



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

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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 (NH₃-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.

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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 Brønsted 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 H₂O₂ 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.

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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.

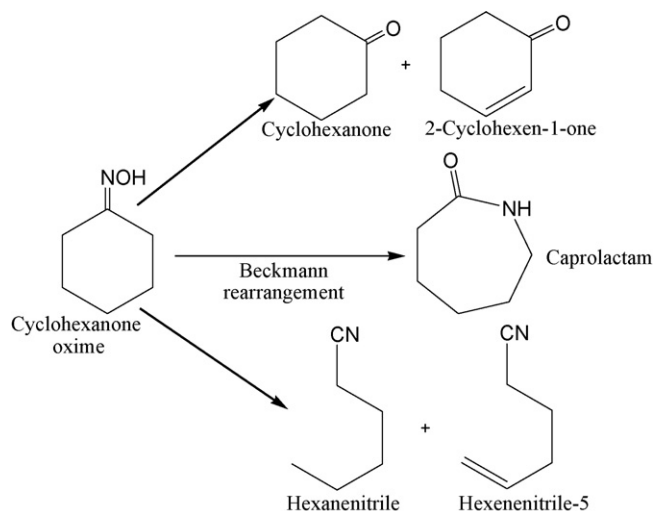
Hexagonally ordered mesoporous $\text{WO}_x/\text{SBA-15}$ nanocomposite materials were synthesized by using TEOS as a silica source and P123 as a structure-directing agent. In a typical synthesis, 4.0 g of P123 block copolymer was dissolved with stirring in a solution of 30 g of water and the required amounts (20, 10, 5 and 2.5 mL) of aqueous sodium tungstate solution ($\text{NaWO}_4 \cdot 2\text{H}_2\text{O}$, 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 $\text{WO}_x/\text{SBA-15}(x)$, 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 $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), 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 (Brønsted 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)



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

with CaF_2 windows. Each $\text{WO}_x/\text{SBA-15}$ 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.

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 \times 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 $\text{WO}_x/\text{SBA-15}$ 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 $\text{WO}_x/\text{SBA-15}$ 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 $p6mm$ space group. The observation is in good agreement with the XRD pattern of pure hexagonally ordered SBA-15 material reported

Table 2
Product distribution of Beckmann rearrangement over $WO_x/SBA-15(20)$ catalyst systems.

Catalyst	Conversion (wt.%)	Selectivity (%)				
		Caprolactam	Hexanenitrile	Hexenenitrile-5	Cyclo hexanone	2-Cyclo-hexen-1-one
SBA-15	36	–	6	14	32	48
$WO_x/SBA-15(2.5)$	47	53	11	–	23	13
$WO_x/SBA-15(5)$	59	66	5	–	19	10
$WO_x/SBA-15(10)$	71	81	3	–	11	6
$WO_x/SBA-15(20)$	79	93	2	–	2	3

Reaction conditions: temperature 350 °C, WHSV = 0.6 h⁻¹, carrier gas (N₂) 20 mL/min oxime concentration 2.5% in MeOH, 3 h, and catalyst 2 g.

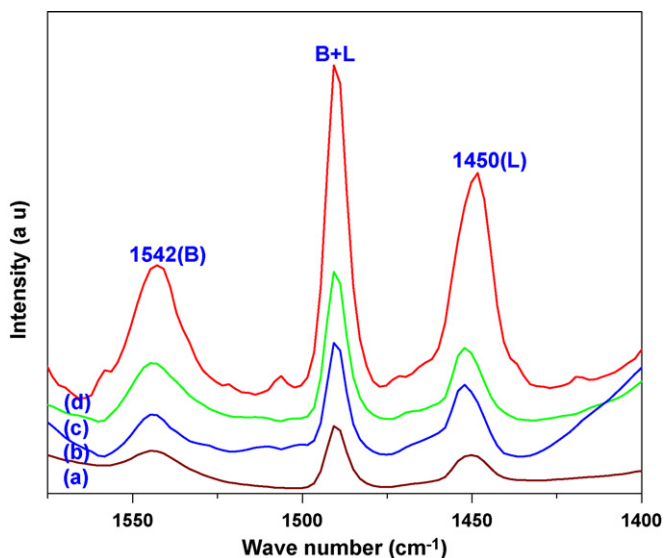


Fig. 3. Pyridine FTIR of $WO_x/SBA-15$ with different concentration of WO_x : (a) $WO_x/SBA-15(2.5)$, (b) $WO_x/SBA-15(5)$, (c) $WO_x/SBA-15(10)$, and (d) $WO_x/SBA-15(20)$.

3.2. Catalytic activity

The product distributions over catalysts of different tungsten contents with methanol as the solvent are depicted in Table 2. The catalyst activity and product distributions attained an equilibrium stage after 3 h, which is consistent with the results of other researchers [21,22]. Therefore all experimental data were collected after the stabilization of the activity. The main product was found to be ϵ -caprolactam. The maximum conversion of cyclohexanone oxime was 79%; this value remained almost constant with time on stream (TOS) up to 10 h (Fig. 4(A)) at temperature of 350 °C. Among the catalysts $WO_x/SBA-15(20)$ showed the highest caprolactam selectivity. Thus, this catalyst was used for further study of different reaction parameters on the conversion of oxime and selectivity toward different products.

3.2.1. Effect of temperature

The effect of temperature on selectivity to ϵ -caprolactam over different catalysts is presented in Fig. 4(B). The rearrangement was studied in the temperature range 250–400 °C. The transformation of oxime was rapid over the catalysts and reached 79% at temperatures >300 °C (Fig. 4(A)) and remained the same thereafter. At low temperature, C–C cleavage products hexanenitrile and hexenenitrile-5 were predominant in the reaction; this result could be due to dehydration/thermal cracking of oxime. The decrease

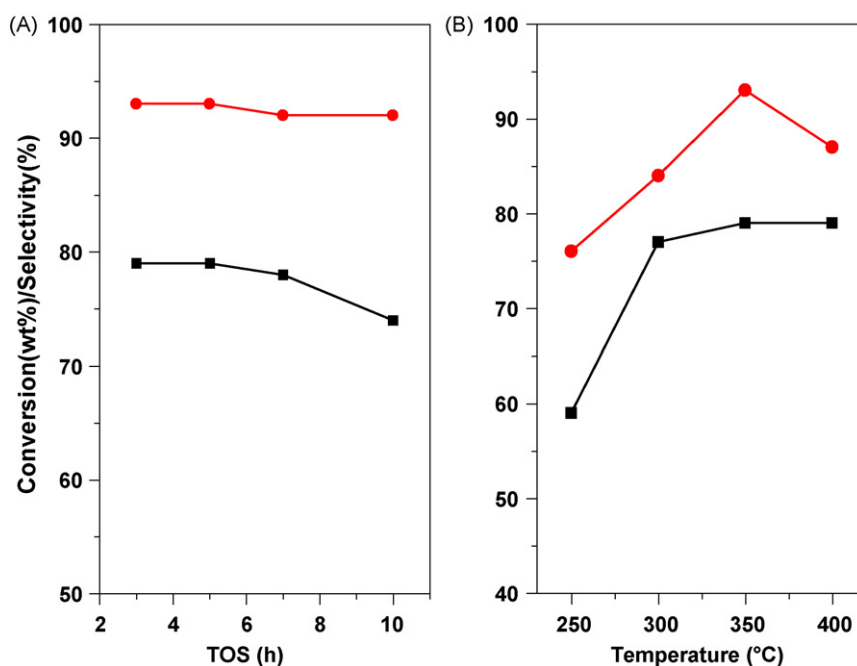


Fig. 4. (A) Influence of time on stream (TOS) on the oxime conversion and selectivity of caprolactam with $WO_x/SBA-15(20)$. Conditions 350 °C, WHSV = 0.6 h⁻¹, carrier gas (N₂) 20 mL/min oxime concentration 2.5% in MeOH and catalyst 2 g ($WO_x/SBA-15(20)$). (B) Influence of temperature on the oxime conversion and selectivity of caprolactam with $WO_x/SBA-15(20)$. Conditions WHSV = 0.6 h⁻¹, carrier gas (N₂) 20 mL/min oxime concentration 2.5% in MeOH, 3 h and catalyst 2 g ($WO_x/SBA-15(20)$) (■: conversion and ●: selectivity).

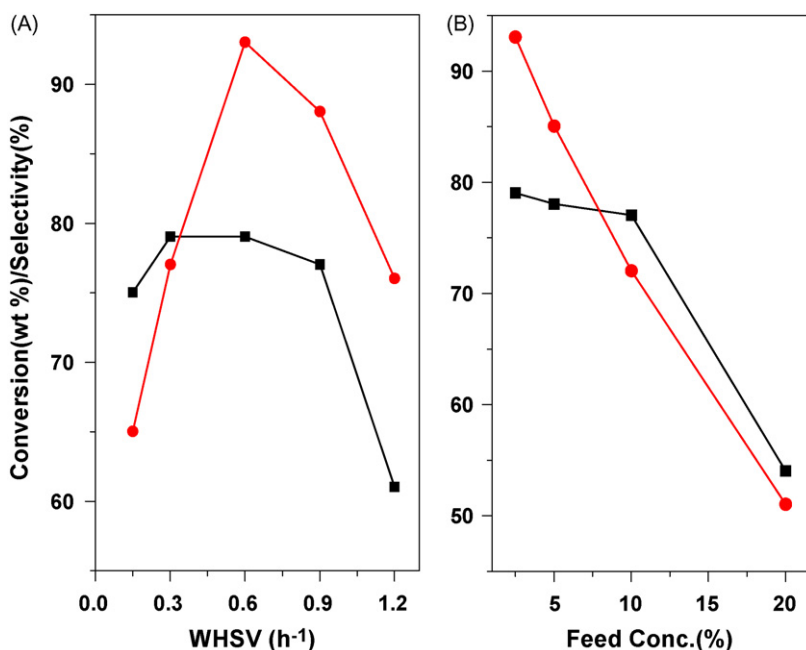


Fig. 5. (A) Influence of WHSV on oxime conversion and selectivity of caprolactam with $\text{WO}_x/\text{SBA-15(20)}$. Conditions carrier gas (N_2) 20 mL/min oxime concentration 2.5% in MeOH, 3 h and catalyst 2 g($\text{WO}_x/\text{SBA-15(20)}$). (B) Influence of feed concentration (%) on oxime conversion and selectivity of caprolactam with $\text{WO}_x/\text{SBA-15(20)}$. Conditions 350 °C, carrier gas (N_2) 20 mL/min oxime concentration in MeOH, 3 h and catalyst 2 g($\text{WO}_x/\text{SBA-15(20)}$) (■: conversion and ●: selectivity).

in caprolactam selectivity at high temperature was also observed, which is probably due to decomposition of ϵ -caprolactam on the catalyst surface and enhancement of the side reactions [21]. Pure siliceous SBA-15 did not show any formation of caprolactam; rather it showed more formation of cyclohexanone (Table 2), which could be due to the presence of neutral surface silanol groups in SBA-15 [21].

3.2.2. Effect of WHSV

The influence of WHSV of the feed on conversion and selectivity to the products over WSBA-15(20) catalyst at 350 °C is illustrated in Fig. 5(A). While the catalyst weight is kept at 2 g, the WHSV was varied in the range 0.15–1.2 h⁻¹ by changing the feed rate. There is a marginal increase of oxime conversion from 74 to 79% that is observed with increasing the WHSV of the feed from 0.15 to 0.6 h⁻¹. The best selectivity of caprolactam was observed at an intermediate WHSV value of 0.6 h⁻¹ (93%).

3.2.3. Effect of feed concentration

It was observed that the dilution of the cyclohexanone oxime in methanol improves the oxime conversion and the caprolactam selectivity (Fig. 5(B)). At low concentration of oxime (2.5 wt.%), the yield of caprolactam was found to be high. At high oxime concentration (20 wt.%), however, the formation of by-products (cyclohexanone and hexanenitrile) was observed in higher amounts, which could be due to faster deactivation of acid sites in the catalyst system [35].

3.2.4. Effect of solvent

The influences of various solvents such as methanol, acetonitrile and benzene on the performance of $\text{WO}_x/\text{SBA-15}$ in cyclohexanone oxime rearrangement were studied, keeping all other parameters constant. An interesting solvent effect has been observed for the selectivity of caprolactam. In the presence of solvents like methanol and acetonitrile, the selectivity of caprolactam was found to be higher than that of benzene, which could be due to the basicity of the solvents. The basic solvents either reduces the acidity of the catalyst system or raise the desorption rate of caprolactam; the pro-

cess is not able to provide sufficient contact time on the surface, and this lowers the probability for acid catalyzed opening of caprolactam to form polymers on the catalyst surface, thus allowing coke formation [5].

Based on the acidic properties obtained from NH_3 -TPD, one could mention that the increase in oxime conversion with WO_x loading could be due to the increase in total acidity. The results were concomitant with the earlier reports that Beckmann rearrangement takes place over Brønsted acid sites of intermediate strength. Conversion of oxime being almost the same, the selectivity of caprolactam depends on reaction variables and is inversely related to side products formation due to the competitive nature of formation of side products from the oxime.

3.3. In situ FTIR study of Beckmann rearrangement of cyclohexanone oxime

The objective of the Beckmann rearrangement by performing *in situ* reactions within the infrared cell is in order to confirm the occurrence of a Beckmann rearrangement of cyclohexanone oxime in presence of $\text{WO}_x/\text{SBA-15}$. For the pure cyclohexanone oxime, there is a strong peak at 1663 cm⁻¹ (C=N group vibration), which is assigned to be the characteristic band of cyclohexanone oxime (Fig. 6(a)) [36]. After 5 min of heating the sample at 300 °C, a new peak appeared at 1631 cm⁻¹ may be attributed to C=O group, which could be assigned to characteristic band for ϵ -caprolactam (Fig. 6(b)) [36]. The C=O peak intensity was found to increased with the time and finally the C=N peak of cyclohexanone oxime disappeared after 180 min (Fig. 6(f)). This means that the Beckmann rearrangement of cyclohexanone oxime to caprolactam did occur in presence of $\text{WO}_x/\text{SBA-15}$ catalyst system only.

4. Catalyst regeneration

To study the regeneration of the catalyst system, we conducted experiment on a deactivated $\text{WO}_x/\text{SBA-15}$ catalyst under non-oxidative gas, N_2 for three recycles. The results based on oxime conversion and caprolactam selectivity are depicted in Fig. 7. The

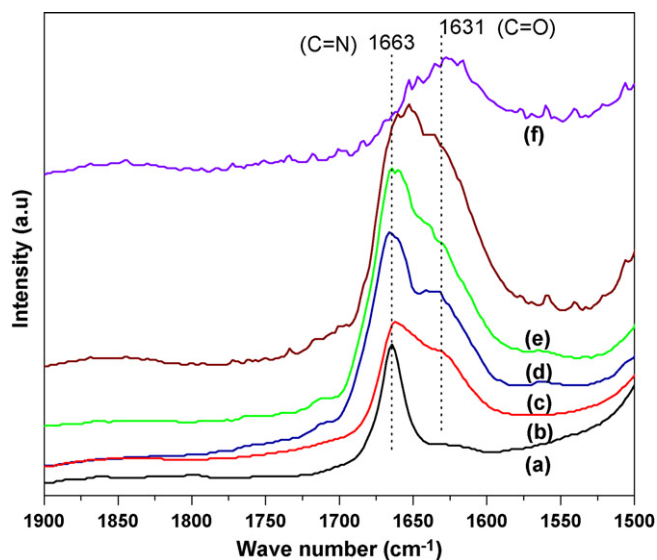


Fig. 6. *In situ* FTIR study of Beckmann rearrangement of cyclohexanone oxime over WO_x/SBA catalyst (a) cyclohexanone oxime adsorbed catalyst ($25^\circ C$), (b) after 5 min at $300^\circ C$ (c) after 30 min at $300^\circ C$, and (d) after 60 min at $300^\circ C$, (e) after 120 min at $300^\circ C$, (f) after 180 min at $300^\circ C$.

regeneration study under N_2 showed almost constant activity for three consecutive cycles. When the catalyst was regenerated in N_2 at $500^\circ C$ for 8 h, the original activity was completely recovered. The main reason for deactivation of the catalyst could be blockage of active sites by coke/oligomers. These oligomers, which are formed by ring opening reactions, can be eliminated with nitrogen at high temperature. The regeneration studies under N_2 indicated that the deactivation is reversible. Moreover, the catalyst system could be regenerated using high temperature according to the literature reports [29,37,38].

We also performed low angle PXRD experiments on the catalyst system after regeneration to check the stability. Fig. 8(a and b) shows low angle PXRD patterns of the $WO_x/SBA-15(20)$ fresh (Fig. 8(a)) and regenerated (Fig. 8(b)) samples. The powder pattern of the sample obtained after regeneration was similar to that of fresh sample with minimal decrease in the peak intensities, indicating negligible structural destruction. The above experiment confirms that $WO_x/SBA-15$ catalyst system could be effectively

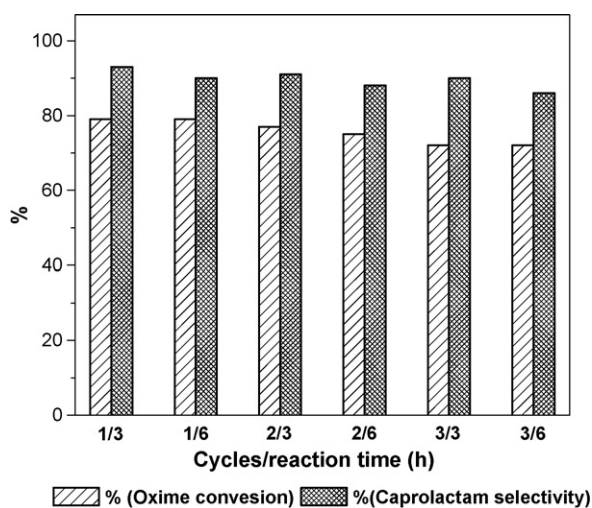


Fig. 7. Catalyst recycle studies under N_2 with $WO_x/SBA-15(20)$. Conditions $350^\circ C$, $WHSV = 0.6 h^{-1}$, carrier gas (N_2) 20 mL/min oxime concentration 2.5% in MeOH, catalyst 2 g, regeneration condition under N_2 at $500^\circ C$ for 8 h.

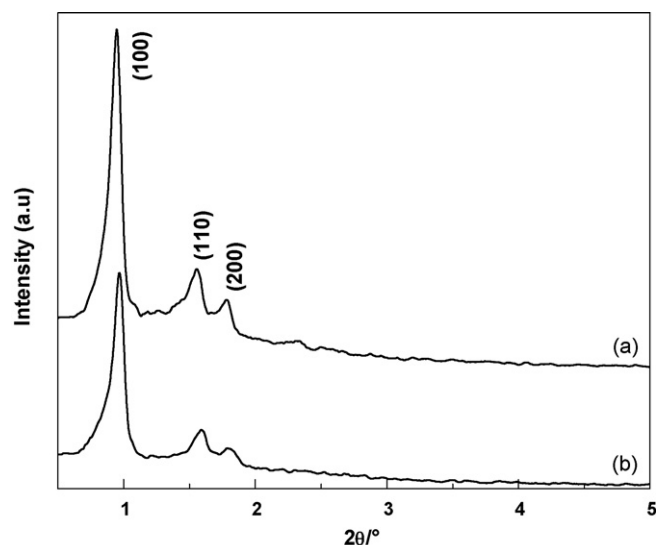


Fig. 8. X-ray diffraction patterns of (a) fresh $WO_x/SBA-15(20)$ and (b) regenerated $WO_x/SBA-15(20)$.

decoated at higher temperature without any substantial mesoporous structural changes.

5. Conclusions

Vapor-phase Beckmann rearrangement of cyclohexanone oxime to ϵ -caprolactam was successfully carried out over solid acid catalyst $WO_x/SBA-15$ with excellent conversion and good selectivity. Selectivity for caprolactam increased with TOS and reached a maximum at 3 h. ϵ -Caprolactam selectivity was found to be 93%, the highest value, with 79% oxime conversion for $WO_x/SBA-15(20)$ at $350^\circ C$ and $WHSV 0.6 h^{-1}$. Pyridine FTIR studies confirmed that the catalyst system contains both Lewis and Brønsted acid sites. The regeneration study has shown that the catalyst system can be regenerated in a non-oxidative gas N_2 and reactions can be carried out without significant loss of catalytic activity. The reaction was environmentally friendly due to the almost complete reuse of the catalyst and of the solvent, without any inconvenience.

Acknowledgements

Ankur Bordoloi gratefully acknowledges Catalysis Centre for Research and Innovation, Department of Chemistry, University of Ottawa, Canada for financial support and instrument facilities. Dr. S.B. Halligudi acknowledges the support of C-MET, Pune.

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