One-step synthesis of ε-caprolactam via the liquid phase catalytic nitrosation of cyclohexane in the presence of concentrated sulfuric acid

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Abstract A simple and efficient approach for the synthesis of ε-caprolactam via the liquid phase nitrosation of cyclohexane and nitrosyl sulfuric acid in the presence of concentrated sulfuric acid has been developed. A series of novel AlVPO composites were prepared by an impregnation method and the composites were then employed to catalyze the nitrosation reaction of cyclohexane and nitrosyl sulfuric acid. Compared to the reaction using fuming sulfuric acid, the selectivity for the desired product was significantly improved using this one-step catalytic process. This method affords a shortcut to prepare ε-caprolactam and its analogs from cyclohexane.

Keywords cyclohexane, ε-caprolactam, AlVPO composite catalysts, one-step synthesis, concentrated sulfuric acid

1 Introduction

ε-Caprolactam is an important monomer for the production of nylon-6 and plastics. Most of the current commercial processes for ε-caprolactam production are based on benzene or toluene [1], as summarized in Scheme 1. Cyclohexanone oxime is also used as a starting material to produce caprolactam via a Beckmann rearrangement. However, this method suffers from the generation of large amounts of low-value ammonium sulfate waste, the corrosion of equipment as well as environmental pollution caused by fuming sulfuric acid. To overcome these problems, many research groups have extensively studied vapor-phase Beckmann rearrangements by using solid acid catalysts instead of fuming sulfuric acid [2–11]. However, vapor-phase reactions have their own drawbacks such as the requirement of a high temperature and the need to use a fluidized bed due to coke formation on the catalyst.

To develop a greener method, several groups have reported a procedure involving the ammoximation of cyclohexanone, NH3 and H2O2 catalyzed by TS-1 [12–14] with a subsequent Beckmann rearrangement of the formed cyclohexanone oxime. Thomas and Raja [15] reported a bifunctional molecular sieve catalyst for a one-step process to make ε-caprolactam from cyclohexanone using O2 and ammonia. This reaction showed very good selectivity and no by-products were formed.

Another industrial process for the production of ε-caprolactam employs cyclohexanecarboxylic acid as the starting material, which is prepared from toluene. This technique has many advantages such as the ready availability of the raw materials and easy operation. However, this method requires the removal of the carboxylic group in the final step which lowers its atom-economy.

Cyclohexane is a cheap and readily available organic compound and has the potential to serve as an ideal starting material for the preparation of ε-caprolactam. However, up to now, only Japan Toray Ltd. has reported a PNC (photonitrosation of cyclohexane) process [16]. In this process, cyclohexane reacts with nitrosyl chloride with the aid of UV radiation in the presence of hydrogen chloride to give cyclohexanone oxime hydrochloride. Compared to traditional thermochemical processes, this photochemical synthesis is very efficient in regards to the starting material cost. Also its overall selectivity for caprolactam is higher than those of the classical routes. However, the formation of NOCl and other chloro-containing compounds is very problematic and not environmentally benign. Therefore, the development of an efficient one-step synthesis of ε-caprolactam from the nitrosation or oximation of cyclohexane under mild conditions has long been desired by chemical industry (see Scheme 2).
Recently, a one-step procedure for the preparation of ε-caprolactam from cyclohexane under liquid phase nitrosation conditions by using nitrosyl sulfuric acid in the presence of fuming sulfuric acid was developed in our laboratory [17–22]. Unfortunately, the selectivity of the reaction was unsatisfactory, and a large amount of benzene sulfonic acid by-product was formed presumably due to the use of fuming sulfuric acid. Therefore, the selectivity of the reaction for ε-caprolactam needs to be improved. Herein, an efficient catalytic system for the selective preparation of ε-caprolactam via the liquid phase nitrosation of cyclohexane by using concentrated sulfuric acid instead of fuming sulfuric acid is reported.

2 Experiment

2.1 Reagents and instrument

Except where otherwise specified, all chemicals were analytical grade and used as received. Nitrosyl sulfuric acid (73.54%) was purchased from Shijiazhuang Chemical Co. Ltd. Concentrated sulfuric acid oleum (98%) was purchased from the Chemical Reagent Factory of Shanghai. High performance liquid chromatography (HPLC) was performed on an Agilent 1100 instrument with an Eclipse XDB-C18 (4.6 × 250 mm) column; Liquid chromatography-mass spectrometry (LC-MS) was run on a Surveyor Liquid Chromatograph coupled with a TSQ Quantum Discovery Max Triple Quadruple Mass Spectrometer (Thermo Electron Corporation, USA). The X-ray diffraction (XRD) patterns of various AlVPO composite catalysts were recorded with a Japanese Rigaku D/Max 2550 VB + 18 kW X-ray diffractometer, using nickel-filtered Cu Kα radiation with a scanning rate of 1°·min⁻¹.

2.2 Preparation of the composite catalysts

The AlVPO precursors were prepared according to our previous procedure [17]. Modified M/AlVPO (M = Cr, Mn, Co, Ni, Cu or Au) composite catalysts were prepared by impregnating the corresponding acetic salt (5.0 wt-% transition metal) into the AlVPO precursor. First, the corresponding acetic salt was dissolved in 20 mL of isobutanol. The resulting solution was then added to a previously prepared precursor and the suspension was allowed to deposit for 5 h at room temperature. After that, the mixture was dried at 373 K for 10 h. Finally, the samples were heated from room temperature to 773 K at a rate of 275 K·min⁻¹ in dry air and kept at this temperature for 5 h. All of these samples were activated in situ before characterization and evaluation of their performance.