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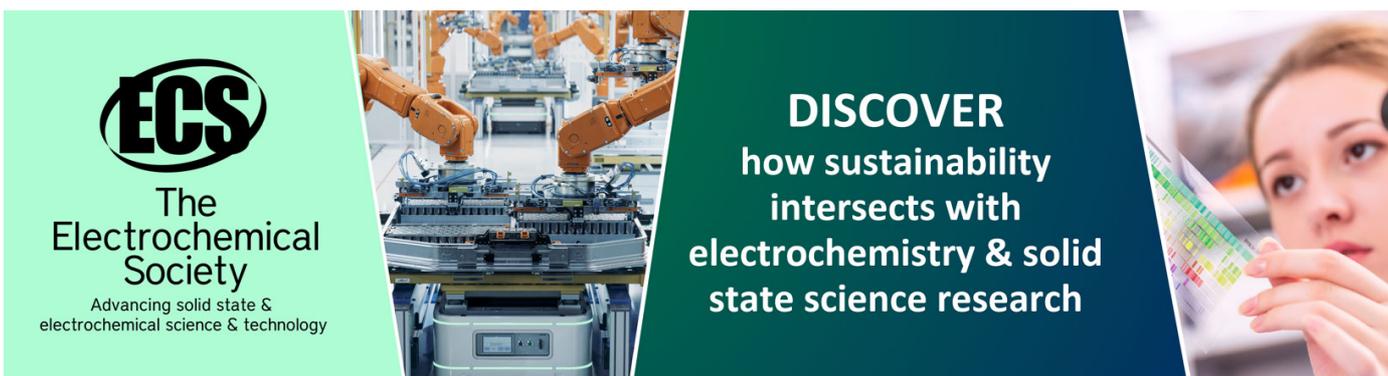
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Polystyrene-supported nickel complex catalysed deprotection of allylic tertiary amine with sodium borohydride

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Abstract. This work represents a green and facile approach for the polystyrene supported nickel catalysed deprotection of allylic tertiary amine. The careful instrumental investigations with XPS, TEM, TGA, XRD and ICP-AES precisely characterized the developed heterogeneous catalyst. Cheap metal, mild reaction conditions, good yields as well as the reusability of the catalyst made this method more environmentally friendly.

1. Introduction

Finding efficient protecting groups and selective deprotection methods is still major motif in organic chemistry [1]. The characteristic of allyl protecting group, such as high selectivity and stability under acidic and basic conditions, which made its wide use of the protection of heteroatoms (nitrogen and oxygen atoms) [2, 3]. The transition metal catalysed methods are the most widely and commonly used for allyl group deprotection. In recent decades, some homogeneous catalysts based on Pd [4, 5], Ru [6], Rh [7], Ni [8] and Co [9] have been used for the deprotection reaction and are capable of obtaining the desired product in high yield. However, the homogeneous catalytic system have drawbacks such as difficulty in separation and recovery of the catalyst which limits its application in the industrial field. Furthermore, the requirement of stoichiometric amounts of nucleophilic compound which act as the allyl group scavenger in the deprotection reaction bring environmental problem. Therefore, it is meaningful that develop a green, economical and simple method to remove allyl groups.

The use of heterogeneous catalysts for organic synthesis has proven to be a good way to minimize waste production and optimize catalyst efficiency. Among those, the heterogenization of homogeneous catalysts onto polymer supports has been well investigated and proven to be more attractive in industrial applications [10]. Polystyrene supported transition metal catalysts are an integral part of this large family and are evoking a renewed interest [11]. They can be easily removed from the reaction mixture, have excellent thermal stability, and can be often reused and regenerated. Polystyrene supported transition metal catalysts has been found to show high catalytic activity towards a wide range of organic reactions, including hydrogenation [12], epoxidation [13], coupling [14, 15] and so on. Even though the efficiency and selectivity of polystyrene supported transition metal, there remains an absence of any reports using them for deallylation of allylic amine.

Herein, we report a new methodologies for the synthesis of a polystyrene supported Ni catalyst that exhibits excellent activity for the deallylation of tertiary amine derivatives with sodium borohydride and



methanol. Reactions were conducted under mild conditions and didn't produce any hazardous waste, which can meet the requirements of environmentally friendly synthesis.

2. Experimental

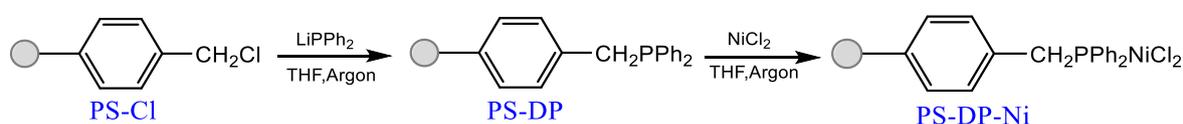
2.1. Materials

Chloromethylated polystyrene and Nickel precursor NiCl_2 were obtained from TCI Development Co., Ltd. Lithium diphenyl phosphate was purchased from Sigma-Aldrich (USA). All the solvents used here were purchased from Sinopharm Chemical Reagent Co., Ltd. Spectrochem.

2.2. Preparation of catalyst

The desired catalyst was prepared cautiously in two step process. Initially, 3.46 g of chloromethylated polystyrene in 30mL tetrahydrofuran was swelled under ultrasound for 1h. Then, swelled chloromethylated polystyrene was mixed with lithium diphenyl phosphate in 45 mL tetrahydrofuran solution in argon atmosphere. Then the solution was continuously stirred under ultrasound until the color of the solution changed from red to colourless. Then resultant mixture was filtered and washed with methanol, ether, toluene and tetrahydrofuran, respectively. Freshly prepared polymer was taken in 50 mL ethanol/toluene mixed solvent (volume ratio 2:1) and continuously stirred under ultrasound for 2 h. The resultant polystyrene was filtered, repeat impregnation and filter for 4 times to remove impure component absolutely and dried in vacuum at 60 °C.

In ethanol/toluene mixed solvent (volume ratio 2:1), the diphenylphosphine methyl polystyrene (PS-DP) (0.5g) and nickel chloride (0.15g) was stirred for 1h in argon atmosphere. The mixture was continuously stirred under ultrasound for another 1h and filtered. The product was washed by ethanol, acetone and ether respectively. Then solid was dried at 60 °C under vacuum. Preparation scheme of the Polystyrene-supported nickel complex is outlined in Scheme 1.



Scheme 1. Preparation of polymer incorporated nickel catalyst.

2.3. General procedure for deprotection of allylic tertiary amine

In a 25 mL glass vial, allylic tertiary amine (1 mmol), PS-DP-Ni catalyst (5% mmol), sodium borohydride (1 mmol) were mixed in 10 mL of methanol at -20 °C. After that the vial was sealed and stirred at room temperature (23–28 °C). The progress of the reaction was monitored by TLC. Upon completion of the reaction, the catalyst was filtered off and the reaction mixture was purified by silica gel chromatography using an appropriate eluent. The solid product was analyzed by NMR, IR and MS.

2.4. Characterization

Transmission electron microscope (TEM) images were performed on FEI Tecnai G2 F30. Ni loading was determined by Thermo ICAP6300 inductively coupled plasma atomic emission spectrometry (ICP-AES). Powder X-ray diffractometer (PXRD) patterns was analyzed by a Bruker D8 Advance X-ray diffractometer equipped with a Cu $K\alpha$ radiation. The scanning 2θ range was 10 – 80°. X-ray photoelectron spectroscopy (XPS) with an AXIS Ultra (Kratos, England) was used to examine the electronic properties of Ni active sites. The binding energies were calibrated using a C1s binding energy of 284.6 eV. Thermal stability of PS-DP-Ni catalyst was measured by a TA-DSC Q2000 differential scanning calorimeter under N_2 atmosphere at a heating rate of 5 °C/min from 30 °C to 600 °C.

3. Results and discussion

3.1. Characterization of the catalyst

3.1.1. *Transmission electron microscope (TEM)*. Image 1(A) and 1(B) are the TEM images of PS-DP-Ni catalyst in two different magnification, where black spherical balls are well dispersed over the whole specimen. These black balls confirm coordination of Ni with polymer supported ligand.

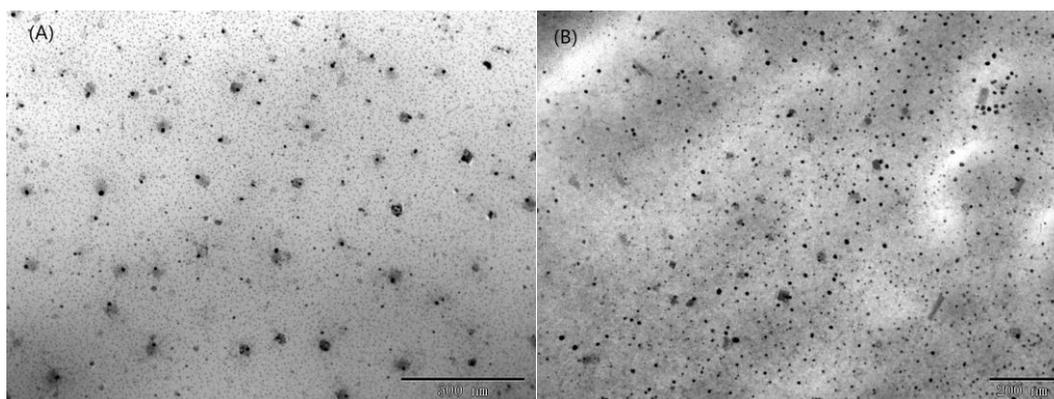


Figure 1. TEM images of polymer supported nickel complex (A) 500 nm, (B) 200 nm

3.1.2. *X-ray photoelectron spectroscopy (XPS)*. The XPS survey spectrum for PS-DP-Ni catalyst is depicted in Fig.2 (A). The spectrum showed a strong existence of C 1s (284.6 eV) core level binding energy peaks along with Ni 2p_{3/2} (860 eV). The Ni 2p_{3/2} spectra of the PS-DP-Ni catalyst were characterized by a main peak with a satellite at higher binding energy (BE). The BE of Ni 2p_{3/2} in PS-DP-Ni of 854.3 eV was close to that of the Ni species in [CH₃PPh₃]₂[NiCl₄]. Its satellite peak due to 860.1 eV (curve-fitted value) also was observed in the XPS spectra shown in Fig. 2 (B).

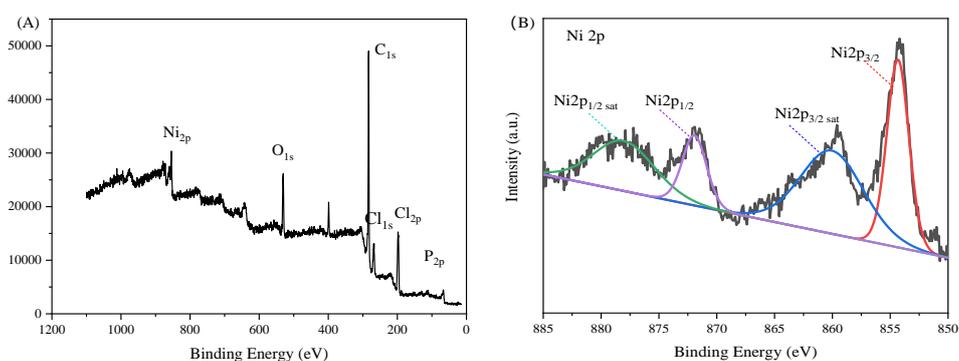


Figure 2. XPS spectrum of the as-synthesized PS-DP-Ni (A) full range (B) Ni 2p

3.1.3. *Powder X-ray diffractometer (PXRD)*. X-ray diffraction measurement was carried out to determine the structure of the polystyrene supported nickel complex (Fig. 3). The broad peaks at 2θ values between 10° and 30° are attributed to the amorphous structure of the polystyrene. It has been observed that the PS-DP show new characteristic peaks at 32° , 45.7° , 56.7° in the XRD measurement than chloromethylated polystyrene. Additionally, after react with NiCl₂, the characteristic peaks at 16.8° and 36° can be found in the patterns of PS-DP-Ni. The loading of Ni in PS-DP-Ni was 0.84wt% by ICP-AES, but in XRD spectrum, no characteristic diffraction peak belonging to Ni were found, indicating that Ni may exist in the form of complexes. This is consistent with the phenomenon that most Ni species is +2 price from XPS, which might be helpful to improve the catalytic performance of the supported catalyst.

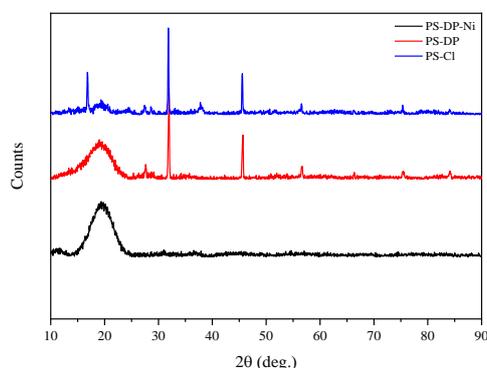


Figure 3. XRD patterns of the PS-Cl, PS-DP and PS-DP-Ni

3.1.4. Thermogravimetric analysis (TGA). Thermal properties of the supported complex was confirmed by TGA over a temperature between 30°C and 600°C at a rate of heating 5°C/min in N₂ atmosphere. A TGA-plot of the chloromethylated polystyrene, PS-DP and PS-DP-Ni catalyst is shown in Fig. 4. The thermal stability of the PS-DP-Ni catalyst is slightly lower compared to PS-DP and chloromethylated polystyrene, which shown that the Ni loading to the surface of the polymer. Additionally, from the TGA curve it can be outlined that thermal degradation of the heterogeneous catalyst occurred after 315°C and the decomposition of the organic structure mainly occurred in one step from 350–480°C. All the above results, suggest that the polystyrene supported nickel complex is thermally stable and can be utilized in a wide range of temperatures.

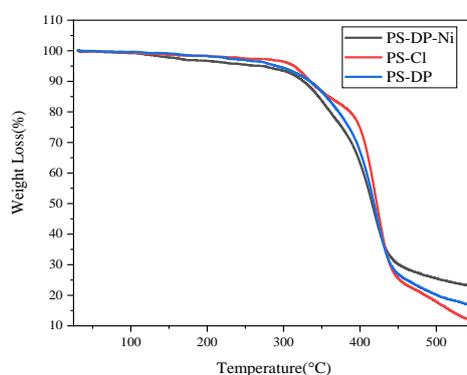


Figure 4. TGA plots of the PS-Cl, PS-DP and PS-DP-Ni

3.2. Catalytic activity of PS-DP-Ni

To evaluate the activity of the polystyrene resin supported nickel complex, it was used in the deallylation of allylic tertiary amine reaction. Initial studies were performed upon the deprotection of N-allyl-N-methylaniline to optimize the reaction parameters including the solvent, catalyst loading and the reaction temperature. The results are summarized in Table 1. The effects of different temperature on the model reaction were first surveyed. It was found that the reaction didn't occur at low temperature while increase the reaction temperature can't improve the yield (Table 1, entry 4). The influence of the solvent on the allyl removal reaction was also investigated. Among the solvents tested, methanol was the most suitable reaction medium for the cleavage of allyl group (Table 1, entry 3). THF was so poor that give the desired product in a yield of 7% (Table 1, entry 6). When the reaction was carried out in toluene or DMF, no conversion of the starting material was observed, probably because the solvents were aprotic solvent (Table 1, entries 7 and 8).

The scope of the N-deallylation reaction under the above-derived optimized reaction conditions was investigated using 0.3mol% of the PS-DP-Ni catalyst in methanol as the solvent at 25 °C. An array of tertiary amine derivatives with different structure were surveyed and the results are outlined in Table 2.

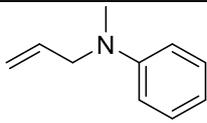
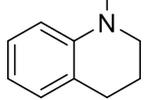
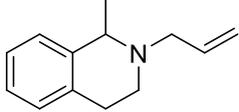
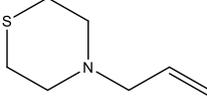
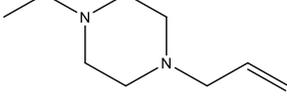
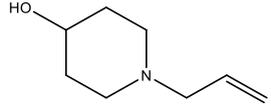
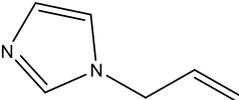
The effectiveness of catalyst was examined with N-allyl-N-methylaniline, 1-allyl-1, 2, 3, 4-tetrahydroquinoline, 2-allyl-1-methyl-1, 2, 3, 4-tetrahydroisoquinoline, 4-allylthiomorpholine, 1-allyl-4-ethylpiperazine. Among them, 4-allylthiomorpholine correspond to the highest yield. However, 1-allylpiperidin-4-ol and 1-allyl-1H-imidazole provides a poor yield of tertiary amine.

Table 1. Optimization of reaction parameter for the .deprotection of allylic tertiary amine

Entry	Solvent	Catalyst (mol % of Ni)	Temp (°C)	Time (h)	Yield ^b (%)
1	MeOH	0.5	-25	24	5
2	MeOH	0.5	0	24	12
3	MeOH	0.5	25	24	52
4	MeOH	0.5	50	24	52
5	EtOH	0.5	25	24	10
6	THF	0.5	25	24	7
7	DMF	0.5	25	24	trace
8	Toluene	0.5	25	24	trace
9	MeOH	0.5	25	16	51
10	MeOH	0.3	25	16	51

^a Reaction conditions: allylic tertiary amine (1 mmol), sodium borohydride(1 mmol), PS-DP-Ni catalyst (0.5% mmol), solvent 10 mL. ^b Determined by GC using n-hexadecane as an internal standard;.

Table 2. Deprotection of allylic tertiary amine.

Entry	Substrate	Time (h)	Yield ^b (%)
1		16	52
2		18	35
3		18	51
4		15	73
5		24	55
6		13	trace
7		9	Trace

^a Reaction conditions: allylic tertiary amine (2 mmol), sodium borohydride (2 mmol), PS-DP-Ni catalyst (0.3% mmol), solvent 10 mL. ^b Isolated yields.

4. Conclusion

In Conclusion, we have developed a novel polystyrene supported Ni (II) complex as an efficient catalyst in the deprotection reaction of various allylic tertiary amine. The allylic tertiary amines are cleaved in the presence of catalyst, sodium borohydride and methanol with moderate to high yields. This heterogeneous catalyst was easily recovered by simple filtration and reused without significant loss of its catalytic activity.

Acknowledgments

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References

- [1] P. Kumar, S.K. Cherian, R. Jain, K. Show, Chemoselective deprotection of N-allylic amines using DDQ. *Tetrahedron letters* 2014, 55 (52), 7172-7176.
- [2] P. Nandi, J.L. Dye, J.E. Jackson, Reductive amine deallyl- and debenzoylation with alkali metal in Silica Gel (M-SG). *Tetrahedron letters* 2009, 50 (27), 3864-3866.
- [3] T. Taniguchi, K. Ogasawara, Facile and Specific Nickel-Catalyzed De-N-allylation. *Tetrahedron letters* 1998, 39, 4679-4682.
- [4] S.Lemaire-Audoire, M. Savignac., J. Pierre Genet, Selective Deprotection of Allyl Amines using Palladium. *Tetrahedron letters* 1995, 36 (8), 1267-1270;
- [5] Z. Dong, S. Pyne, Synthesis of Chiral Allylic Amines via Palladium (0) Catalysed Allylations Of Allylic Carbonates With Chiral Sulfinamide Anions. *Sulfur Letters* 2002, 25 (1), 37-43.
- [6] K. Kajihara, M Arisawa, S. Shuto, A Method for Cleaving an Allyl Protecting Group at the amide nitrogen of peptides by One-pot Olefin isomerization-Oxidation. *The Journal of organic chemistry* 2008, 73, 9494-9496.
- [7] M.J. Zacuto, X. Feng, One-Step RhCl₃-Catalyzed Deprotection of Acyclic N-allyl Amides. *The Journal of organic chemistry* 2007, 72, 6298-6300.
- [8] S. Kamijo, Z. Huo, T. Jin, C. Kanazawa, Y. Yamamoto, Facile Deallylation Protocols for the Preparation of N-Unsubstituted Triazoles and Tetrazoles. *The Journal of organic chemistry* 2005, 70 (16), 6389-6397.
- [9] H. Kumobayashi, S. Akutagawa, S. Otsuka, Metal-assisted terpenoid syntheses. 6. Enantioselective hydrogen migration in prochiral allylamine systems by chiral cobalt catalysts. *Journal of the American Chemical Society* 1978, 100 (12), 3949-3950.
- [10] Y. Zhang, S. N. Riduan, Functional porous organic polymers for heterogeneous catalysis. *Chemical Society reviews* 2012, 41 (6), 2083-94.
- [11] N.E. Leadbeater; M. Marco, Preparation of Polymer-Supported Ligands and Metal Complexes for Use in Catalysis. *Chemical Reviews* 2002, 102 (10), 3217-3274.
- [12] A.S. Sharma; H. Kaur, Microwave assisted hydrogenation of olefins by Pd NPs@polystyrene resin using a gas addition kit: a robust and sustainable protocol. *New Journal of Chemistry* 2018, 42 (23), 18935-18941.
- [13] J. Bartáček, P. Drabina, J. Váňa, M. Sedlák, Recoverable polystyrene-supported catalysts for Sharpless allylic alcohols epoxidations. *Reactive and Functional Polymers* 2019, 137, 123-132.
- [14] B. Movassagh, F. Hajizadeh, E. Mohammadi, Polystyrene-supported Pd(II)-N-heterocyclic carbene complex as a heterogeneous and recyclable precatalyst for cross-coupling of acyl chlorides with arylboronic acids. *Applied Organometallic Chemistry* 2018, 32 (1), e3982;
- [15] A. Ohtaka, A. Sakon, A. Yasui, T. Kawaguchi, G. Hamasaka, Y. Uozumi; T. Shinagawa; O.Shimomura; Catalytic specificity of linear polystyrene-stabilized Pd nanoparticles during Ullmann coupling reaction in water and the associated mechanism. *2018,854,87-93*