



# *In situ* functionalized sulfonic copolymer toward recyclable heterogeneous catalyst for efficient Beckmann rearrangement of cyclohexanone oxime

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## ABSTRACT

Exploring environmentally friendly, efficient and recyclable heterogeneous catalysts for low-temperature liquid-phase organic reactions are important for the development of green and sustainable processes. In this work, we applied an *in situ* sulfonated polymeric solid acid H-PDVB-SO<sub>3</sub>H for catalyzing liquid-phase Beckmann rearrangements for the first time, with post-sulfonated sample and other various counterparts as control catalysts. H-PDVB-SO<sub>3</sub>H was prepared by copolymerization of divinylbenzene with sodium *p*-styrene sulfonate under solvothermal condition, followed by ion-exchanging to convert the polymer into proton form. It possessed a large surface area, plenty of mesopores and high sulfur content, and exhibited the high yield to  $\epsilon$ -caprolactam (75%) with quite steady reusability in the heterogeneous Beckmann rearrangement of cyclohexanone oxime. The catalyst also showed good substrate compatibility with such a high reaction rate that the reaction time was as short as 1 h. No any co-catalysts or metals were used in the catalytic system, making the catalyst an environmentally friendly and efficient candidate for Beckmann rearrangements.

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## 1. Introduction

Transformation from ketoximes to corresponding amides through Beckmann rearrangements produces various vital synthetic intermediates and raw materials for medicines, agrochemicals, fragrances and polymers. Among them, the most important industrial application is the produce of  $\epsilon$ -caprolactam, the starting material for manufacturing nylon fibres and resins [1]. The liquid acids such as concentrated sulfuric acid or oleum are homogeneous catalysts for the commercial process for producing  $\epsilon$ -caprolactam, in which ammonia is used to neutralize the product mixture. This process leads to severely ecological concerns and economical drawbacks, such as the inevitable equipment corrosion, difficulty in product separation, and formation of large amount low value-added ammonium sulphates [2,3]. In order to overcome these problems, solid catalysts have been attempted for this reaction in vapour process, including MCM-41 [4], silicalite-1 [5], WO<sub>x</sub>/Bi-SBA-15 [6,7], TS-1 [8], metal pillared-illerite [9] and so forth. The vapour-phase process is highly energy-consuming because it is usually conducted above 300 °C [10–13], and often leads to low selectivity of lactams and fast catalyst deactivation arising from

coke formation [4,5]. Moreover, it is difficult to produce some important lactams, such as  $\omega$ -laurolactam, in the gas phase due to the instability of the precursors [14]. Therefore, the liquid-phase Beckmann rearrangement has attracted growing attentions; yet, it is still one challenge to explore green and recyclable heterogeneous catalyst under mild conditions.

Many efforts have been made towards liquid-phase Beckmann rearrangement. Various organocatalysts were used for rearrangement of cyclohexanone oxime, such as cyclonic chloride [15], 1-chloro-2,3-diphenylcyclopropenium ion [16], bis(2-oxo-3-oxazolidinyl) phosphinic chloride (BOP-Cl) [17], TsCl [18], trifluoroacetic acid [19] and so on. They exhibited good yields to  $\epsilon$ -caprolactam at relatively low temperatures, but most of them involved environmentally unfriendly halogen with difficulty in catalyst isolation. Task-specific ionic liquids (ILs) tethered with acidic group [20,21] caused liquid–liquid biphasic or homogeneous systems, but excessive IL amount relative to the substrate was needed; in this case, recycling of IL catalyst was not as convenient as a heterogeneous catalyst. In order to improve the catalyst separation and recycling, various solid catalysts were used in the low-temperature liquid-phase rearrangement of cyclohexanone oxime, including H-Beta [22], tungstated zirconia [23], and sulfonated mesoporous silica [24]. However, the catalytic reusability data of those catalysts were not shown in those literatures. There have been a few of studies that reported the reusability of solid catalysts,

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which showed some limitations in catalytic activities. For examples, Al-MCM-41 presented well reusability for rearrangement of cyclohexanone oxime, but showed a low conversion of 50.6% [25]. Titanium-exchanged montmorillonite demonstrated well catalytic conversion (96%) and selectivity (74%) for rearranging cyclododecanone oxime, but required very long reaction time (20 h) [26]. Cs salt of phosphotungstic acid was a recyclable heterogeneous catalyst for rearrangement of cyclohexanone oxime, which however needed the high temperature (150 °C) and long time (6 h) to reach the moderate conversion (80.8%) [27]. Heteropolyanion-based ILS materials demonstrated high activity for the rearrangement of various ketoximes; nevertheless, a co-catalyst such as ZnCl<sub>2</sub> was indispensable and a sluggish deactivation was observed in recycling tests [28,29].

Sulfonic acid group (–SO<sub>3</sub>H) functionalized polymer materials have been developed as effective catalysts for many acid-catalyzed reactions [30–32]. As the typical commercial strong acidic cation exchange resin, Amberlyst-15 has a small surface area and low thermal stability, which limits its practical application in catalysis. For Beckmann rearrangement of cyclohexanone oxime, mesoporous polymers functionalized with –SO<sub>3</sub>H have been designed and used as heterogeneous catalysts. For example, meso-structured polymers FDU-14-SO<sub>3</sub>H demonstrated the conversion of 91.4% and selectivity of 85.8% (yield 78.4%) for liquid-phase Beckmann rearrangement of cyclohexanone oxime, and could be reused for several times with slight decrease of conversion [31]. Hypercrosslinked organic polymer HBS-4 [33] showed the high yield of 83.4% to  $\epsilon$ -caprolactam with the reaction time of 6 h and its reusability was unclear. Generally, these polymeric solid acids avoid the utilization of any metals that may leach in catalytic systems, thus being ecologically sustainable and noncorrosive. However, only post-sulfonated polymers were tested in the Beckmann rearrangement of cyclohexanone oxime and no study is related to their substrate compatibility.

In this paper, sulfonic group is *in situ* incorporated into polymeric skeleton, giving a non-post-sulfonated polymer material (H-PDVB-SO<sub>3</sub>H) that is used as a heterogeneous solid acid catalyst for liquid-phase Beckmann rearrangements for the first time. H-PDVB-SO<sub>3</sub>H with large surface area and high content of the sulfonic group is prepared through copolymerization of divinylbenzene (DVB) and sodium *p*-styrene sulfonate, followed by an ion-exchange. Optimization of reaction conditions, catalytic reusability, and comparison with various control catalysts are systematically investigated. The catalyst is also assessed in the rearrangement of various other ketoximes to evaluate the substrate compatibility. The results show that H-PDVB-SO<sub>3</sub>H is highly active in transforming aromatic oximes, especially cyclohexanone oxime, to the corresponding amides. The advantages of this heterogeneous catalysis system include the very short reaction time of 1 h, easy recovery and steady reuse of the solid acid catalyst, and no need of any co-catalysts.

## 2. Experimental

### 2.1. Materials

All chemicals and solvents were commercially available and used as received without further purification. Cyclohexanone

oxime (98 wt.%), 2,2-azobisisobutyronitrile (AIBN), hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30 wt.%), sodium acetate trihydrate (CH<sub>3</sub>COONa, 99 wt.%), tetrahydrofuran (THF, 99 wt.%) and hydroxylamine hydrochloride (NH<sub>2</sub>OH·HCl, 98.5 wt.%) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium *p*-styrene sulfonate (90 wt.%), divinylbenzene (DVB, 80 wt.%) and styrene (ST, 99 wt.%) were provided by Aladdin Chem. Co., Ltd. Acetophenone (98 wt.%), concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 98 wt.%) and chlorosulfonic acid (ClSO<sub>3</sub>H) were supplied by Shanghai Lingfeng Chemical Reagent Co., Ltd. Acetophenone oxime (98 wt.%), benzophenone oxime (97 wt.%) and cyclopentanone oxime (97 wt.%) were acquired from Tianjin Heowns Co., Ltd.

### 2.2. Catalyst preparation

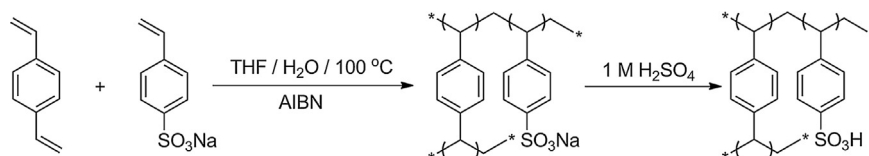
Sulfonic acid group-functionalized polymer H-PDVB-SO<sub>3</sub>H was prepared through two steps (Scheme 1) according to the Ref. [34]. In the first step, H-PDVB-SO<sub>3</sub>Na was synthesized from copolymerization of DVB and sodium *p*-styrene sulfonate under solvothermal condition. In detail, 2.0 g of DVB was added into a solution containing 0.05 g of AIBN and 20 mL of THF, followed by addition of 2.0 mL of water and 3.17 g of sodium *p*-styrene sulfonate. After stirring at room temperature for 3 h, the mixture was solvothermally treated at 100 °C for 24 h. The solvent in the product mixture was evaporated slowly at room temperature, washed successively with water, ethanol and diethyl ether, and dried at 80 °C for 12 h to give the product H-PDVB-SO<sub>3</sub>Na.

In the secondary step, H-PDVB-SO<sub>3</sub>Na compound was further treated by using 1 M (mol L<sup>-1</sup>) sulfuric acid, giving the sample H-PDVB-SO<sub>3</sub>H. In a typical run, 1.0 g of H-PDVB-SO<sub>3</sub>Na was dispersed in 10 mL ethanol, and then 5 g sulfuric acid (1 M) was added dropwise. After stirring for 24 h at room temperature, the solid was obtained by filtration, washed with water until the filtrate was neutral, and then dried at 80 °C for 12 h. (Elemental analysis Calcd: C 65.09 wt.%; H 6.06 wt.%; S 8.19 wt.%.)

For comparison, two other control solid acids, post-sulfonated mesoporous polymer (P(DVB-ST)SO<sub>3</sub>H), sulfonic acid-modified mesoporous silica SBA-15 (SBA-15-SO<sub>3</sub>H) were prepared according to the previous literatures (details are in Supporting Information) [35].

### 2.3. Characterization

Fourier transform infrared spectroscopy (FT-IR) was recorded on a Nicolet iS10 FT-IR instrument (KBr discs) in the 4000–400 cm<sup>-1</sup> region. Lewis acid sites and Brønsted acid sites of the typical sample were measured by the pyridine adsorption FT-IR spectrum [36]. Thermogravimetry (TG) analysis was carried out with a STA409 instrument in dry air at a heating rate of 10 °C min<sup>-1</sup>. Scanning electron microscope (SEM) images were performed on a HITACHI S-4800 field emission scanning electron microscope. Nitrogen (N<sub>2</sub>) adsorption isotherms and Brunauer–Emmett–Teller (BET) surface areas were measured at the temperature of liquid nitrogen (–196 °C) by using a BELSORP-MINI analyzer. The samples were degassed at 120 °C for 3 h to a vacuum of 10<sup>-3</sup> Torr before analysis, and pore size distribution curves were calculated using the Barrett–Joyner–Halenda (BJH) model. CHNS elemental analysis was



**Scheme 1.** Preparation process of sulfonic acid group-functionalized polymer H-PDVB-SO<sub>3</sub>H.

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