Applied Catalysis A: General 379 (2010) 141–147

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Catalytic properties of WO_x/SBA-15 for vapor-phase Beckmann rearrangement of cyclohexanone oxime

Ankur Bordoloi [a,*], S.B. Halligudi [b,*]

[a] Centre for Catalysis Research and Innovation, Department of Chemistry, University of Ottawa, Ottawa, ON, K1N 6N5, Canada
[b] Emeritus Scientist (CSIR), Nanoscience Laboratory, C-MET, Panchawati off Pashan Road, Pune 411008, India

ARTICLE INFO

Article history:
Received 5 October 2009
Received in revised form 3 March 2010
Accepted 8 March 2010
Available online 15 March 2010

Keywords:
Beckmann rearrangement
WO_x/SBA-15
Vapor-phase reaction
Cyclohexanone oxime
ε-Caprolactam

ABSTRACT

WO_x/SBA-15 nanocomposite materials with different WO_x loadings were prepared by one step hydrothermal synthesis and used in the vapor-phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam. The catalysts were thoroughly characterized by X-ray diffraction (XRD), sorption analysis, energy dispersive X-ray analysis (EDAX) and Raman spectroscopy. The acidities of the catalysts were estimated by ammonia temperature programmed desorption (NH_3-TPD) and Fourier transform infrared studies of adsorbed pyridine (pyridine-FTIR). The optimum temperature for the Beckmann rearrangement was 350 °C. Using WO_x/SBA-15(20) under the vapor-phase reaction conditions [temperature = 350 °C, WHSV = 0.6 h^{-1}, oxime concentration = 2.5% (w/w) in MeOH] gave 79% cyclohexanone oxime conversion with 93%, ε-caprolactam selectivity. The ε-caprolactam selectivity was found to be dependent on temperature and space velocity. A correlation has been made between the rearrangement activity and acidity and the structural properties of the catalysts.

1. Introduction

ε-Caprolactam is a large volume commodity chemical used as a monomer in the production of the commercially important Nylon-6. It is produced on an industrial scale almost exclusively by Beckmann rearrangement of cyclohexanone oxime in concentrated sulphuric acid [1]. Although the process is highly selective, it has several disadvantages, including such as corrosion of the reactor system, environmental pollution caused by the use of fuming sulphuric acid and production of large amounts of ammonium sulphate as by-product resulting from the neutralization of sulphuric acid with ammonia. The negative environmental impact of this process motivated research toward the development of greener processes for the synthesis of caprolactam [2,3]. Consequently, gas phase Beckmann rearrangement of cyclohexanone oxime over solid acid catalysis has been studied over the last three decades as a potential green alternative. A number of solid acid catalysts such as silica–alumina [4], tungsten oxide [5], silica–tantalum oxide [6], titanium oxide [7], and boron–silica [8] have been used. Zeolites have also been applied for Beckmann rearrangement reactions [9,10]. These include mordenite [9], ZSM-5 [11], TS-1 [12], TS-2 [13], SAPO 11 [14], Beta, Y [9,15] and monolithic zeolite [16]. It was suggested that the strong Brönsted acidity of the zeolite catalyst enhances the formation of ε-caprolactam [10]. However, many researchers have observed that acid sites of weak or intermediate strength or even neutral silanol groups present on the external surface of zeolites are effective for this rearrangement [14,17–19], and that strong acid sites accelerate the formation of by-products [6,20]. Periodic mesoporous materials such as Si-MCM-41 and Al-MCM-41 were also investigated [21]. In particular, modified B-MFI zeolite and Nb-MCM-41 were found to be highly promising catalysts for gas phase Beckmann rearrangements [22].

There are few reports describing the use of mesoporous silica as a support for tungsten oxide species [23,24]. Zhang et al. [25] described the synthesis of tungsten-containing MCM-41 with good dispersion, however, the segregated crystalline WO_x were detected after mild thermal treatment. The crystalline phases of WO_x that form at low pH in the presence of H_2O_2 were prevented by the use of oxoperoxometalate precursors and the stability was poor, as evidenced by the extensive leaching of tungsten species [26]. Recently, atomic layer deposition (ALD) was used to graft tungsten oxide species onto mesoporous silica (SBA-15) [27]. Moreover WO_x-silicate nanocomposite has also been prepared using silico tungstic acid [28]. In our earlier investigation, we reported on the synthesis of WO_x/SBA-15 catalyst system [29]. Hence, we tried to evaluate the acidic properties of the catalysts and we applied the catalysts for gas phase synthesis of ε-caprolactam from cyclohexanone oxime. The catalytic data has been correlated with the catalyst properties. Furthermore, catalytic performance was investigated under optimum reaction conditions.

---

* Corresponding author. Tel.: +91 9637907056.
E-mail addresses: ankurankurbordoloi734@gmail.com (A. Bordoloi), sb_halligudi123@yahoo.co.in (S.B. Halligudi).

0926-860X/$ – see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.apcata.2010.03.017

2. Experimental

2.1. Materials and catalyst preparation

Sodium tungstate, cyclohexanone oxime, tetraethyl orthosilicate (TEOS), P123 (poly (ethylene glycol)–poly (propylene glycol)–poly (ethylene glycol) block copolymer, with average molecular weight of 5800, and solvents were purchased from Aldrich Chemicals and used as received.

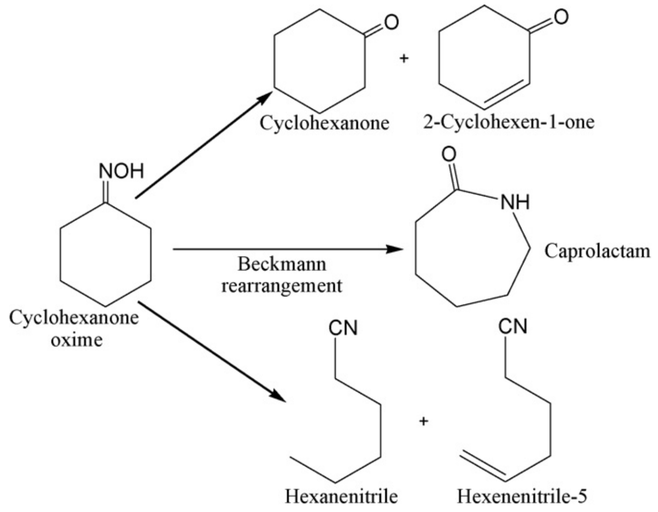
Hexagonally ordered mesoporous WO_x/SBA-15 nanocomposite materials were synthesized by using TEOS as a silica source and P123 as a structure-directing agent. In a typical synthesis, 4.0 g of P123 block copolymer was dissolved with stirring in a solution of 30 g of water and the required amounts (20, 10, 5 and 2.5 mL) of aqueous sodium tungstate solution ($NaWO_4 \cdot 2H_2O$, 0.5 M) were simultaneously and quickly added into the mixture under vigorous stirring. After 1 h, 120 g of HCl (2 M), and 9.1 g of TEOS were added with stirring at 40 °C. After 24 h of constant stirring, the gel composition was kept at 100 °C under static condition for 48 h. After being cooled to room temperature, the solid product was recovered by filtering, washing, drying and calcining at 550 °C. The nanocomposite samples were denoted as WO_x/SBA-15(x), where x is the volume of 0.5 M sodium tungstate solution used [29].

2.2. Catalyst characterization

Tungsten content of the catalyst was determined by energy dispersive X-ray analysis (EDAX) using a Microanalysis Phoenix system. Nitrogen adsorption and desorption isotherms were measured at −196 °C with a Micromeritics ASAP 2020 adsorption analyzer. The samples were out gassed for 3 h at 250 °C under vacuum prior to adsorption measurements. The specific surface area was calculated using the BET model. The pore size distributions were obtained from the adsorption branch of the nitrogen isotherms by the Barrett–Joyner–Halenda (BJH) method with Kruk–Jaroniec–Sayari (KJS) correction [30]. The X-ray diffraction (XRD) patterns of the samples were collected on a Philips X'Pert Pro 3040/60 diffractometer using CuKα radiation ($\lambda = 1.5418$ Å), iron as the filter, and X'celerator as the detector. For high temperature XRD, the data quality of the scan was comparatively good, because the X'celerator detector uses real time multiple strip technology to enhance both the resolution and the intensity of the reflection.

The total amount of acid sites present on the catalysts was evaluated by temperature-programmed desorption (TPD) of NH_3. The NH_3-TPD measurements were performed on an Altamira instrument (AMI-200). A sample weight of ca. 90 mg was loaded in a U-shaped quartz reactor and pretreated in flowing He (50 mL/min) at 300 °C for 1 h. After cooling the sample to 100 °C, we exposed it to ammonia flowing at 50 mL/min. The material was heated to a final temperature of 550 °C at a ramping rate of 10 °C/min. The ammonia consumption was measured by a thermal conductivity detector. Ammonia pulse calibration was performed after each TPD experiment for the quantification of TPD data.

The nature of the acid sites (Brönsted and Lewis) of the catalyst samples were characterized by *in situ* FTIR spectroscopy of chemisorbed pyridine. Circular self-supported wafers of the catalyst samples were prepared while applying 60,000 N/m^2 pressure. Each sample was subjected to vacuum in a glass IR cell until a pressure of 10^{-6} mbar was attained, followed by activation at 300 °C then each sample was cooled to 100 °C. Pyridine vapor was admitted in doses until the catalyst surface is saturated. Pyridine was then desorbed until a pressure of 10^{-6} mbar at a temperature of 200 °C to ensure that there was no more physisorbed pyridine on the wafers. Fourier transform infrared spectra (FTIR) we used were recorded in a Nicolet-Magna 550TM. To follow the Beckmann rearrangement by FTIR, a high temperature DRIFT cell (spectro tech) with CaF_2 windows. Each WO_x/SBA-15 sample was out gassed at 500 °C under vacuum for 2 h. The sample was then cooled to room temperature and one drop of 2.5% of cyclohexanone oxime ethanol solution was added under He gas flow. The sample was then heated at 300 °C (reaction temperature) over time under He gas flow while FTIR spectra was recorded.



Scheme 1. Schematic representation of Beckmann rearrangement of cyclohexanone oxime.

2.3. Beckmann rearrangement of cyclohexanone oxime

The catalytic reactions were carried out in an up flow fixed bed tubular stainless steel reactor (i.d. = 10 mm and 24 cm length) at atmospheric pressure using 2 g of catalyst. The catalyst was compacted in a hydraulic press, and the pellets were broken and then sieved to 16–20 mesh size prior to use. The reactor was placed inside a temperature controlled vertical furnace. The thermocouple tip was centered at the middle of the catalyst bed. A solution of cyclohexanone oxime (2.5 wt.%) in methanol was fed using a high pressure pump (Eldex, US). The weight hourly space velocity (WHSV) was calculated based on the oxime solution injected. The catalyst was activated *in situ* in a flow of N_2 (20 mL/min) at 500 °C for 6 h. The reactor outlet was connected to a cooling trap containing ice; and the collected liquid effluent taken at specified intervals was analyzed using a Hewlett-Packard gas chromatograph (5880A) with a capillary column (cross-linked methyl silicone gum, HP1, 50 m × 0.2 mm i.d.) and a flame ionization detector (FID). The product identification was achieved by GCMS (Agilent). Regeneration of the catalyst was done by calcination at 500 °C for 8 h under N_2 flow. A schematic representation of the Beckmann rearrangement of cyclohexanone oxime is given in Scheme 1.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. X-ray diffraction

The wide and low angle XRD patterns of WO_x/SBA-15 catalysts with different loadings are shown in Fig. 1(A and B), respectively. All wide angle diffraction peaks were indexed to monoclinic WO_3 as reported on JCPDS Card No. 83-0951 (Fig. 1(A)). Moreover, low angle XRD measurements showed that WO_x/SBA-15 materials exhibited three peaks at 2θ in the range 0.5–5°; these can be indexed to (1 0 0), (1 1 0), and (2 0 0) reflections of the hexagonal *p*6*mm* space group. The observation is in good agreement with the XRD pattern of pure hexagonally ordered SBA-15 material reported