Recoverable and Reusable V_2O_5/SnO_2 Catalyst for *N*-Boc Protection of Amines under Solvent-Free Conditions

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ABSTRACT

A convenient N-Boc protection of functionalized amines is described by using heterogeneous V_2O_5/SnO_2 as a recyclable catalyst under solvent-free conditions in shorter reaction time. The V_2O_5/SnO_2 catalyst has been prepared from V_2O_5 using impregnation method followed by calcination at 650 °C for 4 hours. The catalyst was fully characterized by SEM, XRD, FT-IR and UV-DRS techniques. V_2O_5/SnO_2 was found to be stable and efficient catalyst in Boc protection of amines under solvent-free conditions. The catalyst can be easily recovered and reused for ten reaction cycles for protection of amines without any significant loss of activity. The advantage of this protocol in straightforward synthesis of V_2O_5/SnO_2 catalyst and its application of Boc protection of amines in the presence sensitive functional groups, easy workup and excellent yields.

Keywords: Heterogeneous catalyst; V_2O_5/SnO_2; *N*-Boc protection; Solvent-free condition
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INTRODUCTION

Protection of the functional groups, particularly amino group is one of the most fundamental and useful alterations during the synthesis of peptides from amino acids. Protection and deprotection are key procedures in multi-step organic synthesis [1,2], therefore the choice of a method for the functional group transformations depends on high yields of the desired products, ease work-up procedures and shorter reaction times. The great importance of stability toward catalytic hydrogenation and resistance to basic conditions and many other nucleophilic reagents [3], for example the *tert*-butoxycarbonyl (Boc) group has been used widely to mask the amino functionality finding general practice in both organic [4] and peptide [5] synthesis. The *tert*-butylcarbamates are easily introduced as well as readily removed under a variety of conditions [6,7]. Besides, protection of amino groups in amino acids as *N*-Boc derivatives is an important strategy in peptide synthesis, as they can be easily converted into the free amines, and is also useful in Merrifield solid-phase peptide synthesis [8]. A wide range of reagents extensively studied for Boc protection of amines, such as acidic, neutral, and basic reagents.

(a) Basic reagents are NaOH [9], K_2CO_3 [10], $Me_4NOH.5H_2O$ [11], $NaHCO_3$ [12], hexamethyldizilazane sodium salt [13], dimethylaminopyridine [14-17];

(b) Neutral reagents are yttria-zirconia [18], $ZrCl_4$ [19], $Zn(ClO_4)_2.6H_2O$ [20], $LiClO_4$ [21], $Cu(BF_4)_2$ [22], I_2 [23];

(c) Acidic reagents are $H_3PW_{12}O_{40}$ [24], montmorillonite K10 or KSF [25], sulfonicacid-functionalizedsilica [26], $La(NO_3)_3$ [27], thiourea [28], hexafluoroisopropanol [29], and guanidine hydrochloride [30] have been successfully utilised as reagents/catalysts for this transformation. In fact, some of the methodologies effective for Boc-protection of amines, through several difficulties have been associated, for illustration longer reaction times or slower reaction rates, formation of by-products through the catalyzed reactions [15,16], potential hazards (e.g., the high toxicity of DMAP and reagents derived from it). In the case of Lewis acid-catalyzed reactions [31], need to use of excess reagents and the problem of catalyst recovery. For examples, the use of H_2SO_4 at 500 °C to prepare yttria-zirconia, $ZrCl_4$ moisture sensitive and liberates HCl fumes, perchlorate reagents are strong oxidants and explosive in nature. A general *N*-Boc protection reactions of amines have not reported, mainly when amino acids are used as the amine moiety, the protection was unsuccessful. Therefore, a

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new and efficient protocol for synthesis of *N*-Boc amines, amino acids, and peptides, which can widely applicable to a varied substrates in a catalytic process is highly desirable.

On the other hand, heterogeneous acid-based catalysis in organic synthesis has received much attention from the understanding of green and sustainable chemistry because of the possibility of performing environmentally begin chemical processes [32–34]. In this context, V_2O_5/SnO_2 has been used as an acid-based catalyst. It has distinctive properties, particularly in environmental compatibility, low toxicity, reusability, non-corrosiveness, selectivity, stability, and can be used over a prolonged period of time.

Herein, we have disclosed a simple, convenient and eco-friendly approach to the synthesis and characterization of V_2O_5/SnO_2 and its application in catalyzing *N*-Boc protection of amines under solvent-free conditions. The catalyst can be sustainable to recycle and reusable for protection of amines.

EXPERIMENTAL SECTION

Materials
All amines (aromatic and aliphatic) and di-*tert*-butyl dicarbonate were purchased from Aldrich and used without further purification. Silica gel G (ACME) and silica gel finer than 60-120 mesh (ACME) was used for thin layer and column chromatography respectively. All the solvents and reagents were obtained from commercial suppliers. Solvents were purified as per the procedures given in the *"Text book of practical organic chemistry"* by Vogel (6th Edition).

Materials characterization
The IR spectra were recorded on Bruker Infrared model Tensor-27. The ^{1}H NMR spectra were recorded on 400 MHz of Bruker Ultrashield (Avance-III) Nano Bay spectrometers using TMS as internal standard.

Catalyst preparation
The precipitate of $Sn(OH)_2$ was obtained by adding 0.1M of NH_4OH slowly into an aqueous solution of $SnCl_2$ at room temperature with stirring until the pH of the mother liquor reached about 8. The precipitate thus obtained was then washed thoroughly with distilled water until no chloride ions were detected, filtered and dried for 12 hours at 150°C. It was dried and solidified. Dissolved 5 gms of $Sn(OH)_2$ in small amounts of water and taken the 5 wt% of V_2O_5 dissolved in water until a clear solution was obtained, mixed both the solutions and kept it on a water bath until water got evaporates completely and the precipitate was dried to 120 °C and it was calcined in a muffle furnace at 650°C for 4 hours.

Catalyst characterization
The powder X-ray diffraction patterns were recorded on PANalytical B.V Lelyweg 1 7602 EA AlMELO the Netherlands instrument by using nickel filtered CuKα radiation and scintillation counter detector. The scattered intensity data were recorded from 2θ values scanning range from 10 to 800 by scanning at scan speed of 2.000 (deg/min), sampling pitch 0.0200 deg and preset time 60 (sec). Debey-Scherrer equation is used to determine average crystallite size of the particle. Scanning Electron Microscope (SEM) investigations performed on a Hitachi model SEM-EDS S3700N scanning electron microscopy at an applied voltage of 15.0 KV. An FT-IR spectrum of the catalyst was recorded on a SHIMADZU model: A21005002961 spectrometer at ambient conditions. Self-supporting KBr pellets containing the catalyst samples were used to scan the spectra. UV DRS spectra was recorded SHIMADZU UV-3600 for sample preparation using BaSO4.

Initially, we examined the reaction of aniline (1 mmol) and (Boc)$_2$O (1 mmol) in the presence of the 5 wt% V_2O_5/SnO_2 (15 mol%) at room temperature in order to optimize the reaction. The *N*-Boc aniline reaction did not occur in the absence of catalyst, thus, various % of catalyst were examined with 15 mol% giving the high yield (Table 1). Various solvents, including chloroform, toluene, dichloromethane, THF, ethanol, methanol, acetonitrile, 1,4-dioxane, water and without solvent were investigated with the best results achieved based on yields and reaction times under solvent free-condition.

Finally, under the optimized reaction conditions, the generality and scope of this new protocol were explored. A range of functionalized amines were reacted with (Boc)$_2$O to give the corresponding *N*-Boc protected amines (Table 2).

General procedure for the preparation of *N*-Boc amines
The amine (1 mmol) was added to a magnetically stirred mixture of 5 wt% V_2O_5/SnO_2 (15 mol %) and (Boc)$_2$O (1 mmol) at room temperature and stirred for the appropriate amount of time (Table 2) as shown in scheme-1. After completion of the reaction (followed by TLC or GC), the mixture was diluted with EtOAc and filtered to separate the catalyst. Evaporation of the solvent by column chromatography (silica-gel) followed; eluting with EtOAc in n-hexane (5–15%) gave the desired product in good to high yields. In the cases where excess (Boc)$_2$O was used, the products were washed with petroleum-ether or hexane to recover the residual (Boc)$_2$O.

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Table 1: Solvent screening
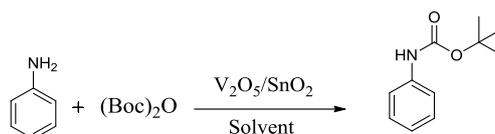
Entry	Solvent	Time (min)	Yield (%)[a]
1	CHCl$_3$	100	95
2	Toluene	90	90
3	CH$_3$CN	90	90
4	Tetrahydrofuran	90	95
5	CH$_2$Cl$_2$	60	95
6	Dioxane	55	90
7	MeOH	30	98
8	EtOH	30	98
9	H$_2$O	10	93
10	**Neat**	**5**	**100**

[a]Yield refers to isolated products
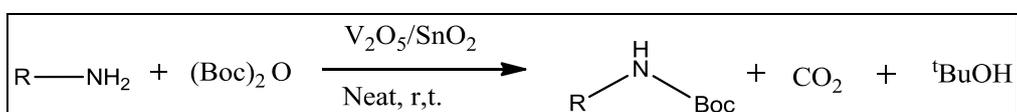
Scheme 1: *N*-Boc protection of amines

Table 2: N-Boc protection of amines in the presence of V$_2$O$_5$/SnO$_2$ under solvent free-conditions

S.no	Reactant	Product	Time (Min)	Yield
1			5	100
2			8	95
3			6	94
4			6	96
5			7	95

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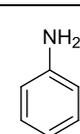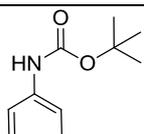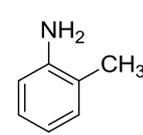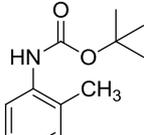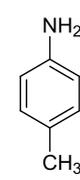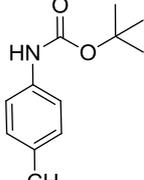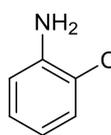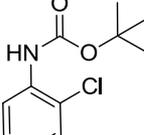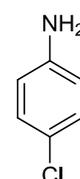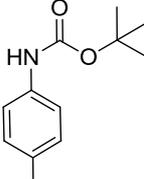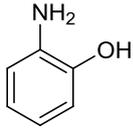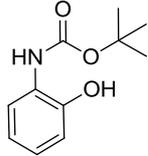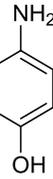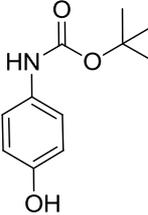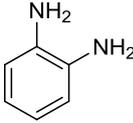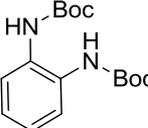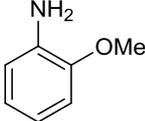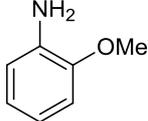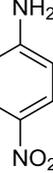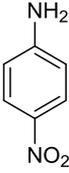
#	Substrate	Product	Time	Yield
6	2-aminophenol (NH₂, OH)	*tert*-butyl N-(2-hydroxyphenyl)carbamate (HN-Boc, OH)	6	92
7	4-aminophenol (NH₂, OH)	*tert*-butyl N-(4-hydroxyphenyl)carbamate (HN-Boc, OH)	10	90
8	benzene-1,2-diamine (NH₂, NH₂)	di-Boc protected (HN-Boc, N(H)-Boc)	8	94
9	2-methoxyaniline (NH₂, OMe)	2-methoxyaniline (NH₂, OMe)	10	93
10	4-nitroaniline (NH₂, NO₂)	4-nitroaniline (NH₂, NO₂)	6	90

Spectral data

tert-butyl N-phenylcarbamate:
^{1}H NMR (400 MHZ CDCl$_3$): δ, ppm =1.52 (s,9H, Boc),6.60 (br s, 1H, NH), 6.81–7.26(m, 4H). IR (Kbr, cm^{-1}): 3034, 2984, 1520, 1369, 1219, 1039, 800, 633

tert-butyl N-(2-methylphenyl) carbamate:
^{1}H NMR (400 MHz, CDCl$_3$): δ, ppm = 1.57 (s, 9H), 6.37 (br s, 1H NH), 7.83 (d, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 2.28 (s, 3H). IR (Kbr, cm^{-1}): 3265, 2974, 1682, 1518, 1257, 1219, 1039, 744.

tert-butyl N-(4-methylphenyl) carbamate:
^{1}H NMR (400 MHz, CDCl$_3$): δ, ppm = 1.52 (s, 9H, Boc), 6.57 (br s, 1H, NH), 2.30 (s, 3H, CH$_3$), 7.09 (d, *J* = 7.6 Hz, 2H), 7.25 (d, *J*=7.6 Hz, 2H). IR(Kbr,cm^{-1}): 3342, 2989, 1650, 1520, 1369, 1039,800,663.

tert-butyl N-(2-chlorophenyl) carbamate:
^{1}H NMR (400 MHz, CDCl$_3$): δ, ppm = 1.52 (s, 9H, Boc), 6.57 (br s, 1H, NH), 7.83 (d, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.17 (d, *J* = 7.4 Hz, 1H). 7.03 (t, *J* = 7.4 Hz, 1H), IR (Kbr, cm^{-1}): 3421, 2976, 1730, 1514,1150,1043, 750.

tert-butyl N-(4-chlorophenyl) carbamate:
^{1}H NMR (400 MHz, CDCl$_3$): δ, ppm = 1.49 (s, 9H, Boc), 6.74 (br s, 1H, NH), 7.21 (d, *J*=8.4 Hz, 2H), 7.30 (d, *J*=8.4 Hz, 2H). IR (Kbr,cm^{-1}): 3362, 2980, 1795, 1689, 1504, 1364,1240,1145,806.

tert-butyl N-(2-hydroxyphenyl) carbamate:
^{1}H NMR (400 MHz, CDCl$_3$): δ, ppm =1.53 (s, 9H, Boc), 6.71 (br s, 1H, NH), 6.85 (t *J*= 8.0 Hz, 1H), 6.96 (d *J*=8.0 Hz, 1H), 7.03 (t, *J*= 8.0 Hz, 1H), 7.10 (d, *J*=8.0 Hz, 1H), 5.5 (s, 1H, OH). IR (Kbr, cm^{-1}): 3254, 2966, 1795, 1687, 1527, 1363, 1248, 1155, 864, 793.

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tert-butyl N-(4-hydroxyphenyl) carbamate:
^{1}H NMR (400 MHz, CDCl$_3$): δ, ppm = 1.53 (s, 9H, Boc), 6.71 (br s, 1H, NH), 6.93 (d, *J* =8.4 Hz, 2H), 6.70 (d, *J* =8.4 Hz, 2H). 5.5 (s, 1H, OH). IR (Kbr, cm^{-1}): 3369, 2967, 1620, 1521, 1369, 1219, 814.

tert-butyl N-(2-aminophenyl) carbamate:
^{1}H NMR (400 MHz, CDCl$_3$):δ, ppm = 1.49 (s, 18H, Boc), 6.89 (br s, 2H, NH), 7.06 (d, *J* =7.4 Hz, 2H), 7.43 (d, *J* =7.5 Hz, 2H). IR (Kbr,cm^{-1}): 3397, 3277,2916,1689 1514,1257, 1153, 1043, 750.

tert-butyl N-(2-methoxyphenyl) carbamate:
^{1}H NMR (400 MHz, CDCl$_3$): δ, ppm =1.50 (s, 9H), 3.75 (s, 3H), 6.56 (s, 1H, NH), 6.81–7.26 (m, 4H). IR(Kbr, cm^{-1}): 3433, 2978, 1734,1520, 1367, 1124, 1039,750.

tert-butyl N-(4-nitrophenyl) carbamate:
^{1}H NMR (400 MHz, CDCl$_3$):δ, ppm = 1.52 (s, 9H, Boc), 6.95 (br s, 1H, NH), 7.52 (d, *J*= 9.2 Hz, 2H), 8.16 (d, *J*=9.2 Hz, 2H). IR(Kbr cm^{-1}): 3470, 3344, 2986 1657, 1599, 1492,1354,1217,1071,837.

<div align="center">

RESULTS AND DISCUSSION

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In figure1 shown the FT-IR spectrum of Support SnO$_2$ and V$_2$O$_5$/ SO$_2$ exhibits three shoulders at 1738, 1366 and 1218 cm^{-1}.The 2971 cm^{-1} band intensity corresponding to stretching vibration of hydroxyl groups decreased strongly and better resolved bands are observed clearly at 686 cm^{-1} which were characteristic of crystalline SnO$_2$. From this, it was concluded that, because of calcination, condensation of hydroxyl groups of Sn(OH)$_4$ occurred, leading to a crystallized sample of the species

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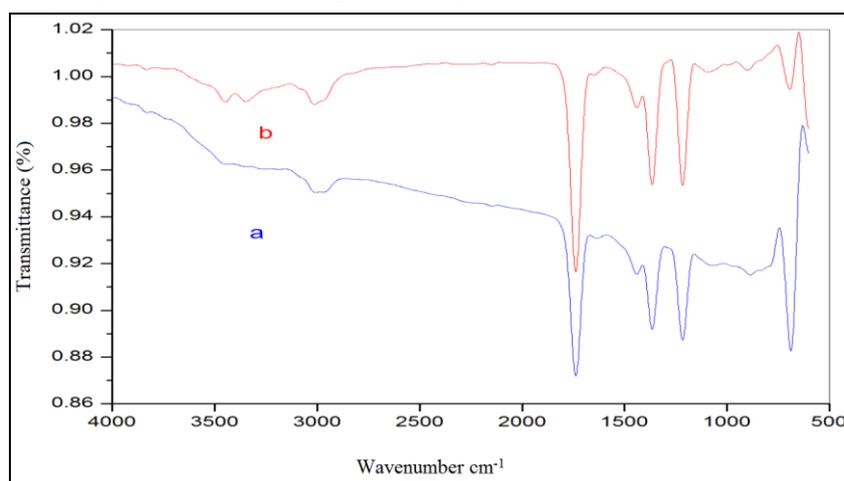
Figure 1: (a) IR spectrum of SnO$_2$ (b) IR spectrum of V2O5/SnO2

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The X-ray diffraction patterns of SnO$_2$ and vanadium promoted SnO$_2$ samples calcined at 923 K are presented in figure 2. In the figure three intense peaks appeared at 2θvalues (26^0,33^0, 37^θ,) can be associated with (100) (101) (200) *hkl* planes respectively it indicates vanadium promoted SnO$_2$ is in tetra gonal phase. (JCPDS card 41-1445) no. The average particle size was calculated using the Scherer equation D = 0.9λ/β cosθ where D is the average crystalline size λ is x ray wave length β is (FWHM) diffraction line θ is the diffraction angle. The average crystalline size is 50 nm for pure SnO$_2$ and vanadium promoted SnO$_2$ but do not have the same activity in the *N*-Boc protection of amines. Derivatives were obtained in 5-12 mins. When vanadium promoted SnO$_2$ is used where as pure stania was totally inactive. Incorporation of vanadium into the stania lattice alters the bulk and surface properties of stania. This higher activity of vanadium promoted SnO$_2$ may be due to lattice defects created by promoter vanadium and notable redox properties.
SEM photographs of both the catalysts were given. There was no much difference in SEM photographs of SnO$_2$ and vanadium promoted SnO$_2$ catalysts indicating small change in structure of SnO$_2$ by incorporating vanadium atom. It was observed that particles were uniformly distributed all over the surface and spherical in shape. This result was agreement with XRD results of both the catalysts having tetragonal phase with same crystallite size. Higher activity for vanadium promoted SnO$_2$ catalyst was due to uniform distribution of spherical particles all over the stania lattice and creating lattice defects by changing surface and bulk properties to the small extent. Average crystallite size of the particles was observed to be same in both the samples from SEM photographs also.

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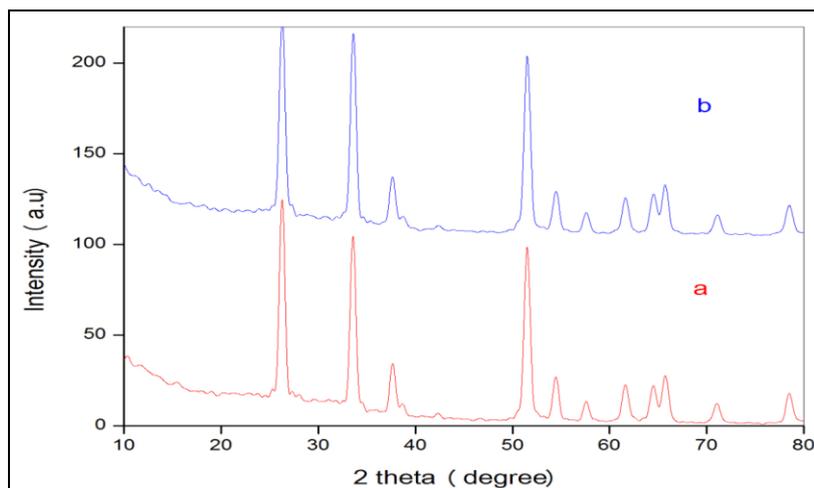
Figure 2: X-ray diffraction patterns of (a) Pure SnO2 (b) V$_2$O$_5$/SnO$_2$
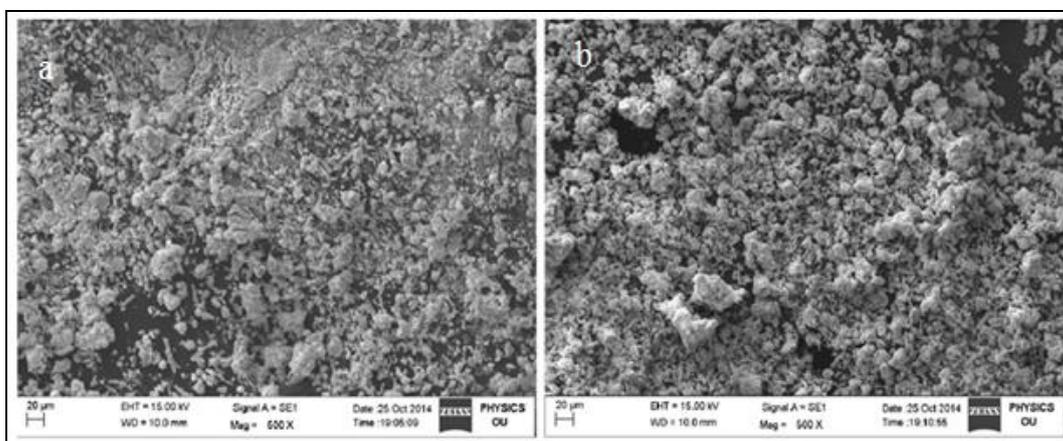
Figure 3: (a) SEM image of Pure SnO2 (b) SEM image of V2O5/SnO2

In figure 4 (a) EDX spectrum of pure SnO$_2$ and V$_2$O$_5$/SnO$_2$ is shown. Pure SnO$_2$ exhibits peaks corresponding to Sn and O whereas V$_2$O$_5$/SnO$_2$ exhibits peaks corresponding to V, Sn, O indicating incorporation of vanadium into SnO$_2$.
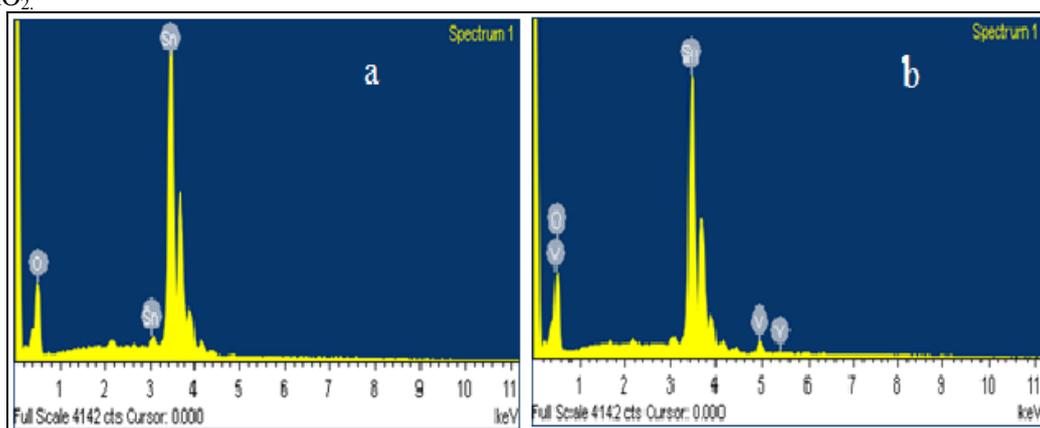
Fig.4 (a) Pure SnO$_2$; (b) V$_2$O$_5$/ SnO$_2$

UV-vis diffuse absorption edge of SnO$_2$ is obtained from the plots of absorbance against wavelength. The interception of the tangent on the descending part of the absorption peak of the wavelength axis gives the value of diffuse absorption edge(nm). The UV–VIS DRS of SnO$_2$ and V$_2$O$_5$/SnO$_2$were presented in Figure 5 The absorption peak of SnO$_2$ can be easily found in the visible region. The wavelength for pureSnO$_2$ was about 420 nm, corresponding to a band gap of2.95 eV, the band gap of the material can be estimated by using the formula:

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$Eg=1240/\lambda$, where Eg is the band gap energy and λ is the wavelength of the absorption edge. A red shift was observed for the V_2O_5/SnO_2 the absorption edge shifted to 550 nm (2.25eV). It may be due to the impregnation of V_2O_5
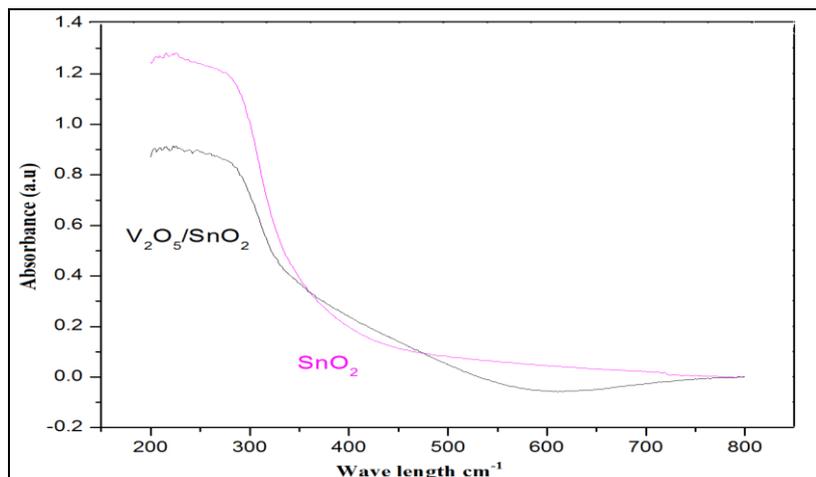
Figure 5: UV-DRS Spectra of SnO₂ & V₂O₅/SnO₂

For practical applications of heterogeneous systems, catalyst recovery is an important aspect. The reusability of the catalyst in the reaction of aniline and $(Boc)_2O$ under solvent-free condition at room temperature in 5 min was studied. In this procedure, after completion of each reaction, ethanol was added to the reaction mixture and shaken and centrifuged for a few minutes to dissolve the product. Then, the clear liquid was separated, and the residue was dried at 50 °C. A new reaction was then performed with fresh aniline under the same condition. The catalyst could be reused at least 10 times without any change in its activity (Figure 5).
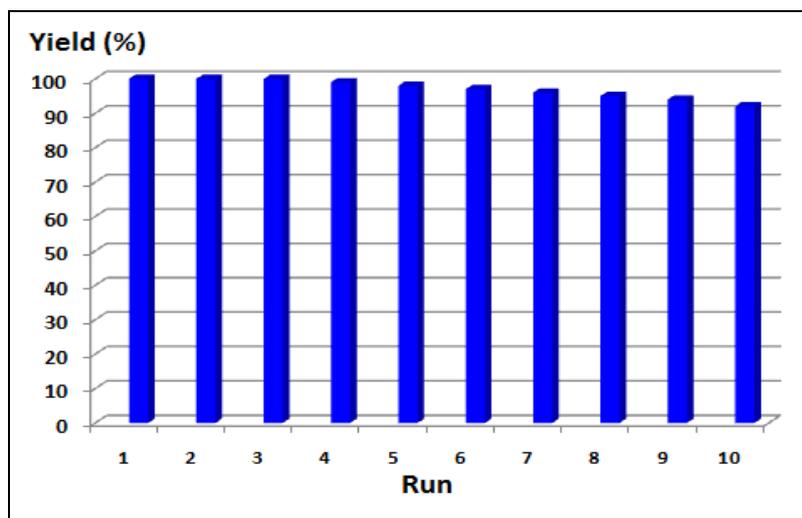
Figure 6: Yield comparison bar chart

Figure 6 Catalytic activity of 5% V_2O_5/SnO_2 in 10 cycles for *N*-Boc protection of aniline Furthermore, structural elucidation of V_2O_5/SnO_2 was performed in detail using X-ray diffraction (XRD) technique after use for five runs. XRD results for the catalyst (Figure 6) showed an ordered mesostructure in large domains with no distinct defects observed for these reaction conditions. Three well-resolved diffraction peaks in the 2θ range of 0.8–2° were observed for V_2O_5/SnO_2 as an organic– inorganic hybrid material. However, the ordered structure of V_2O_5/SnO_2 remained intact, as supported by the XRD results. The patterns feature distinct Bragg peaks in the 2θ range of 20–50°, which can be indexed to (1 0 0), (1 1 0), and (2 0 0) reflections of a two-dimensional hexagonal structure of V_2O_5/SnO_2 material. The presence of these peaks indicates that the crystallographic ordering of the mesopores in V_2O_5/SnO_2 was retained after its use as a catalyst in five runs.

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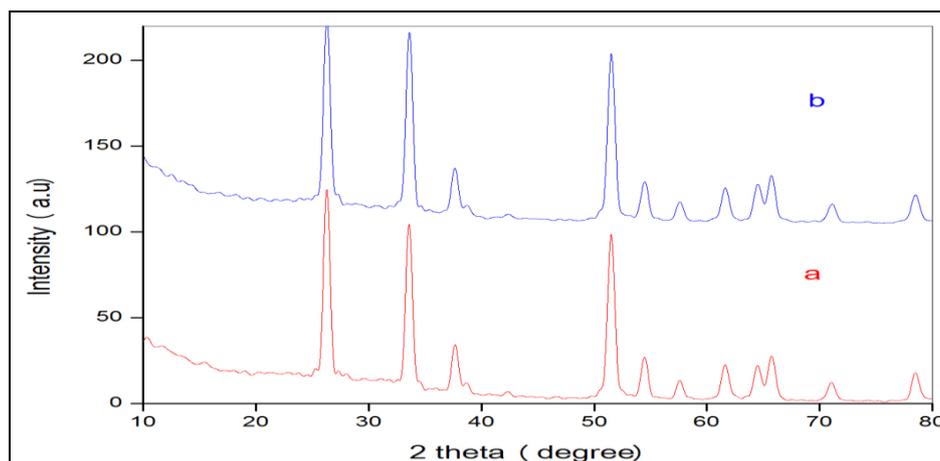
Figure 7: XRD spectrum of V$_2$O$_5$/SnO$_2$: a) fresh b) after use in five runs

CONCLUSION

In conclusion, we have developed a simple method for *N*-Boc protection of amines using V$_2$O$_5$/SnO$_2$ catalyst. The reactions proceeding smoothly under solvent-free conditions and *N*-Boc protection of amines were obtained in good to excellent yields. This heterogeneous catalysis offers the following advantages: (i) ease to prepare the V$_2$O$_5$/SnO$_2$ catalyst, low cost, availability and reusability of the catalyst, (ii) avoid to use of base-, metal-, or acid-reagents, (iii) relatively short reaction times and (iv) clean workup and no side reactions. The catalyst can be easily recovered and reused for ten reaction cycles for protection of amines without considerable loss of activity and yields.

ACKNOWLEDGMENTS

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