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Ionic modified crosslinked salep: A highly loaded and efficient heterogeneous organocatalyst

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ABSTRACT

In this work, a novel heterogeneous organocatalyst was synthesized by immobilization of hydroxide ions on the modified salep as a natural polymer. Because of the grafting of ionic polymer chains onto the salep backbone, catalyst has high loading level of hydroxide ions (3.01 mmol/g). The resulting catalyst shows excellent activity in the synthesis of 4*H*-benzo[*b*]pyrans in water at room temperature in short reaction times. The present catalyst and protocol represent a simple, ecologically safe and cost-effective route to synthesize 4*H*-benzo[*b*]pyrans with high product yield, as well as easy catalyst recycling.

1. Introduction

Base catalyzed organic reactions are very important for the synthesis of pharmaceutical and fine chemicals. Although the industrial scale of base catalyzed transformations are usually catalyzed by alkali hydroxides or alkali alkoxides in the homogeneous phase, these bases material cannot be recycled and reused. Also they have other disadvantages such as waste production, corrosion, and incorporation of metals.

To this viewpoint, there is an increasing interest in the green production of organic materials. Recently, basic organocatalysts have attracted a lot of attention for application in organic syntheses due to their efficiency and selectivity is tunable with structural modifications (Dalko & Moisan, 2004; Ooi & Maruoka, 2004). However, most of them are used in homogeneous systems and their recyclability is still difficult. An innovative way to solve the recyclability problem is immobilization of organocatalysts onto the appropriate solid supports which makes possible the rapid isolation of the product and easy recycling of the organocatalyst. In the past decades, efficient heterogeneous basic organocatalysts were synthesized by immobilization of basic organomolecules onto the inorganic solid supports such as magnetic nanoparticles (Dalaigh, Corr, Gunko, & Connon, 2007; Zhang, Zhao, & Xia, 2009) and mesoporous silica (Parvin, Jin, Ansari, Oh, & Park, 2012; Yuan, Huang, & Chen, 2012). But these heterogeneous catalysts have some serious disadvantages such as (1) several onerous steps for immobilization of homogenous catalysts, (2) low loading level of immobilized catalysts which requires a large volume of solvent for reaction and the catalyst recovery processes, (3) low catalyst activity due to the low penetration of substrates into the catalyst surface and (4) high catalyst leaching due to weak bonds of homogenous catalysts with surfaces.

Recently, there has been more emphasis on utilization of natural materials in catalytic processes. Biopolymers are particularly important candidates for catalysis application because they are versatile, inexpensive, chemically stable, biodegradable, and abundant (Dumitriu, 2005). Among the natural polysaccharides, chitosan is more interesting when used as catalyst because there are free amine groups on chitosan backbone (Chtchigrovsky et al., 2009; Guibal, 2005; Macquarrie & Hardy, 2005; Molvinger, Quignard, Brunel, Boissire, & Devoisselle, 2004; Reddy, Kumar, Reddy, Sreedhar, & Kantam, 2006a; Ricci et al., 2010; Sun et al., 2012; Valentin, Molvinger, Quignard, & Brunel, 2003). Other polysaccharides receive considerably less attention for that their modification is more complicated than chitosan (Budarin, Clark, Luque, Macquarrie, & White, 2008; Gronnow, Luque, Macquarrie, & Clark, 2005; Reddy, Rajgopal, Maheswari, & Kantam, 2006b).

The lack of literature reports about the using of natural polysaccharides as a support for immobilization of homogenous catalysts convinced us to evaluate the potential of salep as a biomaterial bed. Salep is a polysaccharide mainly consisted of glucomannan (Fig. 1) (Kaya & Tekin, 2001). It can be obtained from the dried tubers of certain natural terrestrial orchids and has been

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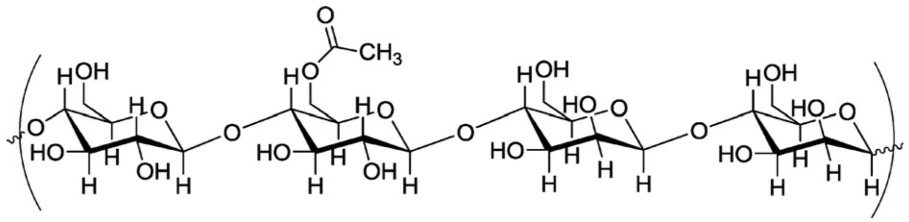


Fig. 1. A portion of the glucomannan repeating unit.

used as thickeners, film formers and emulsifiers in the food industry. Recently, our group used salep as backbone for preparation of biodegradable superabsorbent hydrogels. We prepared poly(acrylic acid) and poly(acrylamide) grafted salep and investigated their swelling behaviors (Pourjavadi, Barajee, & Soleyman, 2009; Pourjavadi, Soleyman, & Barajee, 2008). In another research, we prepared salep phosphate-based hydrogels and used them as a carrier matrix for fertilizer release (Pourjavadi, Doulabi, Soleyman, Sharif, & Eghtesadi, 2012).

In this paper we would like to report the synthesis of a basic organocatalyst based on cross linked salep-grafted-poly(3-(methacryloylamino)propyl trimethylammonium hydroxide). The resulted catalyst was used in the synthesis of 4*H*-benzo[*b*]pyrans in a green way.

4*H*-benzo[*b*]pyrans and their derivatives have been attracted a lot of attention as important heterocyclic compounds because of their wide range of biological properties such as anti-cancer, anti-coagulant, anti-anaphylactic activates (Andreani & Lapi, 1960; Bonsignore, Loy, Secci, & Calignano, 1993). The conventional reported method for synthesis of 4*H*-benzo[*b*]pyrans is using organic solvents such as DMF or acetic acid in reflux temperature which gave poor yields (Singh, Singh, & Singh, 1996; Wang, Shi, Tu, & Yao, 2001). Several acid and base catalysts have been used for the synthesis of 4*H*-benzo[*b*]pyrans such as, ionic liquids (Chen, Li, Huang, & Zheng, 2009; Fang, Zhang, & Liu, 2010; Shaabani, Samadi, Badri, & Rahmati, 2005), tetrabutylammonium bromide (TBAB) (Khurana & Kumar, 2009), rare earth perfluorooctanoate (Wang, Shao, Tian, Wang, & Liu, 2006), fluoride ion (Gao, Tsai, Tseng, & Yao, 2008), inorganic–organic hybrid magnetic nanocatalyst (Khoobi et al., 2012), glycerol (Safaei, Shekouhy, Rahmanpur, & Shirinfeshan, 2012), silica bonded *n*-propyl-4-aza-1-azoniabicyclo[2.2.2]octane chloride (Hasaninejad, Shekouhy, Golzar, Zare, & Doroodmand, 2011), and DBU (Khurana, Nand, & Saluja, 2010). However in most of these methods catalysts cannot be recycled and a large volume of solvent is used for product separation. Therefore, developing a green catalytic protocol for the synthesis of these compounds in mild conditions is still needed.

2. Results and discussion

Salep as a natural biopolymer with high molecular weight is chemically stable, inexpensive and abundant which makes it a good support for immobilization of catalysts in the large scale applications. The large scale preparation of was performed in two simple steps; salep functionalization and ion exchange process. In the first step poly (3-(methacryloylamino)propyl trimethylammonium chloride) (PMAPTAC) was grafted on salep backbone. Addition of ammonium persulfate (APS), initiates the polymerization and PMAPTAC will be grafted onto salep backbone. Using methylenebisacrylamide (MBA) will crosslink the polymer chains to form an insoluble heterogeneous material. A proposed mechanism for thermal initiated preparation of salep-*g*-PMAPTAC is shown in Scheme 1.

After preparation of salep-*g*-PMAPTAC, chlorides are exchanged with hydroxide ions by treatment with KOH solution to form salep-*g*-poly (3-(methacryloylamino) propyl trimethylammonium hydroxide) (salep-*g*-PMAPTAH). After ion exchange process the resulted catalyst was subjected to soxhlet apparatus to remove excess hydroxide ions. Such approaches to preparation of heterogeneous catalysts have some advantages; (1) using degradable biomaterial as support, (2) simple large scale preparation of catalyst, (3) high loading level of immobilization is achieved because of polymer grafting and (4) using water as polymerization medium without the need for toxic solvents.

Fig. 2 shows FT-IR spectra of salep (a), MAPTAC (b), salep-*g*-PMAPTAC (c) and salep-*g*-PMAPTAH (d). The broad band at 3200–3500 cm^{-1} is attributed to stretching vibration of OH groups in the polysaccharide backbone. The peak around 1615 cm^{-1} can be attributed to the stretching band of the C=O group in the glucomannan backbone. Fig. 2b shows FT-IR spectrum of monomer (MAPTAC) with characterization peak at 1641 cm^{-1} corresponded to C=O of amide groups. As seen in Fig. 2c similar peaks with salep and MAPTAC are observed and the results clearly show that PMAPTAC was successfully grafted onto salep backbone. As expected, similar peaks with salep-*g*-PMAPTAC are observed in FT-IR spectrum of salep-*g*-PMAPTAH.

In order to further investigate the grafting of PMAPTAH onto the salep backbone, the TGA curve of the salep-g-PMAPTAH was compared with the TGA curve of salep (Fig. 3). As seen, the TGA curve of salep-g-PMAPTAH is completely different from ungrafted salep. It can be seen that the thermal degradation temperature of catalyst is sufficient for usual catalysis processes.

Surface morphology of salep and salep-*g*-PMAPTAH is shown in Fig. 4. While the SEM image of salep shows uniform structure, the structure of the salep-*g*-PMAPTAH was highly rough. This rough

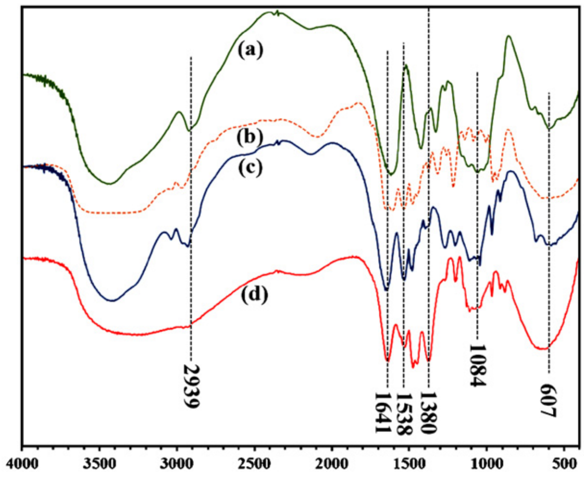
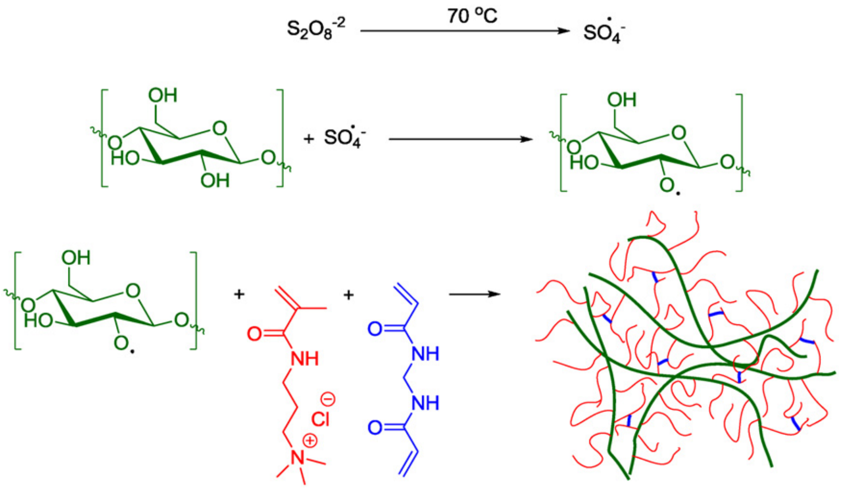


Fig. 2. FT-IR spectra of (a) salep, (b) MAPTAC, (c) salep-*g*-PMAPTAC and (d) salep-*g*-PMAPTAH.



Scheme 1. Proposed mechanism for synthesis of salep-*g*-PMAPTAC.

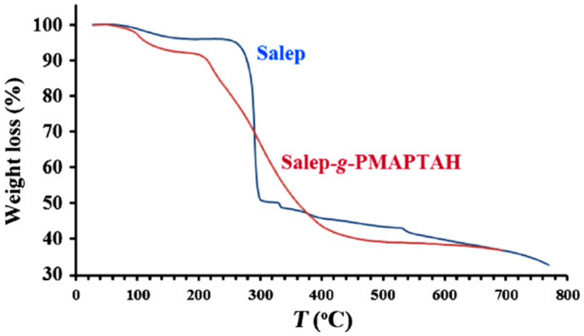
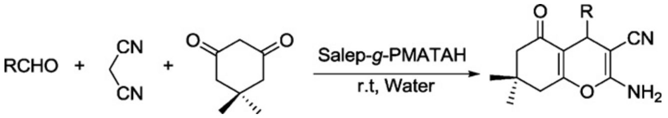


Fig. 3. TGA curves of salep and salep-*g*-PMAPTAH.



Scheme 2. Synthesis of 4*H*-benzo[*b*]pyrans catalyzed by salep-*g*-PMAPTAH.

structure could help to improve the catalytic activity of salep-*g*-PMAPTAH.

The resulted salep-*g*-PMAPTAH was applied in the synthesis of tetrahydrobenzo[*b*]pyrans using three-component reaction between dimedone, aldehydes and malononitrile (Scheme 2).

Table 1 shows optimization of reaction condition using reaction between benzaldehyde, malononitrile and dimedone as a model reaction. As seen in Table 1, in the absence of catalyst, yield of benzopyrene product was only 20% after 3 h at room temperature. The possible catalytic activity of salep was examined by using 50 mg of dissolved salep in water, which gave a 22% yield at room temperature after 2 h. When 20 mg of salep-*g*-PMATAC was charged to the reaction medium, the yield was increased to 57% after 45 min. The possible reason for the observed increase in the yield is the basicity of chloride ion in the salep-*g*-PMATAC matrix. To improve the catalytic activity we exchanged the chlorides with hydroxide ions, and the strong base catalyst was used to perform the reaction. After optimization of amount of catalyst, it was found that using only 5 mg of salep-*g*-PMATAH was enough for 3 mmol scale of reaction in water at room temperature (Entry 7). The reason for high activity of catalyst probably is due to poly ionic nature of surface which makes it easy for penetration of substrate molecules onto the catalyst. Catalyst was used at the same condition in various solvents and the results are shown in Table 1. Although using ethanol–water mixture as reaction solvent gave good yield, but in the view of green chemistry we chose water.

Subsequently, we investigated the generality of the salep-*g*-PMATAH in the synthesis of 4*H*-benzo[*b*]pyrans by the reaction of various aldehydes with malononitrile and dimedone under the optimum conditions (Table 1 entry 7). As seen in Table 2, various aldehydes including hindered aldehydes and highly deactivated aldehydes were also reacted to give excellent yields.

The recyclability of salep-*g*-PMATAH was investigated in the synthesis of benzopyrans by choosing the reaction between benzaldehyde, malononitrile and dimedone as model reaction. Reaction was repeated for five times and after each cycle catalyst was separated and charged into the fresh vessel. The results indicate that no significant loss of catalyst activity was observed even after five cycles (Fig. 5).

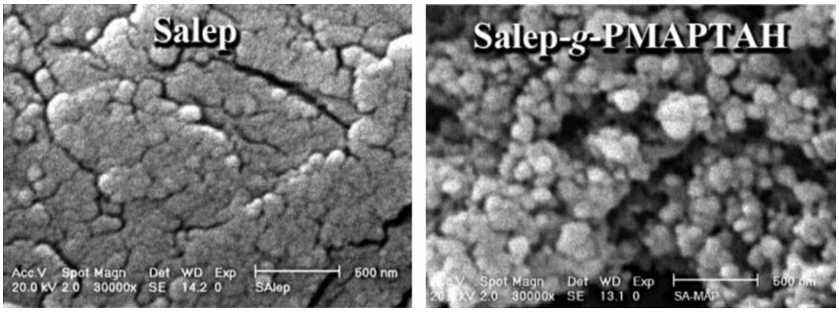


Fig. 4. SEM images of salep and salep-*g*-PMAPTAH.

Table 1
Optimization of reaction condition for synthesis of 4*H*-benzo[*b*]pyrans.[a]

Entry	Catalyst	Amount of catalyst (mg)	Solvent	Time (min)	Yield[b] (%)
1	None	–	H_2O	3 h	20
2	Salep	50	H_2O	2 h	22
3	Salep-*g*-PMATAC	20	H_2O	45	57
4	Salep-*g*-PMATAH	20	H_2O	15	98
5	Salep-*g*-PMATAH	10	H_2O	15	98
6	Salep-*g*-PMATAH	5	H_2O	15	95
7	Salep-*g*-PMATAH[c]	5	H_2O	15	93
8	Salep-*g*-PMATAH[d]	5	H_2O	20	80
9	Salep-*g*-PMATAH	5	H_2O–Ethanol	20	96
10	Salep-*g*-PMATAH	5	$CHCl_3$	20	73
11	Salep-*g*-PMATAH	5	CH_3CN	20	90
12	Salep-*g*-PMATAH	5	EtOH	20	87

[a] Reaction condition: Benzaldehyde (1 mmol), malononitrile (1.2 mmol) and dimedone (1 mmol), solvent volume (5 mL) at room temperature.
[b] Isolated yield.
[c] 3 mmol scale of reaction, same condition.
[d] 5 mmol scale of reaction, same condition

Table 2
Synthesis of 4*H*-benzo[*b*]pyrans by salep-*g*-PMATAH.[a]

Entry	R-CHO	Time (min)	Yield[b] (%)
1	Ph	15	93
2	4-(Cl)Ph	15	96
3	2,4-di(Cl)Ph	20	90
4	4-(Me)Ph	15	92
5	4-(HO)Ph	20	88
6	2-(HO)Ph	20	84
7	4-(MeO)Ph	20	89
8	2-(MeO)Ph	40	80
9	4-(NO_2)Ph	15	96
10	3-(NO_2)Ph	15	97
11	2-(NO_2)Ph	15	91
12	4-(NMe_2)Ph	15	95
13	4-(CN)Ph	15	93
14	Vanillin	40	86
15	Furfural	15	93
16	4-(CHO)Ph	30	89
17	PhCH=CH—	25	85

[a] Reaction condition: Aldehyde (3 mmol), malononitrile (3.6 mmol), dimedone (3 mmol), salep-*g*-PMATAH (5 mg), H_2O (10 mL), room temperature.
[b] Isolated yield.

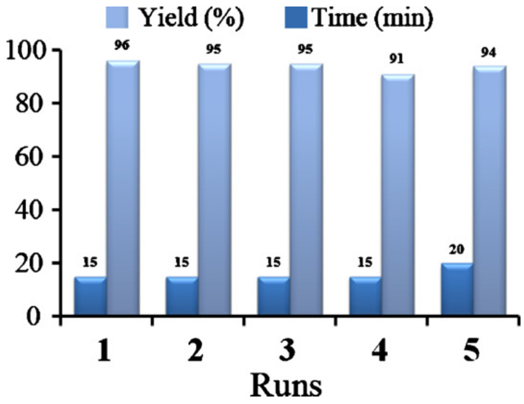


Fig. 5. Recycling experiment.

3. Conclusions

In conclusion we have synthesized a highly loaded organocatalyst using a biopolymer as a means of heterogenizing the hydroxide ions. The resulted catalyst was applied in the synthesis of 4*H*-benzo[*b*]pyrans through a three-component reaction between various aldehydes, malononitrile and dimedone in water at room temperature and the corresponding products were obtained in excellent yields. The method which the catalyst was synthesized was very simple and it could be easily prepared in large scale. We showed that the synthesized catalyst could be separated from the reaction medium and used for five times without significant loss of activity. In the view of green chemistry the present catalyst and protocol could find industrial applications.

4. Experimental

4.1. *General*

The palmate-tuber salep (PTS) was purchased from a supplier in Kordestan, Iran ($M_n = 1.17 \times 10^6$ g/mol, $M_w = 1.64 \times 10^6$ g/mol (high M_w), PDI = 1.39, eluent = water, flow rate = 1 mL/min, acquisition interval = 0.43 s from GPC results). 3-(methacryloylamino)propyl trimethylammonium chloride (MAPTAC, Aldrich) (50 wt% in water) was extracted with ethyl ether five times to remove inhibitors. Methylenebisacrylamide (MBA, Merck) and ammonium persulfate (APS, Merck) were of analytical grade and used without further purification. All other chemicals were also analytical grade.

4.2. *Preparation of salep-g-PMAPTAH*

In a three-necked reactor placed in oil bath and equipped with mechanical stirrer, 1.0 of salep was dissolved in 40 mL deionized water at 80 °C. After the homogenizing of mixture, 4 g of MAPTAC and 0.5 g of MBA were added to solution and the reaction mixture was stirred (200 rpm) for further 15 min. Then the APS (0.015 g dissolved in 5 mL water) was added and after 15 min gel-like product was formed. Reaction was stirred for 45 min and then mixture was cooled down to room temperature. Products were poured into the 200 mL of ethanol for dewatering process and kept there overnight. White precipitates were washed two times with ethanol and dried in vacuum at 50 °C to obtain salep-*g*-PMAPTAC (4.83 g). Titration of resulted salep-*g*-PMAPTAC with AgNO3 (0.01 M) (Mohr method) shows that the 3.19 mmol of chloride ion is presented in the 1 g of catalyst structure. From this, the grafting yield of PMAPTAC onto the salep backbone is found 85.2%.

2 g of powdered (mesh 80) salep-*g*-PMAPTAC was added to 100 mL water and a solution of KOH (30 mL, 3 M) was added and the mixture was stirred for 3 days at room temperature. After completion of ionic exchange process, products were subjected to soxhlet extraction with water for 24 h, and finally dried in vacuum at 50 °C to obtain salep-*g*-PMAPTAH (1.84 g). Standard $AgNO_3$ test shows that there is no significant amount of chloride ions in catalyst (>5%). Titration of catalyst by HCl (0.01 M) shows that the loading of hydroxide ion on salep-*g*-PMAPTAH is 3.01 mmol/g.

4.3. General procedure for synthesis of 4H-benzo[b]pyrans

In a 25 mL round bottom flask, aldehyde (3 mmol), malononitrile or ethylcyanoacetate (3.6 mmol), water (10 mL), salep-*g*-PMAPTAH (5 mg, 5 mol%) was added and mixture was stirred for 5 min at room temperature. Then, dimedone (3 mmol) was added to flask and mixture was stirred for an appropriate time as shown in Table 2 at room temperature. After completion of reaction, monitored by TLC, hot ethylacetate was added and catalyst was filtered and washed two times with ethanol and dried in vacuum at 50 °C. The organic layer was concentrated in vacuum and resulting solid products were recrystallized in ethanol. All compounds gave satisfactory spectral data and they were identical with reported in the literature (Khoobi et al., 2012).

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.carbpol.2012.12.010.

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