



Porous aluminosilicate inorganic polymers (geopolymers): a new class of environmentally benign heterogeneous solid acid catalysts



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ABSTRACT

Aluminosilicate inorganic polymers (geopolymers) were developed as a new class of cost-efficient, environmentally friendly, solid acid catalysts and their performance evaluated in a model liquid-phase Beckmann rearrangement reaction (cyclohexanone oxime to ϵ -caprolactam). The active sites were generated within the structure of the geopolymers by ion-exchange with NH_4^+ followed by thermal treatment. The effect of varying the starting composition on the textural and acidic properties of the geopolymer catalysts was studied and its influence on the catalytic activity was investigated. Catalytic performance was significantly improved by the use of post-synthetic treatments. No significant decrease in the yield of ϵ -caprolactam after recycling for five times suggesting that geopolymer-based catalysts are advantageous over supported catalysts which often lose their catalytic activity due to leaching of the active sites from the support. The catalytic activities obtained in this study are comparable, and sometimes superior, to other solid catalysts suggesting that geopolymers have a great potential as environmentally benign heterogeneous catalysts.

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1. Introduction

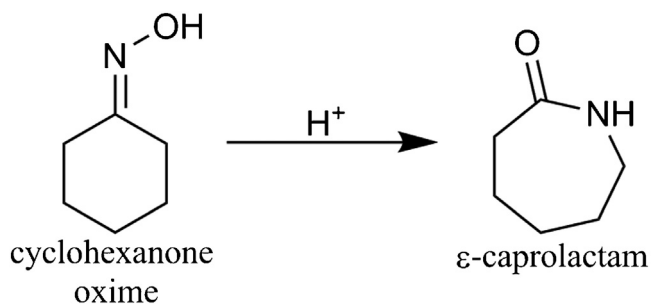
The Beckmann rearrangement is a ubiquitous reaction vital to many industrially important organic syntheses. One such reaction is the production of ϵ -caprolactam, the precursor of polyamide-6 (nylon-6), which is produced in vast amounts; in 2012 alone, five million metric tonnes of caprolactam were produced [1]. The industrial synthesis of caprolactam is by a one-pot ammoxidation of cyclohexanone, followed by the Beckmann rearrangement of the cyclohexanone oxime using concentrated sulphuric acid and/or oleum as the catalyst and solvent [2]. Each tonne of caprolactam produced in this process produces two tonnes of ammonium sulfate waste, formed by neutralisation of the acid with ammonia [3]. Generation of such large amounts of waste presents serious environmental problems and expense involved in its treatment and disposal. Recent increased environmental awareness and the stimulus of greener chemistry has driven the rapid development of new heterogeneous catalysts for a wide range of organic synthesis applications [4].

Solid acid catalysts are reusable, easy to separate from the reaction mixture and usually generate less by-products [5]. Several

of the heterogeneous catalysts employed for the gas phase Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam, Scheme 1, during the last three decades include zeolites (mainly high silicon MFI framework structures [6–8] and nanosheets [9]), molecular sieves [10,11] and functionalised oxides or mixed oxides [12,13]. Large-scale production of ϵ -caprolactam (~90000 tonnes/year) by the Beckmann rearrangement in the gas phase was achieved in 2003 by the Sumitomo Corporation, Japan, using H-ZSM-5 zeolite as the catalyst [14]. However, such vapour-phase systems suffer the drawbacks of requiring high temperatures (often > 623 K) which can also deactivate the catalyst by facilitating side reactions such as polymerisation, with a deleterious effect on the catalyst life time and reusability [1,15–20]. Although the reusability problem can be solved by introducing into the reaction system an additional fluidized-bed reactor for regenerating the catalyst while conducting the reaction [14], such systems are energy consuming. Thus, for both economic and environmental reasons, interest has recently increased in the liquid-phase Beckmann rearrangement of cyclohexanone oxime. Various heterogeneous catalysts have been proposed for this purpose, including zeolites (mainly large pore Y and beta type zeolites [15–17]), molecular sieves [1,21,22], mixed oxides [18,23,24], heteropolyacids [19], MOFs [20] and ionic liquids [25].

The nature and the location of the active sites responsible for catalysing the Beckmann rearrangement reaction are in some

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Scheme 1. xxx.

dispute in the literature. Some reports suggest that the rearrangement is catalysed by Bronsted acid sites located inside the pores of a ZSM-5 zeolite catalyst [26,27], whereas other studies have implicated the strong acidic bridging hydroxyl groups in the strong adsorption of the product to the catalyst, giving rise to its rapid deactivation [28]. However, a more recent general consensus is that the most likely active sites for this rearrangement are the non- or weakly acidic hydrogen-bonded silanol groups (silanol nests) and vicinal silanols located on the outer surface of the catalyst or just under the mouths of the pores [12–14]. Non-acidic silanol groups (isolated Si-OH) located on the outer surface of zeolite nanosheets have also been reported to be active sites for this reaction [9]. The mechanism of the Beckmann rearrangement over solid heterogeneous catalysts and the effect of the solvent type have been reviewed elsewhere [28,29].

The application of solid catalysts for Beckmann rearrangements in the liquid phase is very limited compared with vapour-phase systems. Zeolites suffer from the constraints imposed by the size of their micropores which hinders their efficiency in liquid phase systems by diffusional limitations which cause deactivation and affect the catalyst life time [9,30]. Although mesoporous silicates or molecular sieves (M41S) do not suffer from mass-transfer constraints, they have low hydrothermal stability and low acidity and their synthesis involves the use of costly and sometimes toxic organic structure-directing agents (OSDAs) and lengthy thermal treatments [31–33]. These drawbacks have hindered their use in large scale applications.

Thus, there is still a need for new cost-efficient heterogeneous solid catalysts that are also environmentally benign. Here we report the development and performance of a new class of porous aluminosilicate inorganic polymers (geopolymers) that are easily and cheaply synthesised, environmentally-friendly and with acidic properties that can readily be tailored to the requirements for heterogeneous solid acid catalysis in fine chemical applications.

Geopolymers have been described as amorphous fine-grained analogues of zeolites [34]. Unlike amorphous silica alumina (ASA) that consists of different forms of Al (mainly octahedral and Al_2O_3) grafted into a silica backbone, the geopolymer structure consists of three-dimensional random arrangements of tetrahedral silicate and aluminate units joined through their common oxygen atoms. Charge balance in the tetrahedral aluminate units is achieved by the presence of (usually) monovalent alkali ions that give the geopolymer zeolite-like ion-exchange properties [35]. Historically, geopolymers have been used as ecologically-friendly substitutes for Portland cement, but more recently their ability to be functionalised has led to a range of more advanced applications such as drug delivery agents, photocatalysts and precursors to advanced ceramics [36].

The possible use of geopolymers as a new class of environmentally-friendly heterogeneous solid catalysts arises from their facile and energy-efficient synthesis from simple raw materials (kaolin clay or industrial wastes such as fly ash),

the ability to tailor their porosity to form micro, meso, or even hierarchical structures without using conventional expensive and/or toxic OSDAs [37,38], and the ability to control their acidity and incorporate versatile active sites into their structures either by ion-exchange or metal substitution of the Si or Al in the geopolymer framework [39]. Despite these interesting features, there are only very few reports of geopolymer-based catalysts; Sazama et al. [40] have reported the use of geopolymers as redox catalysts for the reduction of NOx by ammonia and the oxidation of volatile hydrocarbons where the active catalyst was Pt, Fe, Cu or Co, supported or ion-exchanged on a geopolymer matrix. Geopolymers have also been used to support other catalytic nanoparticles such as TiO_2 [41] and CuO [42] for the photocatalytic applications. Sharma and co-workers have also reported the use of geopolymers loaded with Ca^{2+} as base catalysts for the generation of biofuel [43]. However, no workers have reported the use of geopolymers into which suitable solid acidity was incorporated into the structure for catalysing industrially important organic reactions such as the Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam.

In the present work, geopolymers were developed as new solid acid catalysts with active sites generated within the structure of the geopolymer itself, rather than using the geopolymer framework as a catalyst support. The nature of these acid sites was investigated, and the catalytic activity was evaluated in a liquid-phase Beckmann rearrangement of a model system (rearrangement of cyclohexanone oxime to ϵ -caprolactam). The effect of varying the preparation compositions on the textural and acidic properties of the geopolymers was studied and its influence on the catalytic activity was examined. Post-synthetic treatments to improve the catalytic performance of the prepared catalysts were also developed, and their performance over multiple reaction cycles evaluated. The performance of the geopolymer catalysts was compared with zeolites Y and ZSM-5, and with other catalysts that have been reported under identical reaction conditions.

2. Experimental

2.1. Geopolymer synthesis

The geopolymers were prepared from New Zealand kaolinite-type halloysite clay (Imerys Premium Grade), the chemical composition of which is shown in Table 1.

Table 1
Composition of halloysite.

Oxide	% wt.
SiO_2	49.5
Al_2O_3	35.5
Fe_2O_3	0.29
TiO_2	0.09
K_2O	0.01
Na_2O	0.04
CaO	0.02
MgO	0.02
L.O.I.	13.8

The clay was dehydroxylated at 600 °C for 12 hr. and gradually mixed with an aqueous solution of analytical grade NaOH or KOH (Panreac) and sodium silicate (FERNZ Chemical Co, NZ, Type “D”, $Na_2O/SiO_2 = 0.48$, solids content = 41.1 mass %) or potassium silicate (Type K66, Ineos Silicas, UK), depending on whether the sodium or potassium form of the geopolymer was being synthesised. Two sodium and two potassium-based geopolymers were prepared with “normal” composition (e.g. $SiO_2/Al_2O_3 \sim 3.5$), designated Na-N and K-N, and two other compositions, containing

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