

Synthesis and Application of Polycarbosilane Supported Manganese Ions as Catalyst in Mannich Reaction

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ABSTRACT: Polycarbosilane (PCS) with highly crosslinked structure and high surface area was synthesized by the polycondensation reaction between trimethoxyvinylsilane and trichloromethylsilane. The reaction was conducted in the presence of sodium metal. Manganese ion was supported on PCS. The immobilization of transition metal ions to polymer support leads to a number of advantages over homogeneous catalyst, *viz* easy product recovery, increased selectivity, etc. The catalytic activity of PCS supported manganese ion was studied by considering three-component Mannich reaction. Reaction with diverse sets of aldehydes, amines, and ketones was examined. PCS-supported manganese ion catalyst has been prepared for the first time and used successfully in Mannich reaction. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Transition metals have important role as catalysts in various organic reactions. Homogeneous catalysts are often used for these purposes because of their high activity and selectivity. However, they are more expensive and usually cannot be recovered and reused. The immobilization of transition metal ions to heterogeneous supports leads to a number of advantages, like ease of separation, handling, recovery, and regeneration.¹

Polycarbosilane (PCS) is a rather neglected class of organic–inorganic hybrid polymer. Considerable interest has been focused on it recently.^{2–8} PCS represents structural hybrid between polysilanes and polyolefines, a combination of low T_g s and high synthetic versatility similar to that of such inorganic polymers and with good chemical backbone stability as polyolefines. The introduction of metal ions into the polymer creates functional macromolecular and supramolecular materials, which combine processability with interesting redox, preceramic, and catalytic properties.^{9–19}

The Mannich reaction is an important carbon–carbon bond forming reaction in organic synthesis and one of the widely used chemical transformations for constructing β -amino ketones and other β -amino carbonyl compounds, which in turn are important synthetic intermediates for various pharmaceuticals and natural products.^{20–22} There are lots of catalysts reported for the Mannich reaction. Most of these methods have drawbacks, like requirement of large amount of catalyst, expensive reagents or catalyst, long reaction time, and low yield.

However, to the best of our knowledge, there are no reports on the use of PCS as a support for heterogeneous catalysts. In this article, we describe the first example of the manganese ion incorporated PCS catalysts, their preparation, and application in Mannich reaction.

EXPERIMENTAL

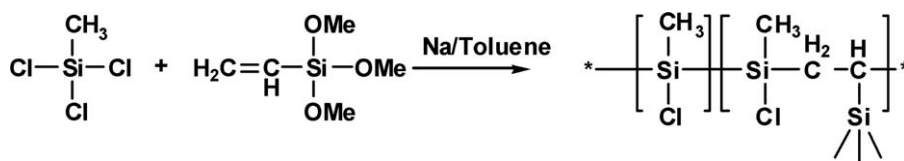
Materials

Monomers, trichloromethylsilane, and trimethoxyvinylsilane, were purchased from Sigma-Aldrich (Bangalore, India). All the other chemicals were purchased from different local suppliers and were used as received. All the solvents were purified according to standard procedures.²³ Toluene was dried initially with anhydrous CaCl_2 , followed by sodium wire and was finally distilled. Acetone was dried with Type 4A Linde molecular sieve, hexane was dried with sodium wire, ethyl acetate was initially dried with anhydrous MgSO_4 and further dried with P_2O_5 before distillation. Absolute ethanol was used without any further purification.

Characterization

FTIR spectra were recorded on JASCO model 4100 FTIR spectrometer as KBr pellets. ^{29}Si -CP-MAS (cross polarized magic angle spinning) NMR spectra and solid state ^{13}C -NMR spectra were obtained from NMR Research Centre, IISc, Bangalore and National Chemical Laboratory, Pune. Thermogravimetric analysis (TGA) was done on Perkin-Elmer Diamond model

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Scheme 1. Synthesis of PCS.

thermogravimetry/differential thermal analysis (TG/DTA) system using platinum as standard. Samples were heated under nitrogen atmosphere from 50 to 1000°C at a rate of 20°C/min. The X-ray diffraction (XRD) analysis was performed using Rigaku (D-MAX Cu-K α) X-ray photometer. The sample was scanned over the range of 20–90° angles with an increment of 0.05° angle and with the rotation speed of 5°/min (SAIF-CUSAT). Surface area and porosity were measured using Micromeritics TriStar 3000 V6.07 A surface area analyzer. The metal ion concentration was estimated using Thermo Electron Corporation atomic absorption spectrometer (AAS). $^1\text{H-NMR}$ spectra were recorded on Bruker 400 MHz instrument with TMS as the internal standard in CDCl_3 (SAIF-CUSAT). In the catalytic activity study, each of the products was analyzed for purity by high performance liquid chromatography (HPLC) on Shimadzu CLASS VP Ver 6.1. Column: Phenomenex Luna 5u C18 (2) 100 Å. Solvent ratio ($\text{CH}_3\text{OH} : \text{H}_2\text{O}$) was 75 : 25 with a run time of 30 min. The Flow rate, detector wavelength, and the temperature were 1 mL/min, 254 nm, and 28°C, respectively.

Synthesis of PCS

PCS was prepared by Wurtz-type coupling of monomers in the presence of sodium metal.^{2,8,24} In a 250-mL round bottom flask, sodium metal (2.5 g, 108.75 mmol) in anhydrous toluene (50 mL) was refluxed and stirred vigorously to make a suspension. A mixture of trichloromethylsilane (6.4 mL, 54.375 mmol) and trimethoxyvinylsilane (8.13 mL, 54.375 mmol) was added drop wise with care. The reaction was highly exothermic. After the addition of monomers, the reaction mixture was refluxed for 12 h. The whole process was performed under nitrogen atmosphere. The reaction mixture was cooled to room temperature and the suspension was filtered, washed with methanol, and dried. Yield: 47%.

The PCS was characterized by halide estimation, FTIR spectroscopy, $^{29}\text{Si-CP-MAS}$ NMR, solid state $^{13}\text{C-NMR}$ spectroscopy, TG-DTA, XRD, and surface area analysis.

Estimation of Chlorine Capacity of the Polymers. Chlorine analysis was done by the modified Volhard's method. The PCS (250 mg) was heated with pyridine (2.5 mL) for 1 h at 100°C, and the suspension was diluted with acetic acid : water (1 : 1) (25 mL). The halide was displaced by the addition of con. HNO_3 (5 mL) and precipitated with a measured excess of standard AgNO_3 solution. AgCl that was formed was coated with toluene, and the excess AgNO_3 was back titrated with standard NH_4SCN solution, using ferric alum [$\text{FeNH}_4(\text{SO}_4) \cdot 12\text{H}_2\text{O}$] as indicator. A red color due to the formation of $\text{Fe}(\text{SCN})_3$ indicated that an excess of SCN^- was present and that the endpoint was reached.

Preparation of Hydroxyl Substituted PCS

The PCS was treated with water to substitute chloro substituent with hydroxyl groups. The reaction was conducted in a round bottom flask; the PCS was refluxed in water for 24 h. It was cooled and the suspension obtained was filtered and dried.

Preparation of PCS Supported Manganese Ion (Mn-PCS)

PCS (1 g) was taken as dispersion by stirring for 12 h in toluene (10 mL). Manganese acetate (1.47 g, 6 mmol) as a solution in ethanol was added drop wise to the swollen PCS and was stirred for 12 h under reflux condition. The reaction mixture was cooled, filtered, and washed with methanol in a soxhlet extractor and dried under vacuum.

Mn-PCS was characterized by FTIR, $^{29}\text{Si-CP-MAS}$ NMR, $^{13}\text{C-CP-MAS}$ NMR spectroscopy, TG-DTA, AAS, and surface area analysis.

Catalytic Activity Study

Mannich reaction was considered as the model reaction to study the catalytic activity of Mn-PCS. The optimum quantity of the catalyst was found out first and the catalytic activity was generalized by conducting the reaction with diverse sets of substrates. General procedure for Mannich reaction: to a mixture of ketone (1 equiv.) and aldehyde (1 equiv.), amine (1 equiv.) was added. To this mixture, Mn-PCS (10 mol %) was added and stirred at room temperature. The reaction was monitored by thin layer chromatography (1 : 4, EtOAc : hexane). On completion of the reaction, the reaction mixture was diluted with ethanol and the catalyst was removed by filtration. Solvent was removed in a rotary flash evaporator and the precipitated solid was recrystallized from acetone. The purity of the products was analyzed with HPLC (Column: C18) in a solvent ratio ($\text{CH}_3\text{OH} : \text{H}_2\text{O}$) of 75 : 25 and the products were purified with column chromatography on silica gel using hexane : EtOAc (20 : 1) as eluent. The products were known compounds and were identified by comparing the spectral data (FTIR, $^1\text{H-NMR}$ spectra, and mass spectra by LCMS) and melting points with those reported.

Recycling of Catalyst. The catalyst can be removed from the reaction mixture by simple filtration. It was washed thoroughly with methanol, acetone, and dried under vacuum for 24 h. The reuse of Mn-PCS as a catalyst for Mannich reaction was studied by conducting reaction with benzaldehyde, aniline, and acetophenone in the presence of recycled Mn-PCS for three more cycles.

RESULTS AND DISCUSSION

Synthesis of PCS

Trimethoxyvinylsilane and trichloromethylsilane were used as the monomers for the preparation of PCS. The sodium metal and monomers were taken in 2 : 1 : 1 ratio. The

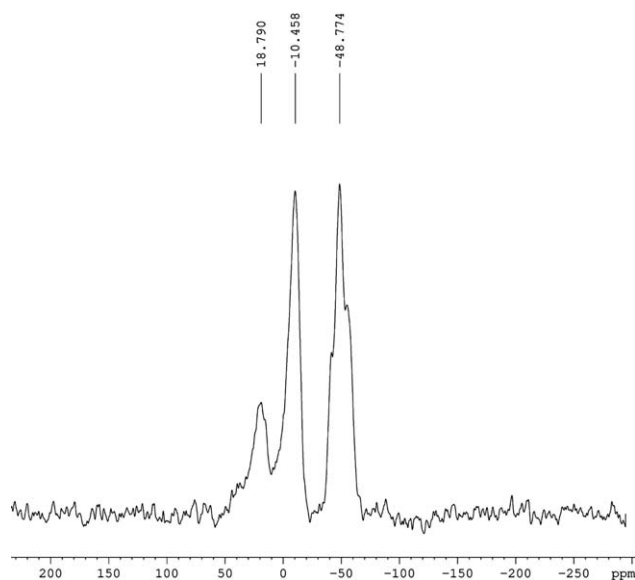


Figure 1. ^{29}Si CP-MAS NMR spectrum of PCS.

polymerization was performed in toluene under nitrogen atmosphere (Scheme 1).

The PCS was characterized by FTIR spectroscopy, ^{29}Si -CP-MAS NMR, solid state ^{13}C -NMR spectroscopy, XRD, TG-DTA, and surface area analysis.

The quantitative estimation of chlorine in the PCS was done by the modified Volhard's method.²⁵ The result showed that 4.10 m equiv./g chlorine was present in the PCS.

The FTIR spectrum of the polymer has the corresponding peaks of the PCS.²⁶ Peaks at 1453, 1270, 1082, and 783 cm^{-1} are clearly seen in the spectrum which corresponded to the CHSiCH_3 and SiC . The spectrum showed a peak at 2929 cm^{-1} which corresponded to the C-H stretching, 1635 and, 1453 cm^{-1} due to Si-CH_3 stretching, 1270 cm^{-1} corresponding to Si-CH_3 deformation, 1082 cm^{-1} due to CH_2 wagging in $\text{Si-CH}_2\text{-Si}$ bond, and 783 cm^{-1} due to Si-CH_3 wagging. The band at 1032 cm^{-1} seen as superimposed on 1082 cm^{-1} was due to the Si-O stretching.

^{29}Si CP-MAS NMR spectrum of the PCS is presented in Figure 1. Spectrum gives a clear idea about the structure of the PCS. Peaks are mainly distributed in two regions. Peak around -10.45 ppm corresponds to $\text{CH}_3\text{Si}(\text{CH}_2)_2$ linkage and -48.77 ppm peak is of Si-Si linkage formed by the head to head polymerization of the monomers. A small peak at 18.79 ppm corresponds to Si-O-Si linkage which might be formed by the oxidation of the polymer.

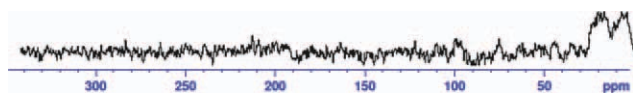


Figure 2. Solid state ^{13}C -NMR spectrum of PCS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

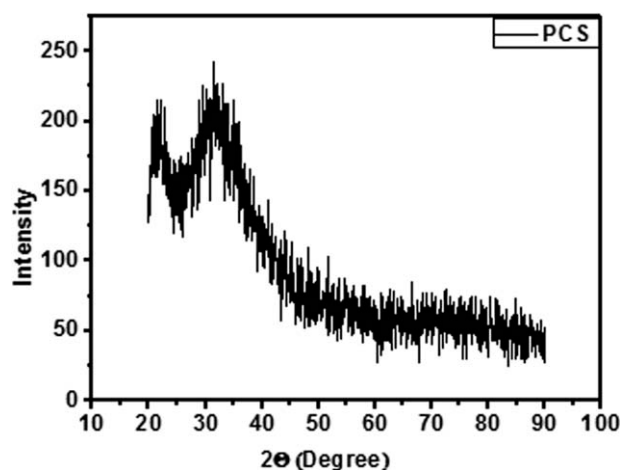


Figure 3. XRD pattern of PCS.

Figure 2 presents the solid state ^{13}C -NMR spectrum of PCS. It exhibits two major broad peaks around 6 and 20 ppm, which are mainly assigned to the signal of SiSiCH_3 units and $\text{CH}_2\text{-CH}_2$, respectively. The absence of signal around 60 ppm indicates the absence of unreacted alkoxy group in the prepared polymer.

The XRD pattern of the PCS (Figure 3) clearly reveals its amorphous nature, which can be explained due to its highly cross-linked structure.

In the TGA curve (Figure 4), 3% weight loss below 300°C is attributed to the vaporization of low molecular weight oligomers and physically adsorbed water from the polymer surface. From 300 to 800°C, the main weight loss indicates that the polymer undergoes Kumada rearrangement and releases gaseous products, such as, methane and hydrogen during the conversion of the Si-Si bond to Si-C bond. No obvious weight loss was observed in the range of 800–1000°C. The weight loss of the polymer at 1000°C was found to be only 14%. High temperature stability is attributed to substantial crosslinking in PCS.²⁷

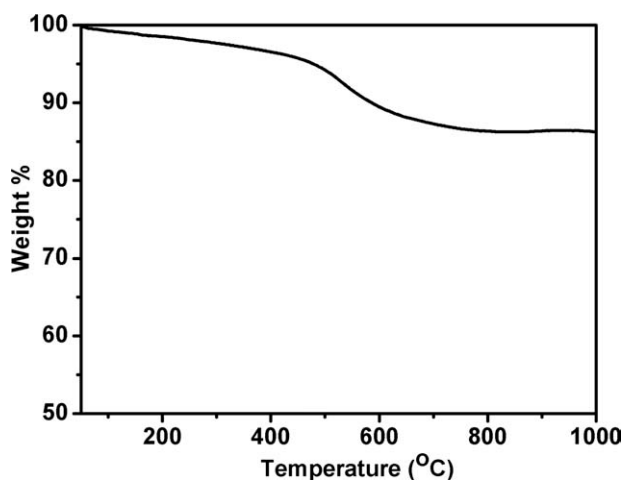
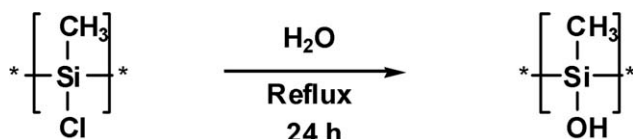


Figure 4. TGA of PCS.



Scheme 2. Conversion of chloro groups of PCS to hydroxyl groups.

Preparation of Hydroxyl Substituted PCS

To substitute the chloride groups with hydroxyl group, the PCS was refluxed in water (Scheme 2).

The hydroxyl group substitution was confirmed by taking FTIR spectrum of the product. The infrared spectrum showed a peak around 3448 cm^{-1} .

Preparation of PCS Supported Manganese Ion

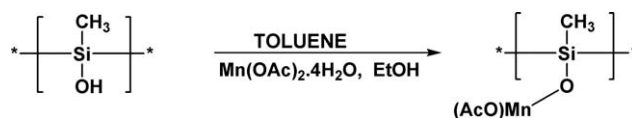
The polymer was allowed to swell in toluene. Ethanolic solution of manganese acetate was added to it and stirred at reflux condition for 12 h and washed in a soxhlet with methanol and dried (Scheme 3).

Mn-PCS was characterized by FTIR, ^{29}Si -CP-MAS NMR, ^{13}C -CP-MAS NMR spectroscopy, TG-DTA, surface area analysis, AAS, and magnetic susceptibility measurement.

The metal content of Mn-PCS was determined using AAS technique. The AAS result showed that 4.35 m equiv./g manganese ion was present on the PCS.

The magnetic susceptibility of Mn-PCS was measured. The result showed that Mn-PCS had a magnetic susceptibility value of 5.40 B.M. From the magnetic susceptibility measurement results, it is clear that Mn-PCS showed paramagnetic nature and possessed five unpaired electrons.

In the infrared spectrum of Mn-PCS, a peak around 960 cm^{-1} was observed and the peak at 3448 cm^{-1} corresponding to Si—OH had diminished intensity.



Scheme 3. Introduction of manganese ion to PCS.

EPR Spectroscopy. The solid state EPR spectrum of Mn-PCS is shown in Figure 5. At an operating frequency of 9450 MHz, the Mn-PCS exhibited six hyperfine splitting with g value centered at 2.02. The six hyperfine splitting due to electron–nuclear spin coupling is observed corresponding to the interaction of the electron spin with the nuclear spin (Mn, $I = 5/2$). Here, six hyperfine splitting lines corresponding to $m_I = +5/2, +3/2, +1/2, -1/2, -3/2,$ and $-5/2$ are observed. The observed g value close to the free electron value is suggestive of the absence of spin orbit coupling in the ground state. The separation between two EPR signals gives a measure of “ A ,” hyperfine splitting constant. The magnitude of “ A ” is determined by the nuclear magnetic moment and density of unpaired electron. $g_{\text{iso}} = 2.02, A_{\text{iso}} = 11.01 \text{ mT}$. This indicates an octahedral geometry around the manganese (II) ion. The broad signal in the EPR spectrum is because of the amorphous nature of the PCS support.

^{29}Si -NMR Spectroscopy. ^{29}Si CP-MAS NMR spectrum of Mn-PCS is shown in Figure 6. New peaks in the region around -102.64 and -111.97 ppm correspond to the Mn—O—Si linkage. It is seen that there is a total up field shift of the PCS peaks. Peak around -10.45 ppm has been shifted to -22.15 ppm and -48.77 to -68.34 ppm , and small peak around 18.79 ppm was shifted to 7.77 ppm . This trend is explained due to the presence of manganese ion attached to the PCS.

^{13}C -NMR Spectroscopy. ^{13}C -CP-MAS spectrum of Mn-PCS is shown in Figure 7. Signals around 130 and -0.79 ppm are observed. Peak around -0.79 ppm is due to the PCS and the former one, that is, 130 ppm corresponds to the peaks of

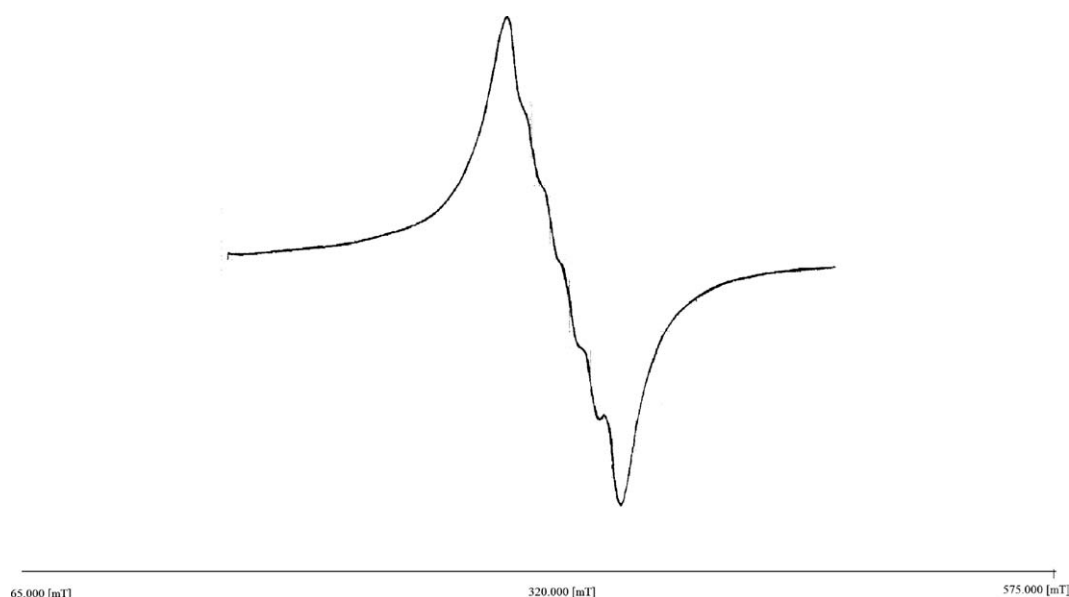


Figure 5. EPR spectrum of Mn-PCS.

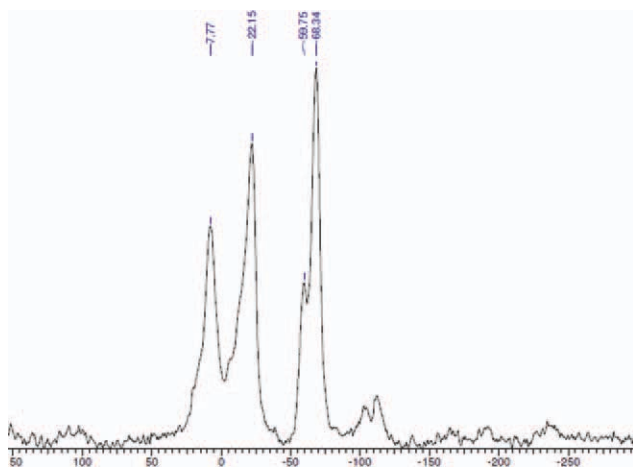


Figure 6. ^{29}Si CP-MAS NMR of Mn-PCS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

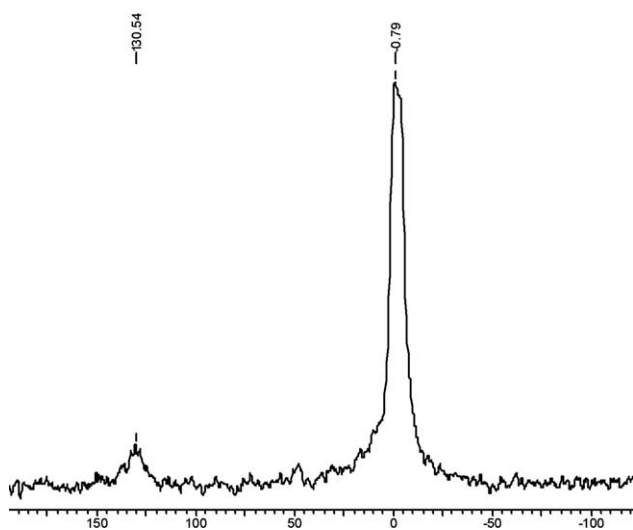


Figure 7. ^{13}C CP-MAS NMR spectrum of Mn-PCS.

acetate moiety. From this, we can confirm the metal ion attachment to the PCS.

The TGA of Mn-PCS shows very small weight loss, which might be because of the evaporation of adsorbed water molecule and low molecular weight fractions of the PCS.

Surface area of PCS and Mn-PCS were determined by Brunauer-Emmett-Teller method (BET) surface area analyzer. Results are shown in Table I. The surface area of both the PCS and the Mn-PCS were found to be considerably high. The high

Table I. Results of BET Surface Area Analysis

Sample	Surface area (m^2/g)		Total pore volume (cm^3/g)	Pore diameter (\AA)
	BET	Langmuir		
PCS	679	1171	1.11	84.58
Mn-PCS	573	988	0.81	77.06

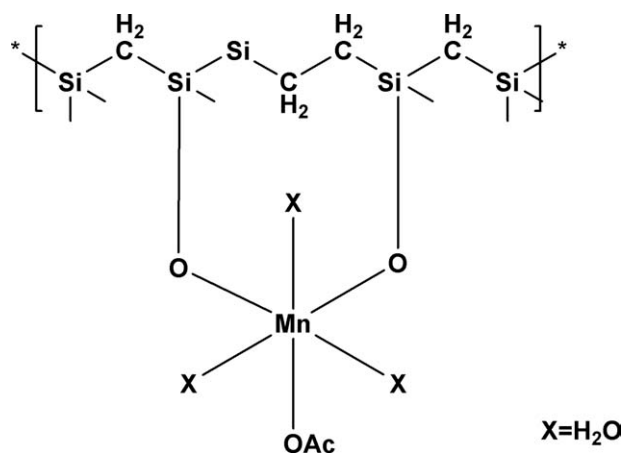
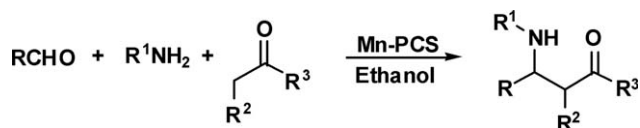


Figure 8. Structure of Mn-PCS.



Scheme 4. Mannich reaction with aldehyde, amine, and ketone.

surface area can be explained by its mesoporous nature. The high surface area is a supportive aspect for the application of PCS in catalysis.

Based on the spectral and analytical data, a possible structure of the Mn-PCS is given in Figure 8. The possibility of bonding between metal ion and neighboring Si—O cannot be ruled out, as this is an immobilized system.

Catalytic Activity Study

The manganese ions attached to the polymer were considered as the catalytic sites and PCS as solid support. The amount of catalyst was estimated in terms of the manganese ions with respect to the substrates. The catalytic activity study of Mn-PCS was investigated by taking Mannich reaction (Scheme 4).

Optimization of Amount of Catalyst. To examine the effect of catalyst concentration, the reaction between benzaldehyde, aniline, and acetophenone in the presence of Mn-PCS was considered. The study is proceeded by conducting the reaction by varying the concentration of Mn-PCS. The reaction period was set as 8 h and with equal concentrations of reactants. The outcome of the study is given in Table II.

It is observed that, as the metal concentration increased, the rate of the reaction also increased. From the results, amount of

Table II. Optimization of the Amount of Catalyst^a

Entry	mol % of the catalyst	Conversion (%)
1	2	65
2	5	75
3	10	81

^aCatalyst, Mn-PCS; solvent, ethanol; time, 8 h.

Table III. Mannich Reaction with Diverse Sets of Substrates^a

Entry	Aldehydes	Amine	Ketone	Conversion (%)
1	Benzaldehyde	Aniline	Acetophenone	81
2	Anisaldehyde	Aniline	Cyclohexanone	76
3	4-Chlorobenzaldehyde	p-Nitroaniline	Cyclohexanone	81
4	Anisaldehyde	p-Nitroaniline	Cyclohexanone	70
5	Formaldehyde	p-Nitroaniline	Cyclohexanone	70
6	4-Chlorobenzaldehyde	Aniline	Acetophenone	85
7	Naphthaldehyde	Aniline	Acetophenone	60
8	Anisaldehyde	Aniline	Acetophenone	80
9	4-Chlorobenzaldehyde	Aniline	Cyclohexanone	79
10	Benzaldehyde	Aniline	Cyclohexanone	72

^aReaction condition, equimolar concentration of aldehyde, amine, and ketone; solvent, ethanol, 10 mol % of Mn-PCS; time, 8 h.

catalyst for the Mannich reaction was optimized as 10 mol % Mn-PCS with respect to the substrates.

The catalytic activity of Mn-PCS can be generalized by conducting the Mannich reaction with a diverse set of substrates. The crude product was purified by column chromatography (hexane : EtOAc, 20 : 1). All the products were characterized by FTIR, ¹H-NMR spectroscopy, liquid chromatography-mass spectrometry (LCMS), and melting point determinations. The details are listed in Table III.

The spectral data of selected entries are listed below.

- Entry 1: 1, 3-diphenyl-3-(phenylamino)propan-1-one, C₂₁H₁₉NO. LCMS ES⁺ (M⁺+1) m/z: 302; FTIR (KBr, cm⁻¹): 3442, 2923, 1665, 1597; ¹H-NMR(400,CDCl₃, δ): 7.91 (dd, 1H), 7.76–7.11 (m, 10H), 6.67 (t, 1H), 6.54 (d, 2H), 5.02 (m, 1H), 3.53 (m, 2H); M. p.: 154–156°C.
- Entry 5: 2-((4-nitrophenylamino)methyl)cyclohexanone, C₁₃H₁₆N₂O₃. LCMS ES⁺ (M⁺+1) m/z: 249; FTIR (KBr, cm⁻¹): 3425, 1647, 1595, 1080; ¹H-NMR (300MHz, CDCl₃): 7.73(m, 2H), 7.35(m, 1H), 7.18(s, 1H), 2.88(m, 1H), 2.09(s, 1H), 1.72(m, 6H), 1.52(bs, 1H), 1.18(m, 2H); M. p.: 114°C.
- Entry 8: 3-(4-methoxyphenyl)-1-phenyl-3-(phenylamino)propan-1-one, C₂₂H₂₁NO₂. LCMS ES⁺ (M⁺+1) m/z: 332; FTIR (KBr, cm⁻¹): 3442, 2921, 1647, 1532, 1021; ¹H-NMR(400, CDCl₃, δ): 7.91 (dd, 2H), 7.57 (m, 1H), 7.46 (m, 2H), 7.36 (m, 2H), 7.10 (m, 2H), 6.86 (m, 2H), 6.65 (t, 1H), 6.57 (d, 1H), 4.97 (m, 1H), 4.50 (bs, 1H), 3.76 (s, 3H), 3.50–3.37 (m, 2H); M. p.: 104–106°C.

Table IV. Recycling of Catalyst^a

No. of cycles	Conversion (%)
1	81
2	78
3	73
4	72

^aCatalyst, 10 mol % Mn-PCS; solvent, ethanol; time, 8 h.

Recycling of Catalyst. The catalyst can be removed from the reaction mixture by simple filtration. It was washed thoroughly and dried. The reuse of Mn-PCS as a catalyst for Mannich reaction was studied by conducting the reaction with benzaldehyde, aniline, and acetophenone in the presence of recycled Mn-PCS for three cycles. The results are given in Table IV.

From the results, it is clear that the recycled catalyst can be used for subsequent reactions without much loss of catalytic activity. Mn-PCS has retained its form and characteristics after the completion of the reaction. Also, they have all the advantages of solid phase catalysts as operational simplicity, filterability, ability for regeneration, and reuse. There was no considerable loss in the activity after recycling.

CONCLUSIONS

Highly crosslinked PCS was prepared and characterized successfully. Because of the highly crosslinked nature, it possessed high surface area, which is one of the main advantages in catalysis. PCS supported manganese ion also has high surface area and its catalytic activity was investigated. The catalytic activity of the Mn-PCS was studied by taking Mannich reaction under consideration. The reactions were efficiently catalyzed by Mn-PCS and good yields were obtained. PCS supported manganese catalyst that has been prepared for the first time and used successfully in Mannich reaction.

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