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1 Introduction

The Beckmann rearrangement of cyclohexanone oxime to ε -caprolactam is an important process in the production of polyamide 6, better known under the trade name 'nylon 6'. Its monomer, ε -caprolactam, is one of the fifty most important bulk chemicals in the world, with an estimated annual production of more than 4.4 million tonnes worldwide.¹ The standard catalyst used in industrial plants for the oxidation and rearrangement is fuming sulphuric acid, where ammonia is used to neutralize the product mixture. The disadvantage of this procedure is the

Niobium doped hexagonal mesoporous silica (HMS-X) catalyst for vapor phase Beckmann rearrangement reaction[†]

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The synthesis of ε -caprolactam, a demanding monomer, through a heterogeneous catalytic pathway has remained a key area of research in the last decade. The Beckmann rearrangement reaction in the vapor phase using a solid acid catalyst was found to be very effective for producing ϵ -caprolactam. It is observed that niobium incorporated into mesoporous silica serves as a good catalyst for the Beckmann rearrangement reaction. Recently developed mesoporous silica, having an ordered honeycomb structure, is very useful as it can lead to effective diffusion of reactants and products for several reactions. In this study, Nb-doped mesoporous HMS-X nanocomposite materials with different Nb loadings were prepared by a one step hydrothermal synthesis and characterized by BET surface area and porosity measurements, wide and small angle XRD, SEM, HR-TEM, elemental mapping, FTIR, ²⁹Si-NMR and NH₃-TPD techniques. The activity of the Nb-HMS-X catalyst was evaluated for the vapour phase Beckmann rearrangement reaction. The catalyst characterization study shows that Nb is highly dispersed on the HMS-X matrix at lower Nb loadings. At higher Nb loadings it is present in the extra-framework position as revealed from XRD, HR-TEM and ²⁹Si-NMR studies. The NH₃-TPD result shows the presence of acidic sites on the catalyst surface, which are active sites for the Beckmann rearrangement reaction. Using the Nb-HMS-X catalyst (Si/Nb = 13) under vapour-phase reaction conditions [temperature = 350 °C, weight hourly space velocity (WHSV) = 15 h⁻¹, cyclohexanone oxime in benzene, cyclohexanone oxime : benzene weight ratio of 1:11] gave 100% cyclohexanone oxime conversion with 100% ϵ -caprolactam selectivity, with a space time yield of 1.4–1.6 \times 10⁻³ mol h⁻¹ gcat⁻¹. The catalyst was highly recyclable up to 9 times without significant loss of catalytic activity.

enormous production of ammonium sulphate, as high as 1.9 tons per ton of product,² causing some ecological concerns in addition to an economical drawback. Starting with the optimization and reengineering of the old reaction pathways, important producers nowadays focus their efforts on new synthetic routes. A solution to the problem, even for the world scale plants, could be to change from homogeneous to heterogeneous catalysis, wherein, due to vapour phase reactions, the catalytic material need not be separated and can be used after recycling.³

Metal oxides can be used as catalysts, alone or in combination with other materials during vapour phase catalytic reactions. It is believed that a mixture of oxides brings out a combined effect or a sort of synergistic behaviour enhancing the catalytic activity.⁴ Early studies showed that such diverse materials as tungsten oxide,⁵ and tantalum oxide⁶ are active for vapour phase Beckmann rearrangement. Recently Mao *et al.* reported B₂O₃/TiO₂– ZrO₂ as an effective catalyst for vapour phase Beckmann rearrangement,⁷ suggesting that doped oxide catalysts are more promising in catalytic reactions than pure metal oxides. Guo *et al.*⁸ demonstrated that silica-pillared layered niobic acid can be



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an efficient catalyst for the vapour phase Beckmann rearrangement reaction in the presence of 1-hexanol.

After the discovery of mesoporous silicious and non-silicious groups of materials, several catalytic systems were reported for the synthesis of fine chemicals.⁹⁻¹² The report by Schüth *et al.* showed that acid treated SBA-15¹³ had an activity to produce ε -caprolactam from cyclohexanone oxime and revealed the necessity of acidic sites for the reaction. The incorporation of niobium into mesoporous silica has been widely reported for Beckmann rearrangement, where more acidity can be generated resulting in better catalytic activity.^{14,15}

The recently developed ordered mesoporous material with a hexagonal honeycomb structure¹⁶ and high thermal stability is used for versatile catalytic applications. In this study we assumed that incorporation of niobium into the mesoporous silica framework would generate more acidic sites and might result in better catalytic activity towards the Beckman rearrangement reaction.^{14,17} We prepared Nb-doped HMS-X materials with three different Si/Nb ratios and characterized them by BET surface area and porosity measurements, XRD, SEM, HR-TEM, FTIR, elemental mapping, ²⁹Si-NMR and NH₃-TPD techniques. The catalytic activity for the Beckmann rearrangement reaction was determined in a fixed bed reactor operating at atmospheric pressure. The catalyst characterization results have been correlated with the activity studies, where the optimum catalyst composition for a higher space time yield of ε-caprolactam was obtained.

2 Experimental

2.1 Catalyst preparation

Hexagonally ordered mesoporous Nb-HMS-X nanocomposite materials were synthesized by using triblock copolymer as a template under acidic conditions. In this synthetic procedure, Pluronic P123 (Aldrich) (4 g) was dissolved in 150 mL distilled water and 7-8 g 35% HCl (Merck) by continuous stirring. After 4 h of stirring a clear solution was obtained and then 4 g n-butanol (Merck) was added to this solution and the stirring continued for 1 h. Then tetraethyl orthosilicate (8.4 g) (TEOS, Acros) and an ethanolic solution of niobium pentachloride (0.81 g) (Aldrich) were added to this solution. The resulting gel composition of the mixture was $P123 : H_2O : HCl : n$ -butanol : TEOS : NbCl₅ = 0.017: 200: 5.4: 1.325: 1: 0.075 (molar ratio) and it was stirred for 24 h at room temperature. Then the mixture was taken in a closed polypropylene bottle and aged at 100 °C for 24 h under static hydrothermal conditions. After hydrothermal treatment the material was filtered in hot conditions without washing and then dried at 100 °C for 12 h in air, followed by calcination at 540 °C for 24 h. The final material obtained after calcination was stored in a vacuum desiccator. The gel composition and thermal treatment of the different samples are shown in Table S1 (ESI[†]).

The Nb-HMS-X was silvlated following the procedure reported in the literature.¹⁸ Before silvlation, the Nb-HMS-X material was dried at 200 °C under vacuum. After vacuum drying, 1 g Nb-HMS-X was suspended in 15 mL anhydrous toluene. Then 0.652 g hexamethyldisilazane (HMDS, Aldrich)

was added and the whole mixture was stirred for 7 h at 120 $^{\circ}$ C under Ar atmosphere. After complete stirring the material was filtered and washed with anhydrous toluene along with anhydrous ethanol.

2.2 Catalyst characterization

2.2.1 BET surface area and porosity measurements. The BET surface area and pore size analysis of the samples was measured at liquid nitrogen temperature with a Quantachrome Autosorb-1C-TPD at 77 K. Pre-treatment of the samples was done at 473 K for 3 h under high vacuum. The surface area was determined by the Brunauer–Emmett–Teller (BET) equation. Pore size distributions were calculated using the NLDFT (Non-linear Density Functional Theory) model of cylindrical pore approximation.

2.2.2 X-ray diffraction (XRD). The small and wide angle X-ray diffraction (SWAX) analysis was carried out by using a Bruker AXS D-8 advance diffractometer operated at a 40 kV voltage and 40 mA current and calibrated with a standard silicon sample, using Ni-filtered Cu K_{α} ($\lambda=0.15406$ nm) radiation.

2.2.3 Scanning electron microscopy (SEM). The SEM images were obtained from a Hitachi S-3400N. The powder samples were supported on lacey carbon and then coated with gold by plasma treatment prior to measurement.

2.2.4 High resolution transmission electron microscopy (HR-TEM) and elemental mapping. The HR-TEM investigation was done on a JEOL JEM 2100 microscope operated at a 200 kV acceleration voltage using a lacey carbon coated Cu grid of 300 mesh size. The STEM-EDS used was from Oxford Instruments (model x-sight).

2.2.5 Fourier transform infrared spectroscopy (FTIR). The FTIR measurements were carried out using a Perkin Elmer GX spectrophotometer. The spectra were recorded in the range $400-4000 \text{ cm}^{-1}$ using a KBr pellet.

2.2.6 Magic-angle spinning nuclear magnetic resonance (MAS NMR). ²⁹Si MAS NMR was recorded at 500 MHz on a Bruker advanced II-500 spectrometer equipped with a magic angle spin probe at room temperature.

2.2.7 Temperature programmed desorption (TPD). TPD profiles of the samples were recorded with a ChemiSorb 2720 (Micrometrics, USA) equipped with a thermal conductivity detector (TCD). The TPD was carried out by first heating under He flow from room temperature to 350 °C for 30 minutes. The dried catalysts were cooled to ambient temperature. The NH₃-TPD profile was obtained by a temperature programme under 4% NH₃ in He with a flow rate of 20 mL min⁻¹ raising the temperature from ambient to 1000 °C at a rate of 10 °C min⁻¹. The amount of NH₃ desorbed in the TPD peak area was evaluated by pulses of NH₃ in a flow of He.

2.3 Catalytic activity for the Beckmann rearrangement reaction

The catalytic reaction was carried out in a fixed bed catalytic reactor (quartz made, 1.5 cm inner diameter). The catalyst, Nb–HMS-X (85 mesh size), was packed into the reactor and then pre-

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treatment was carried out by flowing air (moisture free, 30 mL \rm{min}^{-1}) at 500 °C for 5 h. After pre-treatment the reactor was cooled to the desired reaction temperature and then N₂ gas (purity 99.999%, 30 mL min⁻¹) was passed through the catalyst bed for 15 min. To prepare the feed mixture, cyclohexanone oxime (CHO, Acros) was dissolved in anhydrous benzene (CHO : benzene weight ratio of 1 : 11). The solution was injected into the reactor by a piston pump (B/BRAUN) along with N₂ (purity 99.999%) as a carrier gas (30 mL min⁻¹). The reactor outlet was connected to a cooling trap, which was immersed into a salt-ice freezing mixture. The reactor effluent was collected at different time intervals and analyzed by a gas chromatograph (CIC, India) equipped with a flame ionization detector and SE-30 column.

3 Results and discussion

3.1 Catalyst characterization

3.1.1 Nitrogen sorption isotherms. The BET surface area and porosity measurement results are depicted in Fig. 1, and show a decrease in surface area, pore volume and pore diameter with an increase in Nb loading on the HMS-X matrix. The N₂ adsorption isotherm for the calcined siliceous HMS-X showed a sharp inflection at a relative pressure in the range of 0.6–0.75, indicative of a highly mesoporous material.¹⁹ The shape of the N₂ adsorption isotherm of the Nb–HMS-X (Si/Nb = 13) sample was similar to that of the original HMS-X except for some reduction in the height of the hysteresis loop and the surface area, and the pore diameter remained almost the same as it is in HMS-X [9.5 nm for HMS-X and 9.3 nm for Nb–HMS-X (Si/Nb = 13)]. This suggests that niobium occupies some of the Si atom sites of the porous architecture of HMS-X. Upon increasing the Nb loading, a not sharp but steep inflection at a lower pressure range was observed in the case of Nb–HMS-X (Si/Nb = 3 or 2), together with a gradual decrease in the surface area and pore diameter. This indicates the formation of niobium oxide species at the surface of the mesopores for the Nb-rich samples.¹⁴

3.1.2 X-ray diffraction. The small angle XRD patterns of the Nb–HMS-X catalysts with different Nb loadings are shown in Fig. 2. The XRD patterns show excellent structural order with



Fig. 2 Low angle XRD patterns of HMS-X and Nb-HMS-X catalysts with different Nb loadings.



Fig. 1 Surface areas, pore volumes and pore dimensions of (a) Nb–HMS-X (Si/Nb = 2), (b) Nb–HMS-X (Si/Nb = 3), (c) Nb–HMS-X (Si/Nb = 13) and (d) HMS-X only.

highly ordered hexagonal pore apertures for HMS-X and Nb-HMS-X (Si/Nb = 13).²⁰ The structural ordering of HMS-X and Nb-HMS-X (Si/Nb = 13) was confirmed by the presence of basal peaks corresponding to (100) at 2θ = about 1° with several higher order reflections corresponding to (110), (200), (210) in the region $2\theta = 1.5-2^{\circ}$.^{19,21,22} Here we have used a Fourier-based deconvolution/convolution method to determine the position of the peak maximum. The unit cell values are determined through REFLEX and CELSIZ unit cell fitting programs. As the level of Nb metal loading was increased up to (Si/Nb = 2 or 3), the basal diffraction peak (110) of the HMS-X material disappeared and the peak at the lower 2θ value broadens compared with the undoped siliceous HMS-X and the Nb-HMS-X (Si/Nb = 13) materials. This decrease in basal plane spacing upon higher Nb loading compared to the Nb-HMS-X (Si/Nb = 13) analogue confirms the presence of niobium on the outside of the silicate framework. From HMS-X to Nb-HMS-X (Si/Nb = 13), the Nb atoms are incorporated inside the porous silicate framework by replacing the structural Si atoms of the porous architecture. Hence, due to the large atomic size of Nb compared to Si, the d spacing (which corresponds to the (100) plane) increases with the increment of the pore wall thickness (D). But when the concentration of niobium increases to a very high level (Si/Nb = 2 or 3), Nb is no longer incorporated into the mesoporous silicate framework and is rather deposited outside the porous framework of the material. This is reflected in the lower value of d (interplanar spacing) and higher pore wall thickness (D). The results of the small angle powder XRD patterns of the Nb-HMS-X samples are shown in Table 1. The Nb-HMS-X (Si/Nb = 13) sample showed the highest Nb incorporation as its unit cell is much higher than the other samples. For the Nb-HMS-X (Si/ Nb = 2 or 3) catalysts, the hexagonal order has been lost and the wall thickness increases gradually with increasing Nb concentration. These results also support the BET analysis and HR-TEM analysis. For the HMS-X and Nb-HMS-X (Si/Nb = 13) samples, both the materials have type-IV isotherms with a strong capillary uptake for the adsorbed gas at relatively high pressure (0.6-0.75), suggesting the presence of ordered mesopores in the framework, but for the Nb-HMS-X (Si/Nb = 2 or 3) materials no such capillary condensation is observed and this confirms that the hexagonal ordering of the pores is disturbed in the Nb-HMS-X (Si/Nb = 2 or 3) samples.

The wide angle XRD patterns of the Nb–HMS-X materials with different Nb loadings are depicted in Fig. 3. For the Nb–

Table 1 Quantitative analysis of the small angle XRD patterns of the Nb-HMS-X catalysts



Fig. 3 Wide angle XRD patterns of HMS-X and Nb-HMS-X catalysts with different Nb loadings.

HMS-X material with the lower Nb loading, the absence of diffraction at higher 2θ values, corresponding to niobium oxide, indicated that niobium is present either well dispersed with less than 2 nm size in the framework of HMS-X or attained as an XRD amorphous form outside the framework.¹⁴

3.1.3 SEM and HR-TEM micrographs. SEM analysis was carried out for all the catalysts and the SEM images are depicted in Fig. 4. An interconnected network, with particles of similar size (\sim 2–3 µm) with a wormlike morphology, was observed in the Nb–HMS-X (Si/Nb = 13) catalyst, as depicted in Fig. 4(a). The presence of interconnections between the hexagonal pore channels could be observed clearly. However, the shape of the particles in the Nb doped HMS-X materials depends on the Nb/Si ratio during synthesis. Fig. 4(b) and (c) imply that on increasing Nb loading the shape of the particles becomes much more irregular.

The HR-TEM images of the Nb–HMS-X catalysts are depicted in Fig. 5. They show an ordered hexagonal structure, which is highly crystalline in nature. The parallel layer by layer assemblies are observed in the higher magnification HR-TEM images. These observations agree with the N₂-adsorption and XRD results described earlier.²³ With Si/Nb = 2 loading, the dark spots observed at higher magnification might be due to the presence of Nb₂O₅ on the framework of the silica matrix. As observed from the elemental mapping (Fig. 6) of a selected region for the three different Nb–HMS-X materials, the Nb

	2D-hexagonal planes									
	(100)		(110)		(200)		(210)			
Catalyst	2θ	d	2θ	d	2θ	d	2θ	d	<i>a</i> (nm)	Wall thickness $(D)^a$ (nm)
HMS-X	0.87	10.15	1.54	5.737	1.76	5.08	2.38	3.712	11.72	2.22
Nb–HMS-X (Si/Nb = 13)	0.82	10.77	1.43	6.178	1.64	5.39	2.12	4.167	12.43	3.13
Nb–HMS-X $(Si/Nb = 3)$	0.86	10.39	_	_	_	_	_	_	11.99	3.99
Nb–HMS-X (Si/Nb = 2)	0.89	9.93	—	—	_	—	—	—	11.46	5.76

^{*a*} Wall thickness (*D*) = $(2d100/\sqrt{3})$ – pore diameter.



Fig. 4 SEM images of the (a) Nb-HMS-X (Si/Nb = 13), (b) Nb-HMS-X (Si/Nb = 3) and (c) Nb-HMS-X (Si/Nb = 2) catalysts.



Fig. 5 HR-TEM images of (a) Nb-HMS-X (Si/Nb = 13), (b) Nb-HMS-X (Si/Nb = 3) and (c) Nb-HMS-X (Si/Nb = 2).



Fig. 6 Elemental mapping (Nb) of (a) Nb-HMS-X (Si/Nb = 13), (b) Nb-HMS-X (Si/Nb = 3) and (c) Nb-HMS-X (Si/Nb = 2).

element is distributed in an ordered pattern, which matches with the HR-TEM images. A uniform distribution is also found in the case of the Si and O elements (Fig. S1, ESI†). It is an established fact that scanning transmission electron microscopy (STEM) with a high-angle annular dark field (HAADF) mode is *Z*-contrasted, *i.e.* the contrast of the STEM image comes from inelastic forward Rutherford electron scattering by the nuclei of the elements. The scattering is proportional to Z^2 , where *Z* represents the atomic number of the element.²⁴ Interestingly, with an increase in the Nb loading, the crystallinity of the materials is more affected compared with lower loadings of niobium in the silica matrix.

3.1.4 FTIR spectroscopy. The FTIR spectra of the HMS-X materials with the three different Nb loadings are shown in Fig. 7. The peaks at 1085 cm^{-1} and 1195 cm^{-1} (Fig. 7) are attributed to the asymmetric stretching vibration of framework Si–O–Si bridges, as observed in the Nb–HMS-X materials with the three different loadings of niobium.¹⁵ The strong peak at

817 cm⁻¹ is attributed to Si-O-Si symmetric stretching.²⁵ The gradual decrease of peak intensity at 817 cm⁻¹ with increasing loading of Nb might be signifying the successive formation of Si–O–Nb moieties. The peak at 960 cm^{-1} has been interpreted as the stretching vibrations of Si–OH and Si–O^{δ–} groups.²⁶ Here, a simultaneous slight shifting of this band is observed in Nb-HMS-X at higher loadings, supporting the strong interaction of Si– $O^{\delta-}$ with Nb.^{27,28} As found in the literature, the peak ascribed in this region can be considered as evidence of the isomorphous substitution of Si by Nb metal ions, i.e. as Si-O-Nb connectivity.29 This peak is also widely used to characterize the presence of transition metal atoms near the silica framework, as the Si-O stretching vibration mode is perturbed by the neighbouring metal ions.³⁰ At higher loadings this peak ramifies, probably due to more extra-framework Nb in the silica matrix. In the hydroxyl region, the weak band at 1633 cm^{-1} and the broad band at 3500 cm⁻¹ can be attributed to a combination of the stretching vibration of silanol groups or silanol "nests" with



Fig. 7 FTIR spectra of the catalysts of (a) HMS-X, (b) Nb–HMS-X (Si/Nb = 13), (c) Nb–HMS-X (Si/Nb = 3) and (d) Nb–HMS-X (Si/Nb = 2).

cross hydrogen-bonding interactions and the H–O–H stretching mode of physisorbed water.³¹

3.1.5 ²⁹Si-NMR spectroscopy. The ²⁹Si-NMR spectra of the Nb–HMS-X materials depicted in Fig. 8 show three different signals at –91, –101 and –110 ppm, which are similar to those obtained for doped mesoporous silica as reported in the literature.³² The first peak at around $\delta = -110$ ppm can be assigned to $(-O-)_4$ Si with no OH group attached to the silicon atom (Q⁴). The second peak at $\delta = -102$ ppm is assigned to $(-O-)_3$ Si(OH) with one OH group (Q³). The last peak at $\delta = -90$ ppm, is assigned to $(-O-)_2$ Si(OH)₂ with two OH groups (Q²).³³ A close look at the ²⁹Si-NMR spectra of the different niobium loaded HMS-X materials reveals the decrease of Q³ peak intensity at higher loadings.

3.1.6 NH₃-TPD profiles. The surface acidic properties of all four catalysts were determined by NH₃-TPD studies (Fig. 9). While comparing the TPD profiles of HMS-X and Nb-HMS-X



Fig. 8 29 Si-NMR spectra of the catalysts; (a) Nb–HMS-X (Si/Nb = 13), (b) Nb–HMS-X (Si/Nb = 3) and (c) Nb–HMS-X (Si/Nb = 2).

(Si/Nb = 13) it is found that Nb⁵⁺ incorporation increases the density of weak acid sites in the HMS-X material, as well as medium and strong acid sites.^{34,35} It can be hypothesized that expanding co-ordination of Nb⁵⁺ increases the surface silanol density, along with some co-ordinatively unsaturated Nb⁵⁺ species, which act as Lewis acid sites. Interestingly, there is no significant change in the amount of NH₃ uptake with increase in Nb loading, which emphasizes the formation of polyniobate clusters at higher loadings.

3.2 Catalytic activity

The catalytic activities of the niobium doped and undoped HMS-X materials towards the Beckmann rearrangement reaction are shown in Table 2. The results indicate inherent acidity in the HMS-X network, which is active upon longer reaction time and can convert about 61% of cyclohexanone oxime into product. This inherent acidity is capable of performing essential 1,2 alkyl shifts that result in caprolactam formation. Similar findings were observed in different studies based on MCM and SBA-15 materials.^{13,36,37}

The Nb-doped HMS-X catalysts showed higher catalytic activity compared to undoped HMS-X. The catalytic activity decreased for higher niobium loading as shown in Table 2. On increasing loading, the surface area and pore size were decreased (as per the surface area and porosity measurements) due to an increasing number of extra-framework niobium species in the pores. From the ²⁹Si-NMR studies it is found that the acidic vicinal silanol intensity (Q³) decreased with increasing Nb loading, which might be the reason for the lower catalytic performance. Interestingly the amount of NH₃ uptake was low for higher Nb loadings because of the formation polyniobate clusters on the catalyst surface.

Therefore it can be argued that only framework niobium (*i.e.* Nb–O–Si linkages) is essential for high activity. While comparing the prepared Nb-doped MCM-41 and HMS catalysts (ESI: catalyst preparation procedure†) we found that the catalytic activity was inferior to that of the Nb–HMS-X materials. All the catalysts have a hexagonal pore structure, however the MCM-41 has a unidirectional hexagonal pore structure and HMS-3 has a short range hexagonal pore structure.^{38,39} This



Fig. 9 NH₃ desorbed from TPD profiles of the catalysts.

Table 2	Catalytic activities of	of different niobium loaded N	b–HMS-X catalysts towards	the Beckmann rearrangement reaction ^a
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		Selectivity (%)					
Catalyst	Conversion (%)	ε-Caprolactam	Cyclohexanone	Aniline	WHSV (h^{-1})	Mass balance (%)	
HMS-X	61.47	51.97	44.59	3.42	15	99.79	
Nb–HMS-X (Si/Nb = 20)	96.17	100	0	0	15	100	
Nb–HMS-X $(Si/Nb = 13)$	100	100	0	0	15	100	
Nb–HMS-X (Si/Nb = 3)	76.56	78.97	15.33	5.69	15	100	
Nb-HMS-X $(Si/Nb = 2)$	75.64	74.85	24.13	1.01	15	100	
Nb-HMS-3(Si/Nb = 13)	84.06	82.94	4.05	13	15	100	
Nb-MCM-41(Si/Nb = 13)	89.62	97	1.55	1.44	15	100	

^{*a*} Reaction conditions: reactant (solution of cyclohexanone oxime in benzene, cyclohexanone oxime : benzene weight ratio of 1 : 11) flow = 5 mL h⁻¹, carrier gas (N₂) flow = 30 mL min⁻¹, catalyst pre-treatment temperature = 500 °C, catalyst pre-treatment time = 5 h, TOS (time on stream) = 1 h.

difference is probably due to the high dispersion of Nb species in the hexagonally interconnected network of the HMS-X species.⁴⁰

3.2.1 Effect of pre-treatment time and temperature. The effect of pre-treatment time and temperature on the conversion and ε -caprolactam selectivity over Nb–HMS-X (Si/Nb = 13) are shown in Tables 3 and 4. With longer pre-treatment times and higher pre-treatment temperatures, sub-layer niobium oxide species present in the mesopores diffuse to the surface generating more active sites, resulting in high oxime conversion and ε -caprolactam selectivity, even at the highest weight hourly space velocity (WHSV) (15 h⁻¹). So, a longer pre-treatment time (5 h) and higher pre-treatment temperature (500 °C) are favourable for optimum catalytic performance in this present case.

3.2.2 Effect of reaction temperature. The effect of temperature on the conversion and ε-caprolactam selectivity over the

Nb-HMS-X (Si/Nb = 13) catalyst is presented in Table 5. Desorption is not fast enough at lower temperatures causing enhancement of intrinsic residence time, which can result in decomposition of cyclohexanone oxime.13 It is clear that at lower temperatures the hydrolysis product cyclohexanone is the main product competing with the Beckmann product ε-caprolactam. At lower temperatures the mass balance was lower, which may be due to different products, such as cyclohexanone, aniline, 5-hexenenitrile, 2-cyclohexen-1-one etc., sticking onto the catalyst surface.14 Upon increasing the reaction temperature up to 350 °C, the oxime conversion and ε-caprolactam selectivity are also increased, whereas the selectivity for cyclohexanone decreases continuously. At a temperature of 400 °C there is no reaction and the catalyst bed turned black in colour, which emphasizes that thermal cracking products are formed on the catalyst surface.36

Fable 3	Catalytic activity	of Nb-HMS-X (Si/Nb =	13) with different pre-treatment times towa	ards the Beckmann rearrangement reaction ^a
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			Selectivity (%)			WHSV (h^{-1})	Mass balance (%)
Catalyst	Catalyst pre-treatment time (h)	Conversion (%)	ε-Caprolactam	Cyclohexanone	Aniline		
Nb-HMS-X	2	95.05	94.53	5.46	0	15	99.62
Nb-HMS-X	3	90.99	92.29	7.7	0	15	100
Nb-HMS-X	4	89.07	91.76	6.81	1.42	15	100
Nb-HMS-X	5	100	100	0	0	15	100

^{*a*} Reaction conditions: reactant (solution of cyclohexanone oxime in benzene, cyclohexanone oxime : benzene weight ratio of 1 : 11) flow = 5 mL h⁻¹, reaction temperature = 350 °C, carrier gas (N₂) flow = 30 mL min⁻¹, catalyst pre-treatment temperature = 500 °C, TOS (time on stream) = 1 h.

Table 4	Catalytic activity of Nb-	–HMS-X (Si/Nb = 13) wi	th different pre-treatmer	nt temperatures toward	s the Beckmann rearrangement reaction ^é
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				Selectivity (%)				
Catalyst	Pre-treatment temperature (°C)	Reaction time (min)	Conversion (%)	ε-Caprolactam	Cyclohexanone	Aniline	WHSV (h^{-1})	Mass balance (%)
Nb-HMS-X	300	60	97.82	94.45	3.54	1.99	15	98.82
Nb-HMS-X	400	60	95.98	94.15	5.26	0.58	15	99.19
Nb-HMS-X	500	60	100	100	0	0	15	100

^{*a*} Reaction conditions: reactant (solution of cyclohexanone oxime in benzene, cyclohexanone oxime : benzene weight ratio of 1 : 11) flow = 5 mL h⁻¹, reaction temperature = 350 °C, carrier gas (N₂) flow = 30 mL min⁻¹, catalyst pre-treatment time = 5 h.

Table 5Catalytic activity of Nb-HMS-X (Si/Nb = 13) at 14 h^{-1} WHSV at different reaction temperatures^a

				Selectivity (%)				
Catalyst	Reaction Temperature (°C)	Reaction time (min)	Conversion (%)	ε-Caprolactam	Cyclohexanone	Aniline	WHSV $\left(h^{-1}\right)$	Mass balance (%)
Nb-HMS-X	250	60	81.7	52.57	47.42	0	14	87.99
Nb-HMS-X	300	60	95.21	84.04	15.95	0	14	95.21
Nb-HMS-X	350	60	99.28	97.51	2.48	0	14	99.28
Nb-HMS-X	400	60	No reaction		—	—		

^{*a*} Reaction conditions: reactant (solution of cyclohexanone oxime in benzene, cyclohexanone oxime : benzene weight ratio of 1 : 11) flow = 5 mL h⁻¹, carrier gas (N₂) flow = 20 mL min⁻¹, catalyst pre-treatment temperature = 500 °C, catalyst pre-treatment time = 5 h.

3.2.3 Effect of WHSV. The effect of WHSV and N₂ flow rate on cyclohexanone oxime conversion and product selectivity over Nb–HMS-X (Si/Nb = 13) are shown in Table 6. The WHSV is varied in the present case keeping other reaction parameters constant. Though many authors reported decreasing conversion, selectivity or both on increasing WHSV, which might be due to faster deactivation of the catalyst,^{17,22} the Nb–HMS-X catalyst system retains high conversion and selectivity even at 15 h⁻¹ WHSV, which demonstrates the optimum production of ε -caprolactam on an industrial scale.

3.2.4 Effect of silylation. Organic modification of mesoporous silica catalysts has been well practised for different reactions.⁴¹ The Beckmann rearrangement reaction was carried out under the same conditions (Table 7) with silylated Nb–HMS-X (Si/Nb = 13). The FTIR study of silylated Nb–HMS-X shows a band at 2800–3000 cm⁻¹ (Fig. S3, ESI†), which is due to C–H species present on the surface, indicating the formation of Si–O–Si(CH₃)₂ connectivity in the sample.¹⁸ The silylated catalyst had lower productivity corresponding to its lower surface silanol concentration.³⁷ However, the substantial activity for the silylated catalyst implies the presence of silanols in the micropores.¹³

3.2.5 Catalytic regeneration. Catalyst deactivation remains a key problem in gas phase reactions.⁴² To study the regeneration of the catalyst system, the reaction was carried out on a deactivated Nb-HMS-X (Si/Nb = 13) catalyst after regenerating in the presence of a N₂ atmosphere. The results based on oxime conversion and ε-caprolactam selectivity are depicted in Fig. 10. The regeneration study under N2 showed almost constant activity with high conversion and selectivity (more than 80% in each cycle) for ten consecutive cycles. When the catalyst was regenerated in flowing N₂ gas (30 mL min⁻¹) at 500 °C for 4 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 in the presence of acidic sites, can be eliminated with nitrogen at high temperature.¹³ The regeneration studies under N₂ indicated that the deactivation is reversible.

Though there are several reports for the reaction mechanism of Beckmann rearrangement, no undisputed understanding of the reaction mechanism has been achieved so far.^{4,43} The active sites for the Beckmann rearrangement are thought to be the surface Brönsted acid sites of the catalyst. It was suggested that the Beckmann rearrangement on the oxide surfaces proceeds

able 6 Catalytic activity of Nb-HMS-X (Si/Nb = 13) at different WHSVs and N ₂ flow rates"	Table 6	Catalytic activity of Nb–HMS-X (Si/Nb = 13) at different WHSVs and N ₂ flow rates ^a
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				Selectivity (%)				
Catalyst	$ m N_2~flow \ (mL~min^{-1})$	Reaction time (min)	Conversion (%)	ε-Caprolactam	Cyclohexanone	Aniline	$WHSV\left(h^{-1}\right)$	Mass balance (%)
Nb-HMS-X	10	60	96.07	94.78	5.21	0	12	99.30
Nb-HMS-X	20	60	99.28	97.51	2.48	0	14	99.28
Nb-HMS-X	30	60	100	100	0	0	15	100

^{*a*} Reaction conditions: reactant (solution of cyclohexanone oxime in benzene, cyclohexanone oxime : benzene weight ratio of 1 : 11) flow = 5 mL h⁻¹, reaction temperature = 350 °C, catalyst pre-treatment temperature = 500 °C, catalyst pre-treatment time = 5 h.

Table 7 Catalytic activity of silylated Nb-HMS-X (Si/Nb = 13) material towards the Beckmann rearrangement reaction^a

		Selectivity (%)				
Catalyst	Conversion (%)	ε-Caprolactam	Cyclohexanone	Aniline	WHSV (h^{-1})	Mass balance (%)
Nb–HMS-X (silylated)	88.76	90.25	8.89	0.85	15	100

^{*a*} Reaction conditions: reactant (solution of cyclohexanone oxime in benzene, cyclohexanone oxime : benzene weight ratio of 1 : 11) flow = 5 mL h⁻¹, reaction temperature = 350 °C, catalyst pre-treatment temperature = 500 °C, catalyst pre-treatment time = 5 h.

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Fig. 10 Catalyst regeneration studies under the following reaction conditions: reactant (solution of cyclohexanone oxime in benzene, cyclohexanone oxime : benzene weight ratio of 1 : 11) flow = 5 mL h⁻¹, carrier gas (N₂) flow = 30 mL min⁻¹, reaction temperature = 350 °C, catalyst pre-treatment temperature = 500 °C, catalyst pre-treatment time = 4 h, TOS (time on stream) = 1 h.

via a fast step where a Brönsted acid site interacting with a nitrogen atom is transferred to the oxygen atom of the oxime. In the rate determining step, the transfer of the alkyl group and the elimination of the hydroxyl group from the oxide are feasible to produce caprolactam.⁴⁴ Cyclohexanone, a major by-product, is formed due to the hydrolysis of cyclohexanone oxime.

Based on the catalyst characterization results and catalytic activity sites the reaction mechanism is depicted in Fig. 11. The hydrogen atom bound to the bridging oxygen, *i.e.* the Si–O–Nb linkage, is known to exhibit the strongest acidity. In the present study we found from TPD measurement that Nb–HMS-X (Si/Nb = 13) has the highest acidity due to the presence of framework Si–O–Nb moieties and major amounts of surface hydroxyl groups compared to the other two Nb doped HMS-X (Si/Nb = 3



Fig. 11 Reaction mechanism for the vapor phase Beckmann rearrangement reaction.

and Si/Nb = 2) materials. Due to the presence of agglomerated niobium oxide species, the acid site density did not alter at higher Nb loading. Therefore a mutual balance between the niobium and silica ratio is a key factor for the surface acidity.

4 Conclusions

From this work the following conclusions are drawn:

• Nb-HMS-X catalysts with different Si/Nb ratios have been synthesized and characterized by various spectroscopic techniques. These analytical results provided strong evidence that Nb has been incorporated into the mesoporous HMS-X silica framework.

• The small angle XRD results revealed that all four catalysts were mesoporous in nature with a hexagonal pore structure. With increasing Nb loading, the crystal plans are badly affected and the peaks become broader.

• N₂ sorption studies revealed that the Nb–HMS-X materials have a very high surface area and porosity. With increasing Nb content, partial loss of the mesoporous structure occurred. The continuous decrease of surface area, pore volume and diameter indicates formation of more Nb₂O₅, which might block the mesopores.

• The HR-TEM image of Nb–HMS-X (Si/Nb = 13) shows the presence of a well-shaped, uniform, honeycomb-like surface morphology with mesoporous channels. With increasing Nb loading the channel like morphology of Nb–HMS-X was destroyed.

• The FTIR spectroscopy results revealed a strong interaction of Nb with silanol groups, as indicated by the presence of the Si– O–Nb vibration mode. However at much higher loading this peak ramified, probably due to the increased amount of extraframework Nb.

• The ²⁹Si-NMR result indicated the presence of three different types of silica species and Si–O–Nb linkage, confirming Nb incorporation into the Si framework.

• The NH₃-TPD results revealed that with increasing Nb loading, acidity decreases and the intensity of the surface hydroxyl groups, Si(OH), are suitable for Beckmann rearrangement.

• Rearrangement of cyclohexanone oxime carried out on Nb– HMS-X materials with different Si/Nb ratios showed that the catalysts are highly active with the highest Si/Nb ratios. Thus, the catalytic activity mainly depends on the acidity of the catalyst and the acidity of the samples is strongly dependent upon the effect of niobium content in the sample.

• The WHSV studies suggested that a reaction temp. of 350 °C, a N₂ flow rate of 30 mL min⁻¹, a pre-treatment temp. of 500 °C and a pre-treatment time of 5 h are the optimum reaction conditions for this reaction, obtaining 100% cyclohexanone oxime conversion and 100% ϵ -caprolactam selectivity.

• The time on stream studies indicated that the catalyst maintained constant activity for up to 40 h, after which the conversion started to decrease. Nevertheless, constant ε -caprolactam selectivity was observed during 1 h time on stream. This indicates that the catalyst deactivates due to poisoning of the catalyst active sites either by coke or by oligomers.

• The successful regeneration of the Nb-HMS-X (Si/Nb = 13) catalyst for ten cycles in the presence of nitrogen and the ordered, thermally stable honeycomb mesoporous structure of Nb-HMS-X (Si/Nb = 13) makes this catalyst viable as per industrial requirements.

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