the lower equilibrium concentrations of substrate, which results into higher conversion of styrene oxide.

The effect of agitation speed on the conversion and selectivity of styrene oxide hydrogenation was also studied by varying the stirring rates at 500, 750, 950, 1150 and 1350 rpm, respectively, in order to confirm the impact of gas liquid mass transfer resistance. The other reaction parameters were kept the same. At low



Fig. 7 Effect of partial pressure of hydrogen on the AFCTS-2Pd catalyzed hydrogenation of styrene oxide. Reaction conditions: styrene oxide = 25 mmol, catalyst (AFCTS-2Pd) = 60 mg, temp. = 40 °C, methanol = 30 mL, reaction time = 60 min.

stirring rate (500 rpm), the reaction proceeds slowly and is diffusion-limited. Whereas an increase in stirring rate from 500 to 950 rpm substantially enhanced both the conversion and 2-PEA selectivity. With the further increase in stirring rate from 950 to 1350 rpm, no significant change in conversion and selectivity were observed. Therefore, in all the experiments the stirring rate was maintained at 950 rpm.

Effect of solvent

The choice of solvent was found to be critical for the reaction as the side product formation was affected by solvent used. Different solvents were studied to find the effect of solvent on AFCTS-2Pd catalyzed hydrogenation of styrene oxide (Fig. 8). The hydrogenation of styrene oxide proceeds well with high



Fig. 8 Effect of solvent on AFCTS-2Pd catalyzed hydrogenation of styrene oxide. Reaction conditions: styrene oxide = 25 mmol, catalyst (AFCTS-2Pd) = 60 mg, temp. = 40 °C, hydrogen pressure = 2.0 MPa, solvent = 30 mL, reaction time = 60 min.

activity and selectivity in MeOH and EtOH, while in THF, 1,4dioxane and n-hexane, low conversion was observed. The highest conversion was observed with MeOH as the solvent. A similar observation had been reported by Chaudhari *et al.*²⁶ The use of protic solvents such as methanol and ethanol indicates the presence of weak, or the absence of, metal Pd-epoxide interaction, which increases the conversion and selectivity.

Recyclability of the catalyst

The kinetic profile for conversion of styrene oxide and formation of 2-phenyl ethanol with respect to time is shown in Fig. 9. In 30 min, 41% conversion of styrene oxide was observed, which increased to 71% in 60 min of reaction time. The complete conversion of styrene oxide was obtained at 105 min. The catalytic hydrogenation of styrene oxide yielded mainly 2-phenyl ethanol. However, a small amount of phenyl acetaldehyde was observed at the initial stage of the reaction. As the reaction proceeded, the formation of phenyl acetaldehyde increased up to 3%.

In order to determine Pd leaching from the catalyst, the hydrogenation of styrene oxide (with 41% conversion) was stopped after 30 min, the catalyst was removed by filtration and the reaction was allowed to proceed at 40 °C and 2.0 MPa hydrogen pressure for a further 6 h without catalyst. No further increase in the conversion of styrene oxide into 2-phenyl ethanol was observed. Moreover, Pd in the reaction mixture after the reaction could not be detected by the ICP-OES (detection limit of ICP-OES instrument is ~0.2 ppm). This indicates that leaching of Pd, if any, is very low. Catalyst recycling tests were also conducted. For reusability experiments, the catalyst was filtered from the reaction mixture, washed with methanol and dried before reuse. The regenerated catalyst was used for the hydrogenation of styrene oxide under similar reaction conditions as used for the fresh catalyst. No significant change in TONs (see ESI[†]) as well as in selectivity to 2-PEA were observed up to five cycles suggesting that the catalyst is reusable under the



Fig. 9 Progress of hydrogenation of styrene oxide with respect to time using the AFCTS-2Pd catalyst. Reaction conditions: styrene oxide = 25 mmol, substrate/Pd = 2216, temp. = 40 °C, hydrogen pressure = 2.0 MPa, methanol = 30 mL.

employed reaction conditions. The ICP analysis of spent catalyst after the fourth cycle showed ~1.92 wt.% of Pd in the catalyst further confirming that Pd leaching into the organic phase is negligible. Moreover, the recycled catalyst was checked for elemental analysis to study the leaching of the APTMS, if any. The obtained results were %C: 43.78, %H: 6.82, %N: 10.59. This confirms the stable functionalization of APTMS in the AFCTS and the increase in %C can be attributed to the adsorption of substrate or/and products. In order to check any loss of APTMS from the AFCTS-2Pd, the fresh catalyst was taken in toluene and the supernatant solution was separated. In the separated supernatant solution salicylaldehyde was added and the solution was checked by UV-vis spectroscopy for a characteristic imine peak. No characteristic imine peak was observed, indicating that there is no loss of APTMS from the AFCTS-2Pd catalyst.

Conclusions

The catalytic hydrogenation of styrene oxide to 2-phenyl ethanol by Pd supported on a chitosan catalyst was investigated. Chitosan has been modified using APTMS avoiding the use of acid or alkali. The Pd supported on modified chitosan was found to be an efficient catalyst compared to the Pd supported on non functionalized chitosan for the selective preparation of 2-PEA. The more basic site in AFCTS with respect to the non-functionalized counterpart provided better selectivity thus leading to high 2phenyl ethanol selectivity (97–98%) at total conversion of styrene oxide under optimized conditions. The catalyst was separated and effectively used up to five cycles without significant loss in its activity and selectivity.

Acknowledgements

Authors are thankful to analytical section of the institute for assistance with analyses and CSIR for financial support under CSIR Network Programme NWP 010. AAD and NS thank to CSIR, New Delhi, for the award of Senior Research Fellowship.

Notes and references

- B. D. Mookherjee and R. A. Wilson, *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed.*, Vol. 17, John Wiley & Sons, New York, 1994.
- 2 K. Bauer, D. Garbe and H. Surburg, *Common Fragrance and Flavour Materials*, New York, 1990.
- 3 G. A. Olah, V. P. Reddy and G. K. Surya Prakash, *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed.*, vol. 11, John Wiley & Sons, New York, 1994.
- 4 E. T. Theimer, *Theimer in Fragrance Chemistry*, Academic Press, New York, 1982, p. 271.
- 5 H. Fujitsu, S. Shirahama, E. Matsumura, K. Takeshita and I. Mochida, J. Org. Chem., 1981, 46, 2287.
- 6 S. Krishnamurthy, R. M. Schubert and H. C. Brown, J. Am. Chem. Soc., 1973, 95, 8486.

- 7 M. Bartok and K. L. Lang, in: A. Weissberger and E. C. Taylor (ed.), *The Chemistry of Heterocyclic Compounds-Small Ring Heterocycles*, Wiley, New York, 1985.
- 8 G. Smith and Janice, Synthesis, 1984, 8, 629.
- 9 C. Bonini, R. D. Fabio, G. Sotgiu and S. Cavagnero, *Tetrahedron*, 1989, 45, 2895.
- 10 M. Yamada, K. Tanaka, S. Araki and Y. Butsugan, *Tetrahedron Lett.*, 1995, 36, 3169.
- 11 W. B. Smith, J. Org. Chem., 1984, 49, 3219.
- 12 R. Sreekumar, R. Padmakurmar and R. P. Rugmini, *Tetrahedron Lett.*, 1998, **39**, 5151.
- 13 B. C. Ranu and A. R. Das, J. Chem. Soc. Chem. Commun., 1990, 1334.
- 14 K. Yamaguchi, K. Ebitani and K. Kaneda, J. Org. Chem., 1999, 64, 2966.
- 15 W. Hölderich, M. Hesse and F. Näumann, *Angew. Chem. Int. Ed.*, 1988, **27**, 266.
- 16 T. F. Wood and N. J. Clifton, U.S. Patent, 2524096, 1950
- 17 T. F. Wood, GER. Patent, 1918852, 1969
- 18 H. Hopff and H. Kuhn, U.S. Patent, 2822403, 1958; T. F. Wood and J. N. Wayne, U.S. Patent, 3579593, 1971
- 19 O. Priese, GER. Patent, 86812, 1972
- 20 F. Fujitsu, S. Shirahama, E. Matsumura, K. Takeshita and I. Mochida, J. Org. Chem., 1981, 46, 2287.
- 21 C. A. Gibson, L. F. Theiling Jr., U.S. Patent, 4064186, 1977
- 22 W. F. Hoeldrich, N. W. Goetz and L. F. Hupfer, U.S. Patent, 4943667, 1990
- 23 S. Mitsui, S. Imaizumi, M. Hisashige and Y. Sugi, *Tetrahedron Lett.*, 1973, **29**, 4093.
- 24 V. G. Yadav and S. B. Chandalia, Org. Process Res. Dev., 1998, 2, 294.
- 25 C. V. Rode, M. M. Telkar and R. V. Chaudhari, U.S. Patent, 6166269, 2000
- 26 C. V. Rode, M. M. Telkar, R. Jaganathan and R. V. Chaudhari, J. Mol. Catal A: Chem., 2003, 200, 279.
- 27 R. Dimitrova, V. Minkov and N. Micheva, *Appl. Catal. A: Gen.*, 1996, **145**, 49.
- 28 O. Bergada, P. Salagre, Y. Cesteros, F. Medina and J. E. Sueiras, *Appl. Catal. A. Gen.*, 2004, **272**, 125.
- 29 O. Bergada, P. Salagre, Y. Cesteros, F. Medina and J. E. Sueiras, *Appl. Catal.A. Gen.*, 2007, 331, 19.
- 30 I. Kirm, F. Medina, X. Rodriguez, Y. Cesteros, P. Salagre and J. E. Sueiras, J. Mol. Cat. A: Chem., 2005, 239, 215.
- 31 T. Vincent and E. Guibal, *Ind. Eng. Res. Chem.*, 2002, **41**, 5158; L.-M. Tang, M.-Y. Huang and Y.-Y. Jiang, *Macromol. Rapid Commun.*, 1994, **15**, 527; H.-S. Han, S.-N. Jiang, M.-Y. Huang and Y.-Y. Jiang, *Polym. Adv. Technol.*, 2002, **7**, 704.
- 32 M.-Y. Yin, G.-L. Yuan, Y.-Q. Wu, M.-Y. Huang and Y.-Y. Jiang, J. Mol. Catal. A: Chem., 1999, 147, 93.
- 33 F. Quignard, A. Choplin and A. Domard, Langmuir, 2000, 16, 9106.
- 34 W. Sun, C.-G. Xia and H.-W. Wang, New J. Chem., 2002, 26, 755.
- 35 Y. Chang, Y. Wang and Z. Su, J. Appl. Polym. Sci., 2002, 83, 2188; D. Hu, Y. Cui, X. Dong and Y. Fang, React. Funct. Polym., 2001, 48, 201.
- 36 J. Zhang and C.-G. Xia, J. Mol. Catal. A: Chem., 2003, 206, 59.
- 37 K. Kojima, M. Yoshikuni and T. J. Suzuki, Appl. Polym. Sci., 1979, 24, 1587.
- 38 M. N. V. Ravi Kumar, React. Funct. Polym., 2000, 46, 1.
- 39 E. Guibal, Prog. Polym. Sci., 2005, 30, 71.
- 40 D. J. Macquarrie and J. J. E. Hardy, Ind. Eng. Chem. Res., 2005, 44, 8499.
- 41 R. Valentin, K. Molvinger, F. Quignard and D. Brunel, New J. Chem., 2003, 27, 1690.
- 42 K. R. Reddy, K. Rajgopal, C. U. Maheswari and M. L. Kantam, New J. Chem., 2006, 30, 1549.
- 43 N. Sudheesh, S. K. Sharma and R. S. Shukla, J. Mol. Catal A: Chem., 2010, 321, 77.