

## Solvothermal synthesis of nanoporous, polymeric solid bases with controlled wettability and good catalytic activity



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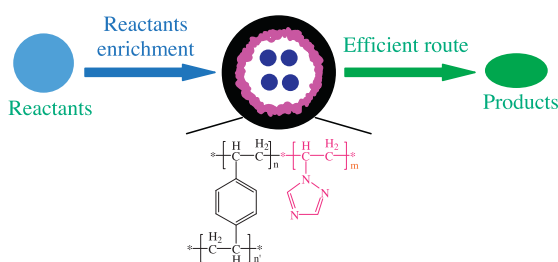
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### HIGHLIGHTS

- Nanoporous polymeric solid bases were synthesized under solvothermal conditions.
- The nanoporous solid base showed superhydrophobicity and good air-stability.
- The nanoporous solid base showed controlled wettability for various reactants.
- Hydrophobic-oleophilic network results in high exposition degree of basic sites.
- The solid bases showed good catalytic activity in base catalytic reactions.

### GRAPHICAL ABSTRACT

Superhydrophobic, sponge-like nanoporous solid bases with controlled wettability and unique adsorption properties for various organic reactants have been synthesized from copolymerization of divinylbenzene with basic monomers under solvothermal conditions.



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### ABSTRACT

Nanoporous, polymeric solid bases with controlled wettability have been successfully prepared under solvothermal conditions, the basic site of imidazole or triazole group could be easily introduced into the samples from copolymerization of divinylbenzene (DVB) with 1-vinylimidazole (VI) or 1-vinyl-1,2,4-triazole (VT). The solid bases possess abundant nanopores, good stability, controlled wettability and excellent adsorption properties for various organic reactants. The synergistic effects of abundant nanoporosity and good wettability for reactants largely promote the fast diffusion of reactants and products, further enhancing the compatibility between reactants and catalysts, which result in their much improved catalytic activities and recyclability in Knoevenagel condensation and Michael addition in comparison with conventional solid bases of Amberlite 400, hydrotalcite and CaO.

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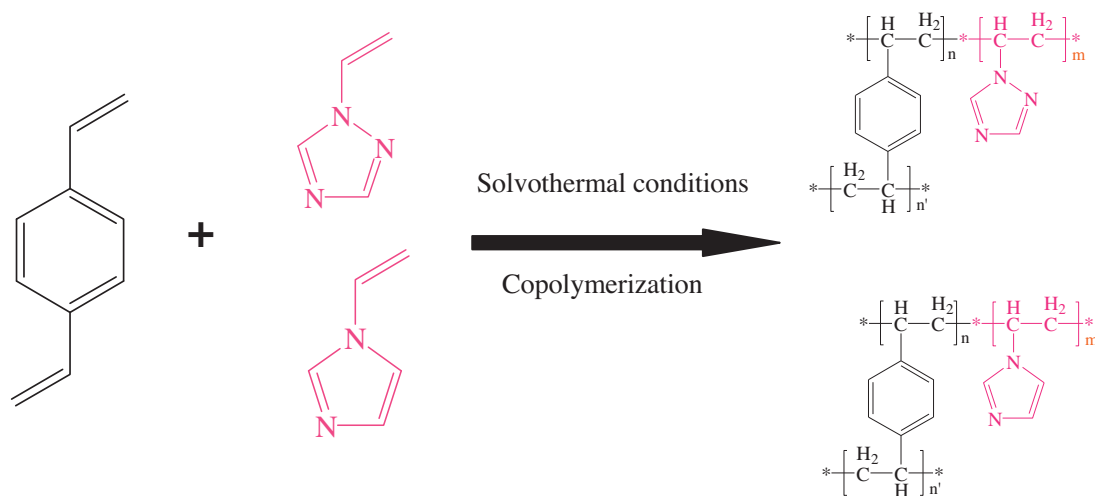
## 1. Introduction

Acid and base catalysts remain of significant current research interest due to their range of applicability in industrial processes

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[1–4]. In recent times, research on replacement of homogeneous acid or base catalysts with their heterogeneous counterparts has received considerable attention from the point of view of green and sustainable chemistry. The obvious drawbacks of homogeneous acid and base catalysts include difficult separation of catalysts from reaction media, equipment corrosion while being deleterious to the environment [1–15]. Up to now, various kinds of solid acid and base catalysts have been used in industrial processes. Compared with acid catalysts, base catalysts have been widely used in the areas of production of perfumes, pharmaceuticals and agro-chemicals,



**Scheme 1.** Solvothermal synthesis of nanoporous, polymeric solid bases.

which usually show very good catalytic activities under rather mild conditions [11–13].

Typical solid base catalysts such as alkaline earth oxides, basic resin, and hydrotalcite, have been widely used in various base catalytic reactions with good catalytic performances [2,16]. However, their poor porosity results in the low degree of exposure of catalytically active sites to the reactants. Furthermore some of these active sites can be covered by reactants and products during the progress of the reaction, resulting in further lowering of catalytic activities and bad recyclability. Immobilization of basic sites onto porous materials such as zeolites, ordered mesoporous materials, and carbon nanotubes opens up an alternative way of overcoming the embedding and coverage of active sites [10,17,18]. Typical nanoporous solid bases such as alkali ion-exchanged resins, X and Y type of zeolites, amino groups functionalized mesoporous silicas of MCM-41 and SBA-15, and N doped carbon nanotubes showed good catalytic activities in various base reactions such as Knoevenagel condensation, Michael addition and transesterification [7,9,14–17]. However, these catalysts suffer from drawbacks such as poisoning of basic sites by water and CO<sub>2</sub> in the air, which results from their intrinsic hydrophilic character. This seriously constrains their wide applications in industry [2,8]. In principle, the hydrophilic feature in solid bases usually promotes the adsorption of CO<sub>2</sub> [8,19], and hence the synthesis of solid bases with good hydrophobicity is expected to enhance their stability in the air.

Synthesis of efficient and hydrophobic solid bases with good air-stability remains a challenge, in particular, preparation of porous and air-stable solid bases with superhydrophobicity, good wettability and adsorption properties for organic reactants. We demonstrate here synthesis of a series of superhydrophobic solid bases from copolymerization of DVB with basic monomers such as 1-vinyl-1,2,4-triazole (PDVB-VT-*x*s) or 1-vinylimidazole (PDVB-VI-*x*s, where *x* stands for molar ratio of DVB with VT or VI) under solvothermal conditions. The obtained novel solid bases possess abundant sponge-like nanopores, good air-stability, superhydrophobicity and superwettability for various organic compounds, which result in their very high adsorption capacities for various organic reactants. More interestingly, PDVB-VT-*x*s and PDVB-VI-*x*s show much improved catalytic activities and good recyclability in Knoevenagel condensation and Michael addition in comparison with reported solid bases such as hydrotalcite, CaO and basic resin of Amberlite 400, which should be attributed to their novel structural and interfacial properties. The synthesis of PDVB-VI-*x*s and PDVB-VT-*x*s will develop effective routes for synthesizing efficient

and stable solid bases, which would be potentially important for the wide applications of solid bases in industry.

## 2. Experimental

### 2.1. Chemicals and reagents

All reagents were of analytical grade and used as purchased without further purification. Divinylbenzene (DVB), 1-vinylimidazole (VI), 1-vinyl-1,2,4-triazole (VT), Amberlite 400 were purchased from Sigma–Aldrich Co. Azobisisobutyronitrile (AIBN), acetylacetone, acrylonitrile, benzaldehyde, propanedinitrile, methyl acrylate, ethyl acetate, THF, iodomethane, NaOH, CaO, Na<sub>2</sub>CO<sub>3</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, and Al(NO<sub>3</sub>)<sub>3</sub> were obtained from Tianjin Chemical Co. Hydrotalcite was synthesized according to the literature [20].

### 2.2. Synthesis of nanoporous polymer based solid bases

Imidazole or triazole functionalized superhydrophobic nanoporous polymers of PDVB-VI-*x*s or PDVB-VT-*x*s were solvothermally synthesized from copolymerization of DVB with VI or VT (As shown in Scheme 1), which was achieved with the starting system of DVB:VI or VT:AIBN at molar ratios of 1:0.2–0.5:0.027. As a typical run, 2.0 g of DVB and 0.478 g of VI or 0.48 g of VT were added into a solution containing 0.07 g of AIBN and 30 mL of ethyl acetate. After stirring of the mixture at room temperature for 3 h, which was then transferred into an autoclave and heated at 100 °C for 24 h, after slowly evaporating the solvent at room temperature for 2 days, the solid base with monolith morphology designated as PDVB-VI-0.33 or PDVB-VT-0.33 was obtained.

Quaternary ammoniation of PDVB-VI-*x*s or PDVB-VT-*x*s was achieved by treating PDVB-VI-*x*s or PDVB-VT-*x*s with CH<sub>3</sub>I at room temperature under dark condition, ion-exchanging with NaOH solution (1 M) for two times. As a typical run, 2.0 g of PDVB-VI-0.33 was added into a mixture containing 40 mL of ethanol and 2.0 mL of methyl iodide. After reaction for 12 h at room temperature under dark condition, the sample was obtained by washing with ethanol, filtering, and drying at 80 °C. After treating the sample with 100 mL of NaOH solution (1 M) for 24 h at room temperature for two times, strong base ionic liquid functionalized nanoporous polymer designated as PDVB-VI-0.33-Q was obtained.

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