

Silica supported polyvinyl pyridine as a highly active heterogeneous base catalyst for the synthesis of cyclic carbonates from carbon dioxide and epoxides

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Abstract

Reaction of epoxides and carbon dioxide to corresponding cyclic carbonates using silica supported polyvinyl pyridine as a highly active heterogeneous base catalyst has been reported. Typical optimized PVP/SiO₂ catalyst can be prepared from 10 wt.% loading of PVP using silica of surface area of 800 m² g⁻¹. The reaction gives 91% yield of propylene carbonate at 5.5 MPa CO₂ pressure, 150 °C and 6 h. The catalyst was found to be recyclable over four recycles without any loss in the catalytic activity.

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Keywords: Cyclic carbonates; Polyvinyl pyridine; Carbon dioxide fixation; Epoxide and silica supported catalyst

1. Introduction

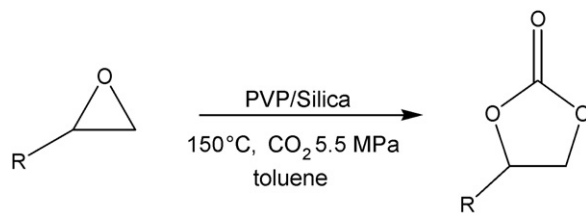
The use of solid heterogeneous catalysts in the chemical industry is a theme of extreme importance for the development of clean processes. Extensive work has been carried out using heterogeneous base catalysis for the variety of transformations [1]. Several heterogeneous base catalysts such as metal oxides, supported alkali metal catalysts, basic Zeolite and mixed oxides are known, however they suffers from the drawbacks of deactivation poor conversion, selectivity performance, recycle, etc. It is therefore essential to develop suitable base catalyst, via heterogenization of homogenous base catalysts, which can retain original selectivity and activity performance and provide an additional advantage of recyclability essential for the clean synthesis.

Carbon dioxide is one of the green house gases, which leads to the environmental pollution. In order to prevent environmental pollution various methodologies are developed for the chemical fixation of carbon dioxide to valuable chemicals, and the synthesis of five member cyclic carbonates via coupling

of carbon dioxide with epoxide is one of the promising reaction in this direction. The five member cyclic carbonates have several applications such as they act as a precursor for polymeric synthesis, ingredient for pharmaceutical/fine chemicals in biomedical applications [2], they are also used as an intermediate for the manufacture of several important chemicals such as glycol, carbamates, pyrimidines, purins and so on [3]. In recent decades numerous homogenous and heterogeneous catalysts system such as alkali metal halides [4], onium salts [5], organic bases [6], mixed oxides [7], Zeolite [8], smectites [9], and ionic liquids [10], have already been explored for this transformation. However, many of these catalysts suffer from disadvantages like low stability, low catalyst activity and/or selectivity [11–13]. For example alkali metal halides, onium salts and organic bases are homogeneous catalysts and they offer excellent activity/selectivity performance, however, suffer from a major drawback of catalyst product separation and hence affect the recyclability of the catalysts. Heterogeneous base catalysts offers lower activity performance, e.g. Zeolite (TOF 27 h⁻¹), metal oxides (TON 2–10 h⁻¹), PEG supported quaternary ammonium salts (TOF 20 h⁻¹), although they are offers the advantage of catalyst recyclability. There are some reports, which showed heterogeneous catalyst with high TOF 2712 h⁻¹ [14]. There is sufficient scope for the development of an active and recyclable catalyst for this transformation. In this

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paper we report novel homogenous base catalyst such as vinyl pyridine heterogenized to give polyvinyl pyridine (PVP), which is supported on high surface area silica and used as a heterogeneous base catalyst for the CO₂ fixation reaction for synthesis of cyclic carbonates (Scheme 1).

2. Experimental

2.1. Materials

Silica gel of different surface area was procured from Sigma–Aldrich (Davisil grade), Epoxides were supplied by Merck Company and Carbon dioxide with a purity of 99.99% was obtained from Alchemie Gases India, Propylene carbonates (PC) was obtained from Lancaster and other carbonates were synthesized by using reported methods. Other reagents were analytical grade and used as received without further purification.

2.2. Catalyst preparation and characterization

2.2.1. Preparation of poly-4-vinyl pyridine

Poly-4-vinyl pyridine (PVP) was prepared by radical polymerization of 4-vinylpyridine [15]. The polymer obtained was characterized by using, IR, ¹H NMR spectra, XRD and DSC/TGA analysis.

2.2.2. Preparation of silica supported PVP

Polyvinyl pyridine 0.5 g was dissolved in methanol 20 ml to this solution silica 5 g (Aldrich Davisil Grade) having known surface area (e.g. 800 m² g⁻¹) was added with constant stirring. The resulting slurry formed was stirred for 2 h and then methanol was removed under reduced pressure to form free flowing PVP–Silica catalyst. Similarly other PVP/SiO₂ catalysts were prepared using silica of different surface area.

2.2.3. Characterization of poly-4-vinyl pyridine and PVP/SiO₂

The IR spectrum of poly-4-vinyl pyridine was recorded on Buck Scientific Spectrophotometer using KBr pallet. The IR spectrum showed peaks at 3461 cm⁻¹ due to for N–H stretching, 2937 cm⁻¹ for aromatic C–H stretching, 1605 cm⁻¹ for C=C stretching and 1427 cm⁻¹ for C=N stretching in ring, 865 cm⁻¹ for C–H deformation out of plane. These are in accordance with the available spectrum of poly-4-vinylpyridine [16]. The IR spectra of typical supported catalyst PVP/SiO₂ with SiO₂ and active species PVP was illustrated in Fig. 1, indicating successful immobilization of active catalyst in the support silica.

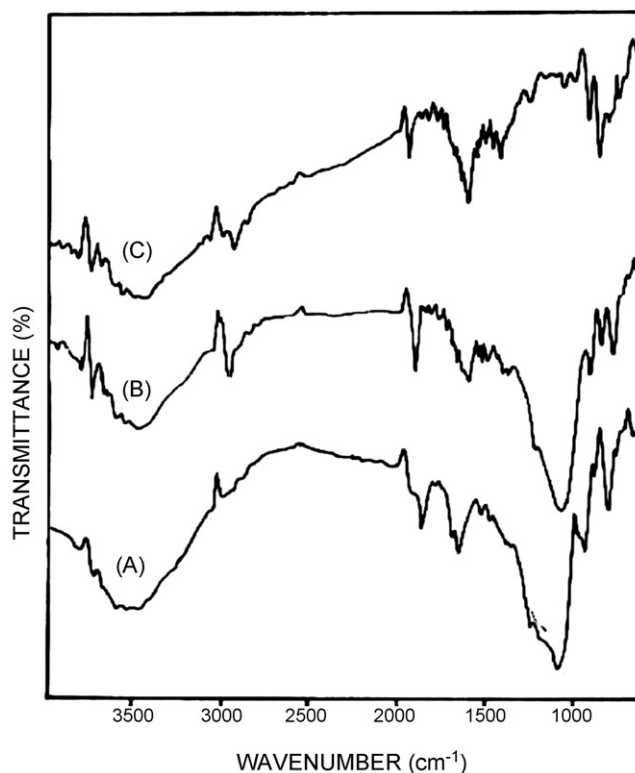


Fig. 1. IR spectrum (KBr) of poly-4-vinyl pyridine. IR spectra comparisons of the (A) SiO₂; (B) PVP/SiO₂; and (C) PVP.

The ¹H NMR spectrum of poly-4-vinylpyridine was recorded in its CDCl₃ solution containing a drop of CD₃OD, for complete solubilization of the polymer (Fig. 2). The spectrum showed a broad peak at 1.46 due to the ethylene group of the polymer chain. The benzylic type methylene protons give a fine multiplet at 3.33. Pyridine ring in the polymer has two distinct groups of protons at the α and β positions. α-Position, being highly deshielded.

The corresponding two protons appear as a multiplet at 8.25, while β protons appear as a multiplet at 6.39. These peaks and the nature of the spectrum clearly indicated the formation of the desired polymer.

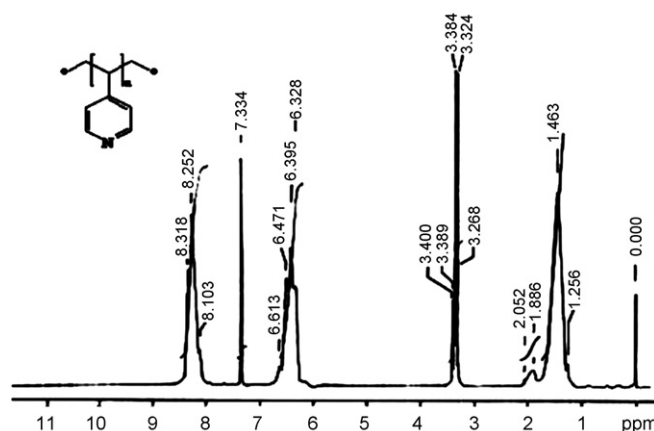


Fig. 2. ¹H NMR spectrum of poly-4-vinylpyridine.

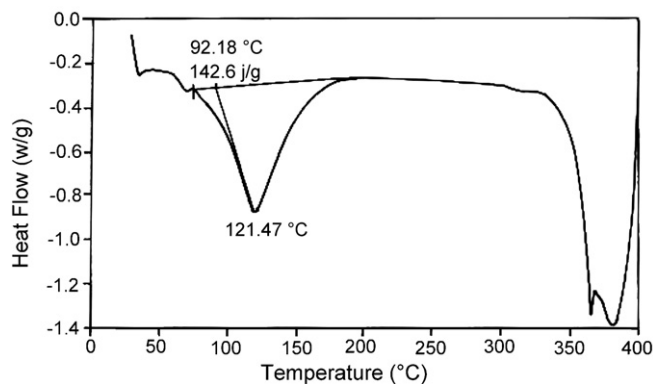


Fig. 3. DSC of poly-4-vinylpyridine.

The DSC of the polymer was recorded using Thermal analysis Instrument MDSC-Q100 to know the glass transition temperature as well as decomposition temperature of the polymer (Fig. 3) the polymer had TG 121.47 °C and it underwent decomposition above 350 °C.

The XRD of PVP is shown in Fig. 4. The XRD was recorded using Cu K α (1.5419 Å) source. It showed two well-defined peaks at 2θ value of 7.5 and 21. Thus, the polymer is a crystalline polymer. The XRD of the PVP as such and PVP supported on silica is similar with characteristic peak at $\theta=21$, showing no change in the crystalline nature of PVP after supporting on silica. The some difference in the XRD pattern is due to the additional PVP film in the lattice of silica.

The molecular weight of the polymer was determined by weight average method using viscosity of the dilute polymer solutions. The molecular weight was found to be $2.65\text{--}3.0 \times 10^5$. The DPI (degree of polymerization index) of the polymer was found to be 1.5.

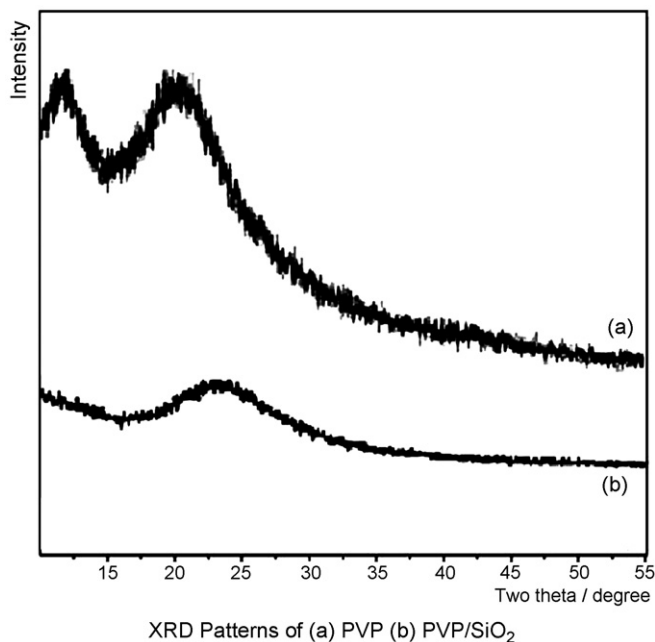


Fig. 4. XRD of Polyvinyl pyridine and PVP/SiO₂. XRD Patterns of (a) PVP; (b) PVP/SiO₂.

The surface area of catalyst was determined using BET method and was found to be $690\text{ m}^2\text{ g}^{-1}$, which is smaller than the area of original silica used as a support, i.e. $800\text{ m}^2\text{ g}^{-1}$.

2.3. Catalytic reaction

All the reactions were carried out in 250 ml stainless steel autoclave. In typical experimental procedure toluene 20 ml, propylene oxide 3.6 ml (50 mmol) and 1 g PVP/SiO₂ catalyst with 10 wt.% PVP loading were charged in to the reactor. CO₂ was introduced to reactor at room temperature. The reactor was heated up to 150 °C, and then initial pressure of CO₂ was adjusted up to 5.5 MPa. The reaction mixture was stirred for 6 h. After completion of the reaction the reactor was cooled to room temperature by ice water and depressurizes by vent valve. The liquid reaction mixture was analyzed compared with authentic sample by gas chromatography. Similar results can be obtained using 100 ml toluene, 18 ml (250 mmol) PO and 5 g PVP/SiO₂ catalyst.

3. Result and discussion

The synthesis of cyclic carbonates by coupling of epoxide with CO₂ in the presence of silica/PVP catalyst was conducted under various reaction conditions and the influence of each reaction parameter was studied in detail. For the initial optimization the reaction was carried out using PO, which leads to formation of PC.

3.1. Influence of loading of PVP on silica

Loading of PVP content on silica in catalyst system has strong influence on the yields of PC from CO₂ and PO. For the initial optimization of loading of PVP content on silica surface, various catalyst samples with variable PVP content in the range of 2.5–12.5 wt.% had been prepared on the silica of known surface area ($800\text{ m}^2\text{ g}^{-1}$) and their activities had been tested under the similar reaction conditions and the results are shown in Fig. 5. It can be seen that the catalytic activity of PVP/SiO₂ catalyst

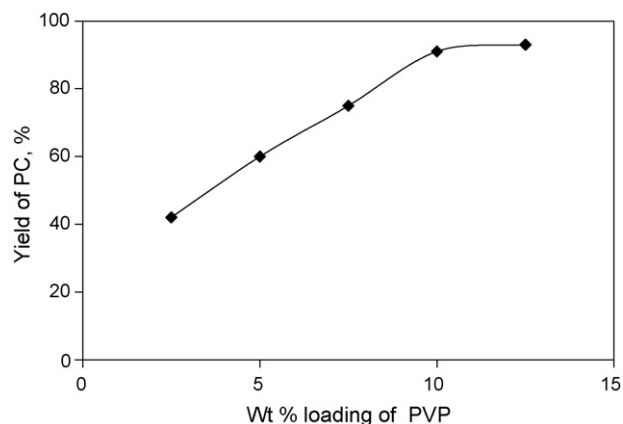


Fig. 5. Influence of loading of PVP. Reaction conditions: propylene oxide, 3.6 ml (50 mmol); catalyst, 1 g; toluene, 20 ml; CO₂ pressure, 5.5 MPa; temperature, 150 °C.

was increases with increasing the PVP loading from 2.5 wt.% to 10 wt.%. The yield of PC increases form 43% to 93% in this range. Above the 10 wt.% loading of PVP, no change in the catalyst activity was observed. The activity is directly proportional to the active basic sites available for the reactant. In case of PVP basicity is mainly due to the free pyridine moieties attached to the backbone of PVP polymer. Pyridine has pK_a value of 5.16 and Vinyl pyridine, which is a monomer of PVP, has pK_a value of 5.66. These pK_a values indicate basicity of the catalyst and hence the pK_a value of PVP polymer should fall in between these pK_a values, as there is no structural variation around pyridine moiety. In case of the reactions using lower PVP concentration to higher PVP concentration active basic sites are linearly increased, which directly reflects in the increase in the yield of PC. TOF and TON values obtained herein are as follows: PVP supported on silica (TON 100, TOF 16.6 h^{-1} 2.5 wt.% PVP; TON 52, TOF 8.7 h^{-1} 10 wt.% PVP see Fig. 5) and these values are comparable with those obtained with many other heterogeneous catalyst systems for similar reaction as mentioned in the introduction section.

3.2. Effect of variation in the surface area of silica

The surface area of silica also had strong influence on the yield of PC. Hence, the experiments with variation in the surface area of silica using similar PVP wt.% were conducted. The typical results obtained are given in Fig. 6. In order to study the role of surface area of support, the reaction was carried out using supported and unsupported PVP. It had been seen that 10 wt.% silica supported PVP catalyst gives higher yields (91%) as compared to that of unsupported PVP (43%) catalyst (PVP). This is due to the fact that in case of unsupported PVP, all basic sites are not exposed to the reactant whereas in the case of silica supported PVP catalyst, and PVP is well dispersed on silica, which leads to increase in the number of basic sites exposed to the reactant. With increase in surface area this effect is more pronounced and results to the increase in yield of PC as shown in the previous section. Hence to study further, the effect of surface area of silica, catalysts was prepared using silica with different surface area ($800, 750, 675, 550, 480\text{ m}^2\text{ g}^{-1}$) for constant PVP

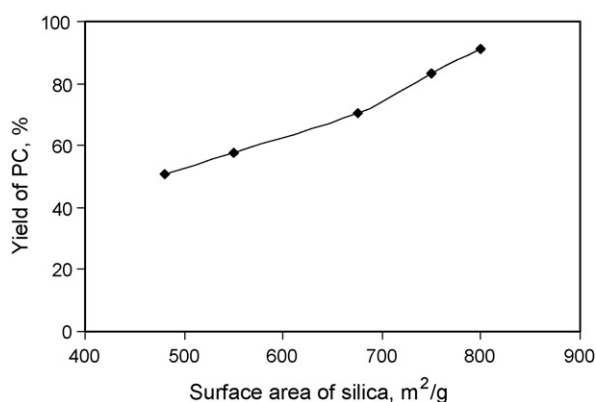


Fig. 6. Effect of surface area of silica. Reaction conditions: propylene oxide, 3.6 ml (50 mmol); catalyst, 1 g; toluene, 20 ml; CO_2 pressure, 5.5 MPa; temperature, 150°C .

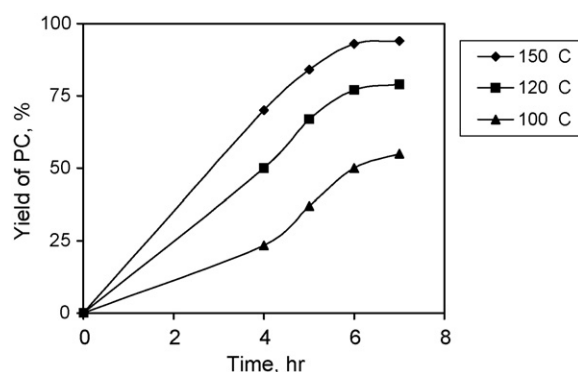


Fig. 7. Influence of temperature/reaction time. Reaction conditions: propylene oxide, 3.6 ml (50 mmol); catalyst, 1 g; toluene, 20 ml; CO_2 pressure, 5.5 MPa.

loading, i.e. 10 wt.% as optimized in the earlier section. It was observed that with increase in the surface area of the silica, yield of PC increases. Higher yield of PC was obtained when the silica having surface area $800\text{ m}^2\text{ g}^{-1}$.

3.3. Influence of temperature/reaction time

The influence of temperature on the yield of PC was investigated and the results obtained are shown in Fig. 7. The reaction was carried out at various temperatures in the range of $100\text{--}150^\circ\text{C}$. The higher temperature was of great advantage for insertion of carbon dioxide into the C–O bond of epoxide thus resulting in the rapid conversion of epoxide to cyclic carbonate. The PC yields increases with increase in the temperature reaching to the highest yield of PC (91%) at 150°C and no side reaction was observed even at high temperature and PC obtained quantitatively. This is one of the major advantages of PVP/ SiO_2 catalyst, since at higher temperature there is possibility of formation of PO oligomers that is eliminated in this case.

The influence of reaction time on the yield of PC is also represented in Fig. 7. It was observed that the yield of PC was increased with the increase in the reaction time. It can be seen that almost quantitative yield (91%) could be achieved at 6 h. no further increase in the yields of PC was observed above 6 h. Same trend of PC yields verses reaction time was observed at 100°C and 120°C . therefore, the reaction time of 6 h is suitable for the synthesis of PC quantitatively at 150°C .

3.4. Effect of CO_2 pressure

The effect of CO_2 pressure was also studied for the reaction and it was observed that the pressure also played an important role on the yield of cyclic carbonate as illustrated in Fig. 8. The yield of PC increases with increase in the pressure in the region up to 5.5 MPa and then remained nearly constant for further increase in the pressure. The low yield of PC below 5.5 MPa CO_2 pressure is due to lower gas–liquid mass transfer. As the pressure increases the concentration of carbon dioxide in the solvent increases and leads to increase in the yield of PC. (Fig. 8) shows the influence of pressure. The results obtained are accordance to some studies reported earlier for same reaction [17–20].

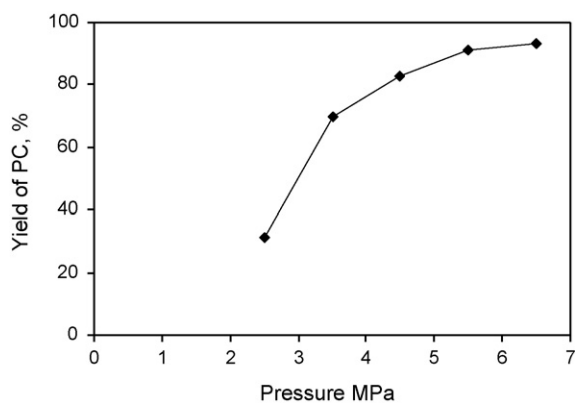


Fig. 8. Effect of pressure. Reaction conditions: propylene oxide: 3.6 ml (50 mmol); catalyst, 1 g; toluene, 20 ml; temperature, 150 °C.

3.5. Catalyst recyclability

A catalytic recycle was studied to investigate the consistency of the catalyst activity and recyclability. In each cycle PVP/SiO₂ catalyst was easily recovered via simple filtration and reused as a catalyst for subsequent reaction. The catalyst recyclability was tested by conducting the reaction at the optimized reaction conditions, i.e. 150 °C and 5.5 MPa CO₂ pressure for 6 h. The results were obtained as shown in the Fig. 9. It is interesting to note that the PC yield in subsequent runs is similar to that of the fresh catalyst, suggesting that PVP/SiO₂ catalyst could be reused up to fourth cycle without any loss in catalytic activity. Hence, the recyclability of the catalyst makes the process economically and potentially viable for commercial applications.

3.6. Substrate study

Under optimized reaction conditions, we examined reaction of terminal epoxide with CO₂, in order to survey the applicability of various epoxide. Various epoxides were converted to their corresponding cyclic carbonates with high yield and selectivity under optimized reaction conditions. The results are summarized in Table 1. Propylene oxide (1a) was found to be the most reactive, while epichlorohydrin (1b) exhibits relatively low activity among the epoxide studied. Probable reason for this observa-

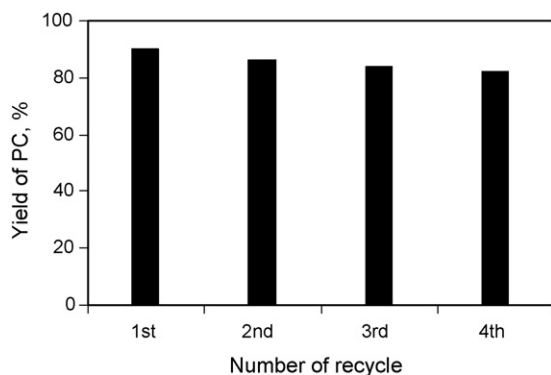


Fig. 9. Catalyst recyclability. Reaction conditions: propylene oxide, 3.6 ml (50 mmol); catalyst, 1 g; toluene, 20 ml; CO₂ pressure, 5.5 MPa; temperature, 150 °C.

Table 1

Synthesis of various carbonates in presence of PVP/silica system at 150 °C for 6 h in CO₂

No	Reactant	Product	Pressure (MPa)	% Yield
1			5.5	93
2			5.5	84
3			5.5	87

Reaction conditions: propylene oxide, 3.6 ml (50 mmol); catalyst, 1 g; 1 toluene, 20 ml; CO₂ pressure 5.5 MPa, temperature, 150 °C.

tion is mainly due to the less steric hindrance in case of PO as compared with other two substrates.

4. Conclusion

Polyvinyl pyridine supported on high surface area silica was found to be highly efficient and recyclable heterogeneous base catalyst for cycloaddition of carbon dioxide and epoxies to give selective formation of cyclic carbonates in high Yield. Typical optimized PVP/SiO₂ catalyst can be prepared from 10 wt.% loading of PVP using silica of surface area of 800 m² g⁻¹. The reaction gives 91% yield of propylene carbonate at 5.5 MPa CO₂ pressure, 150 °C and 6 h. The catalyst showed similar activity and selectivity performance for four consecutive recycles.

Acknowledgement

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