Highly stable In-SBA-15 Catalyst for Vapor Phase Beckmann Rearrangement Reaction

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ABSTRACT: The Indium doped SBA-15 material was prepared by sol-gel method and tested for vapor phase Beckman rearrangement reaction. Among three indium loading, In/Si ratio of 2/100 was found as an optimum composition in terms of caprolactam selectivity (100%) and cyclohexanone oxime conversion (100%). The catalysts were characterized by N₂ adsorption, small-angle X-rays/neutron scattering (SAXS/SANS), XRD, FESEM, HRTEM, EDX, UV, FTIR and NH₃-TPD techniques. In-situ SANS experiment was performed on the adsorption of CO₂ to detect the micropores in the mesopore wall. All catalysts samples have highly ordered hexagonal structure with well dispersed indium in the silica matrix. The fine tuning of weak and strong acid sites were found in indium doped SBA-15 (In/Si = 2/100) catalyst. The same catalyst showed optimum catalytic performance, high space time yield 114.4 mol/h/g_{cat} and high stability till 6 h of reaction without deactivation. The micro-kinetic analysis showed that there were no external and internal diffusion limitations in the SBA-15 catalyst. The reaction mechanism of Beckmann rearrangement over In-SBA-15 has been elucidated.

KEYWORD: Indium, SBA-15, in-situ SANS, SAXS, ϵ -Caprolactam

1. Introduction

The development of mesoporous silica has remained as a demanding research area for material science community. The exploitation of sol-gel chemistry using soft template approach leads to discovery of many advanced mesoporous silica such as SBA-15, KIT-6, FDU-12 etc. The wide application of these materials for adsorption, drug delivery, and catalysis was found in literature. The most scientific challenge in the heterogeneous catalysis is to overcome the mass transfer limitation for easy accessibility of reactants to the active sites.

ϵ -Caprolactam is an important precursor for the production of nylon-6 fiber and plastics. Industrially, it is obtained from sulphuric acid which is itself challenging due to ecological concerns. Use of heterogeneous catalysts could be a solution of this problem, but production cost and yield have always remained as challenge for industries vis-à-vis research community. Due to pore diffusion limitation of micropores [1], mesoporous molecular sieves/mesoporous zeolites have been tested for vapor phase Beckmann rearrangement reaction of cyclohexanone oxime to ϵ -caprolactam [2,3,4,5,6]. Recently our group has reported Bi incorporated SBA-15 catalyst for producing ϵ -Caprolactam where fast deactivation of catalyst remained a challenging problem [7].

Indium is one of the post-transition metals which used for Friedel-Craft alkylation, Wagner-Meerwein rearrangement, and Diels-Alder reactions etc.[8,9,10] Ia3 cubic nanostructure In_2O_3 are known for sensing weak electrical response arises from the interaction between CO_3^{2-} and CO_2 in CO_2 sensing [11,12] as well as hydrogen production via steam reforming of ethanol [13]. Indium was also selected as the metal to be incorporated into silica due to its specific properties like stability in aerial atmosphere and low toxicity [14]. Several indium based catalyst has been reported in the literature for benzoylation [15,16,17], acylation of aromatic compound [18], hydrogenation of crotonaldehyde [19],

1 Meerwein-Ponndorf-Verley (MPV) reduction [20] and photocatalysis [21]. In earlier studies, we have
2 found O₂ polarizing ability of indium oxide stabilized on silica surface resulting styrene oxidation [22]
3 and bayer villager oxidation [23]. By prompted from vibrant catalytic property, higher aerial stability
4 and low toxicity of indium, we have synthesized In-SBA-15 and employed it for vapor phase
5 Beckmann rearrangement reaction in anhydrous high temperature conditions.

6 The In-SBA-15 catalysts with different indium loading are prepared by the sol-gel method and
7 characterized by N₂ physisorption, small angle X-ray/neutron scattering (SAXS/SANS), wide angle X-
8 ray Diffraction (WAXRD), field emission scanning electron microscopy (FESEM), high resolution
9 transmission electron microscopy (HRTEM), ultraviolet-visible spectroscopy (UV-vis), Fourier
10 transform infrared spectroscopy (FTIR) and ammonia temperature programmed desorption (TPD)
11 techniques. Recently, it has been shown that porous materials can be well characterized by the neutron
12 scattering during the gas adsorption [24]. We have shown that in-situ SANS experiment on the CO₂
13 adsorption provides a clear evidence of the micropores present on the mesopore wall which is not
14 detected by other techniques. The developed catalysts are tested for vapor phase Beckmann
15 rearrangement reaction of cyclohexanone oxime to ϵ -caprolactam production. The catalytic activity is
16 optimized with indium loading, reaction temperature, and pretreatment time temperature. The role of
17 solvent and the catalytic activity over long time on stream have also been examined. The catalyst was
18 found quite stable up to six hour run with a space time yield (STY) 114.4 mol h⁻¹ g_{cat}⁻¹. The micro-
19 kinetic studies show that there is no external and internal diffusion limitation in the tested catalyst. The
20 results are highly promising for the development of alternative industrial process to produce ϵ -
21 caprolactam with 100% conversion and 100% selectivity.

2. Experimental

2.1. Catalyst preparation. High quality of hexagonally ordered mesoporous In-SBA-15 was synthesized by using triblock copolymer as a template under acidic condition [7,25]. In this synthetic procedure, Pluronic P123 (Aldrich) (4 g) was dissolved in 150 mL distilled water in the presence of 7-8 g 35% HCl (Merck) under continuous stirring. After 4 h, a clear solution was obtained and then 4 g n-butanol (Merck) was added to this solution for 1 h. Then tetraethyl orthosilicate (8.4 g) (TEOS, Acros) and desired amount of indium nitrate (Merck) dissolved in water was added to the reaction mixture. The resulting gel composition of the mixture was P123 : H₂O : HCl : n-Butanol : TEOS : In(NO₃)₂.6H₂O:: 0.017 : 200 : 5.4 : 1.325 : 1 : 0.02-0.08 (molar ratio). The whole mixture was stirred for 24 h at room temperature. Then, the mixture was transferred in a closed polypropylene bottle and aged at 373 K for 24 h under static hydrothermal condition. After hydrothermal treatment the material was filtered in hot condition and then dried at 373 K for 12 h in presence of air. For template removal, filtered and dried powder was slurred in an ethanol-HCl mixture (1:1) and subsequently calcined at 823 K for 4 h.

2.2. Catalyst characterization. The BET surface area and pore size analysis of the samples were carried out at liquid nitrogen temperature with a Quantachrome Nova 3200e instrument at 77 K. The pretreatment of the sample was done at 473 K for 3 h under high vacuum. The surface area was calculated by Brunauer-Emmett-Teller (BET) equation. Pore size distribution was calculated by using NLDFT (Non-linear Density Functional Theory) model of cylindrical pore approximation. SAXS measurement was performed by using a laboratory based SAXS instrument with Cu K_α ($\lambda = 1.54 \text{ \AA}$) X-ray source. Variation of scattering intensity with wave vector transfer [$Q = 4\pi \sin(\theta)/\lambda$, 2θ is the scattering angle] was measured for the powder samples. Wide angle X-ray diffraction (WAXRD) analysis was carried out by using Rigaku Ultima 4 diffractometer operated at 40 kV voltage and 40

1 mA current and calibrated with a standard silicon sample, using Ni-filtered Cu K α radiation. SANS
2 experiments have been carried out at the General Purpose SANS instrument of the High Flux Isotope
3 Reactor with a neutron wavelength of 4.72 Å and wavelength resolution $\Delta\lambda/\lambda \sim 0.13$ [26]. Two
4 sample-to-detector distance was chosen to cover an extended range of scattering vectors
5 $0.005 < Q < 1.0 \text{ Å}^{-1}$. SANS measurements have been performed on bare SBA-15 and Indium doped
6 SBA-15 specimens. Recently developed high pressure dome cell was used for in-situ SANS
7 experiment on the adsorption of CO $_2$ [27]. The subcritical CO $_2$ was injected into the catalyst sample at
8 296 K at different pressures. The changes in the scattering profiles were monitored. ^{29}Si MAS NMR
9 was recorded at 500 MHz on a Bruker advanced II-500 spectrometer equipped with a magic angle spin
10 probe at room temperature. Field emission scanning electron microscope characterization (FESEM)
11 was carried out by using Supra 55, Carl (Zeiss, Germany) microscope. The sample was supported on
12 lacey carbon and then coated with platinum by plasma prior to the measurement. The HRTEM was
13 done on JEOL JEM 2100 microscope operated at 300 KeV acceleration voltage using lacey
14 carbon coated Cu grid of 300 mesh size. Energy dispersive X-ray spectroscopy (EDX) was
15 carried out using a field emission scanning electron microscopy (FESEM Supra 55, Carl Zeiss,
16 Germany) equipped with an energy dispersive spectrometer (Oxford Liquid Nitrogen free SDD X
17 MAX 50 EDS) detector. The UV-visible measurement was carried out by using Varian Cary 500
18 (Shimadzu) spectrophotometer. The spectra were recorded at the range of 200-800 nm wavelengths.
19 The FT-IR measurement was carried out by using Perkin Elmer GX spectrophotometer. The spectra
20 were recorded at the range 400-4000 cm $^{-1}$ using KBr pellet. Ammonia temperature programmed
21 desorption (TPD) of the samples were done by using a thermal conductivity detector (TCD) in a
22 Micromeritics Chemisorb 2750 (USA) instrument. First of all, sample was degassed in Helium
23 atmosphere at a flow rate of 30 ml/min for 2 h at 473 K. Then it was saturated with 10% NH $_3$ in

Helium at room temperature for 30 minutes. After that, the excess NH_3 was flushed out in a flow of He (flow rate 30 mL/min) for 45 minutes. Then desorption of ammonia (carrier gas He) in various temperature was obtained by heating the catalyst temperature to 773 K at a temperature ramp of 10 K/min.

2.3. Vapor phase Beckmann rearrangement of cyclohexanone oxime. The catalytic reaction was carried out in a fixed bed catalytic reactor (quartz made, 1.5 cm inner diameter). The catalyst, In-SBA-15 (85 mesh size) of 0.3 g amount was packed into the reactor and pretreated by flowing air (moisture free, 30 ml/min flow maintained by Aalborg mass flow controller) at 673 K for 4 h. The catalyst bed temperature was monitored with a thermocouple touching the catalyst bed. After the pretreatment the reactor was cooled to the desired reaction temperature and then N_2 gas (purity 99.999%, 30 ml/min) was passed through the catalyst bed for 15 minutes. To prepare the feed mixture, cyclohexanone oxime (Acros) was dissolved in a solvent (anhydrous benzene or ethanol or methanol) in mole ratio of 0.0088: 0.1408 (cyclohexanone oxime: solvent). To maintain this mole ratio, weight ratio of cyclohexanone oxime: benzene: ethanol: methanol was 1: 11: 6.48: 4.5 ratios. The solution was injected into the reactor by a syringe pump (B/BRAUN) along with N_2 (purity 99.999%) as a carrier gas (30 ml/min). 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. Characterisation results

The N_2 physisorption isotherms of three different In-SBA-15 samples are plotted in **Fig. 1** and the textural data (surface area, pore volume and pore diameter) are depicted in **Table S1**. All In-SBA-15 samples showed type IV adsorption/desorption isotherms with H1 hysteresis loop, which is characteristic of the mesoporous materials with 2D-hexagonal structure [28]. The surface area of 2

1 mol% and 4 mol% indium loaded SBA-15 samples is found much higher than SBA-15 sample. It
2 indicates that indium is successfully incorporated into silica network and expanded the silica
3 framework. The shape of the N₂ adsorption isotherm of 8 mol % indium loading shows fast reduction
4 in the height of the hysteresis loop, surface area, pore volume and pore diameter. It may be due to
5 uneven folding of template by complexation of indium with PEO-based surfactant at higher indium
6 loading [2929]. From the surface area and porosity results, the localization of Indium in the SBA-15
7 channels can be explained in two ways. As reported in the literature isomorphous substitution of Si⁴⁺
8 ions by In⁺³ ions occur in the walls of SBA-15 [30]. These indium ions are deeply incorporated within
9 the silica mesoporous walls, so surface area/pore volume/pore diameter might be increased as in the
10 case of 2-4 mol% indium loaded SBA-15 due to expansion of silica network. Alternatively the
11 incorporated metal-ion may interact with two or three surface hydroxyl groups and contraction of the
12 pore wall occurs [30]. Again, if the concentration of metal ion increases from optimum level, uneven
13 folding or unfolding of template may occur frequently causing fast reduction of surface area/pore
14 volume/pore diameter [29] as in the case of 8 mol% indium loaded SBA-15.

Fig. 1. The N₂ physisorption isotherms of (a) SBA-15 (b) In-SBA-15 (In/Si = 2/100) (c) In-SBA-15 (In/Si=4/100) (d) In-SBA-15 (In/Si = 8/100).

The ²⁹Si-NMR spectra of the In-SBA-15 samples are depicted in **Fig. 2**. It shows three different signals at -91, -101 and -110 ppm, which corresponds to (–O–)₂Si(OH)₂ denoted as Q², (–O–)₃Si(OH) denoted as Q³ and (–O–)₄Si denoted as Q⁴ respectively. With increasing indium loading from 2 mol% to 4 mol%, both Q₃ and Q₄ peaks are intensified. Further, indium loading till 8 mol% results into decrease in Q₃ and Q₄ peaks intensity. It indicates expansion of silicates framework till optimum metal loading (4 mol%) as justified by surface area and porosity results also.

Fig. 2. The ^{29}Si -NMR spectra of the In-SBA-15 samples

The Small angle X-ray scattering (SAXS) of the In-SBA-15 catalysts with different indium loadings are shown in **Fig. 3**. The In-SBA-15 catalyst exhibits an intense diffraction peak corresponding to the (10) plane at 0.64 nm^{-1} which is a typical characteristic of two dimensional hexagonal mesoporous silica material [31,32]. The intensity of the reflection corresponding to the (10), (11) and (20) plane shows long range order structure for the SBA-15 type of material similar to reported in literature [33].

Fig. 3. Small angle x-ray scattering pattern of (a) SBA-15 (b) In-SBA-15 (In/Si = 2/100) (c) In-SBA-15 (In/Si=4/100) (d) In-SBA-15 (In/Si = 8/100)

The wide-angle XRD patterns of In-SBA-15 catalysts with different Indium loadings shows amorphous nature of catalyst as depicted in **Fig. S2** [34]. No phases of bulk In_2O_3 is found in the wide angle XRD pattern [35]. This indicates that even at highest loading indium oxide species were well dispersed over silica surface and cannot be detected by the wide angle XRD pattern.

The SANS profile from SBA-15 and Indium doped SBA-15 specimens are depicted in **Fig. 4** and **Fig. 5** respectively. The scattering profile of SBA-15 in the low-Q range ($0.005 \text{ \AA}^{-1} < Q < 0.02 \text{ \AA}^{-1}$) is found linear in double logarithmic scale. The slope of the linear region is found to be -4, i.e., $I(Q) \sim Q^{-4}$ in the low Q range. Similarly the scattering profile in the high-Q range ($0.2 \text{ \AA}^{-1} < Q < 0.7 \text{ \AA}^{-1}$) is found to be -3.1. This slope corresponds to scattering from highly rough mesopore surface. The roughness of the mesopore is expected to originate from the presence of random-shaped micropores in the mesopore pore-wall. The presence of the micropores has been predicted previously using the high resolution SAXS instrument at synchrotron source [36]. The scattering in the intermediate Q-range bears the signature of the hexagonal ordered mesopore. The crystalline structure of the SBA-15 is

found to be quasi two dimensional pore structures [37]. Two reflection peaks (10) and (11) are clearly visible in the scattering profiles. The high ordered reflection peaks are not observed due to low resolution of SANS technique.

Fig. 4. SANS profile from SBA-15

Fig. 5. SANS profile from SBA-15 as a function of Indium doping

The lattice parameter can be estimated using the primary (10) peak using the following equation:

$$Q_{10} = \frac{4\pi}{a\sqrt{3}} \quad (1)$$

Where “a” is the lattice parameter and it represents interval of adjacent mesopore centers. The mesopore diameter can be estimated using the intensity ratio of diffraction peaks using the equation [27,37] below:

$$\frac{I_{hk}}{I_{h'k'}} = \frac{M_{hk}}{M_{h'k'}} \frac{J_1(2\pi\gamma\sqrt{g/3})^2}{J_1(2\pi\gamma\sqrt{g'/3})^2} \frac{g'}{g} \quad (2)$$

M_{hk} is called the multiplicity factor for the (h k) peak. The multiplicity factor of (h 0), (h h) and (h k: h≠k, k≠0) diffraction peaks is 6, 6 and 12, respectively.

$$g = h^2 + hk + k^2 \quad (3)$$

$$g' = h'^2 + h'k' + k'^2 \quad (4)$$

γ is the mesopore diameter normalized by lattice parameter, i.e., $\gamma=2R/a$. The value of the γ has been estimated using the experimentally observed intensity ratio of (hk) and ($h'k'$) peaks for different doped samples.

Interestingly the value of γ is found to be 0.68 for all the specimens, i.e., the ratio of the mesopore diameter to lattice parameter remains independent of doping. **Table 1** depicts the important structural parameter of the SBA-15 with and without Indium doping. It is evident that the crystalline structure of In-doped samples has not changed significantly. Indium doped samples show additional scattering at high-Q as compared to the SBA-15 due to Indium nano-particles.

Table 1. The structural parameter of the SBA-15 with varying doping concentration

Catalyst `	Q_{10} ($\text{\AA}^{-1}$)	Lattice parameter (nm)	Mesopore diameter (nm)
SBA-15	0.067	10.8	7.3
In-SBA-15 (In/Si = 2/100)	0.064	11.3	7.7
In-SBA-15 (In/Si = 4/100)	0.063	11.5	7.8
In-SBA-15 (In/Si = 8/100)	0.066	11.0	7.5

The SANS profiles of SBA-15 at different CO_2 pressures and variation of the scattering intensity at different Q values is depicted in **Fig. 6** and **Fig. 7** respectively. It is evident that the variation of the scattering intensity is different in the different Q -range.

Fig. 6. The SANS profiles of SBA-15 at different pressures

Fig. 7. Variation of the scattering intensity in the different Q-range at different pressure

The scattering intensity from the hexagonally ordered pores can be written as,

$$I(Q) = n(\Delta\rho)^2 P(Q) S(Q) \quad (5)$$

Where n is the number density of the pores. $P(Q)$ is the form factor of the pore which depends on the shape and size of the pore. $S(Q)$ is the structure factor which gives information about the arrangement of the pores. $(\Delta\rho)^2$ is known as contrast factor and depends on scattering length density (SLD) difference between the pore wall and the pore fluid, i.e., $(\Delta\rho)^2 = (\rho_w - \rho_f)^2$. ρ_w and ρ_f is the SLD of the pore wall and pore fluid, respectively. The SLD of the bulk CO_2 has been estimated for different pressures and is shown in the **Table 2**. The SLD of the silica matrix is found $\sim 3.0 \times 10^{10} \text{ cm}^{-2}$. As there is no fluid in the pores for powder samples under vacuum, the injection of CO_2 in SBA-15 is expected to reduce the contrast. The contrast factor should decrease as pressure increases. However, opposite trend has been observed. The increase in the scattering intensity at high-Q may originate from the

densely adsorbed CO₂ in micropores. The increase in the low-Q intensity confirms this proposition as the densely adsorbed CO₂ in the micropores causes higher density of the porous grains [27]. The intensity in the intermediate Q-range showed non-monotonic trend with pressure. The intensity of the (10) peak was increased up to 29 bar and decreased subsequently. The intensity of (11) peak continuously decreases with pressure. The non-monotonic variation of peak intensity with pressure could be linked to the formation of the adsorbed liquid phase CO₂ along cylindrical pore wall.

Table 2. The density and scattering length density of the bulk CO₂ at various pressures at 296 K on SBA-15

Pressure (bar)	Density (g/cm ³)	SLD (10 ¹⁰ cm ⁻²)
0	0	0
14	0.027	0.0674
29	0.062	0.155
55	0.153	0.382

The FESEM images for three different indium loaded SBA-15 (In/Si=2/100, In/Si=4/100 and In/Si=8/100) catalysts and HRTEM images of In-SBA-15 (In/Si = 2/100) are shown in **Fig. 8** and **Fig. 9** respectively. It is observed that morphology of catalyst samples are vermicular stalks. The HRTEM images of In-SBA-15 (In/Si=2/100) shows perfectly hexagonal channels having pore like honeycomb pattern. **With increasing indium loading, orderness of materials is more affected compared with lower indium loading.** The EDX profile showed the real surface composition of indium and Silica to be 0.17/100 over In-SBA-15 (In/Si=2/100) (**Fig. S3** and **Table S4**).

Fig. 8. FESEM image of (a) In-SBA-15 (In/Si = 2/100) (b) In-SBA-15 (In/Si = 4/100) (c) In-SBA-15 (In/Si = 8/100)

Fig. 9. HRTEM image of (a) In-SBA- 15 (In/Si = 2/100) with the incident electron beam perpendicular to the direction of channel b) In-SBA- 15 (In/Si = 2/100) with the incident electron beam parallel to the direction of main channels (c) In-SBA-15 (In/Si = 4/100) (d) In-SBA-15 (In/Si = 8/100). The inset image shows HRTEM images in 5 nm range.

SBA-15 and indium-containing SBA-15 samples shows UV band centered around 215 nm and 250 nm (**Fig. 10**). A band around 210 nm assigns to In^{3+} in a tetrahedral environment and absorption band at 250 nm is due mesoporous pure silica [38,39]. Both of the peaks intensified

and broadened at higher dopant levels presumably due to a ligand-to-metal charge transfer [38,40]. Shift of band with the introduction of Indium dopants could be related to the mixed valence states of the In and Si affecting the band energy of the mesoporous materials. The absence of absorption band in the region of 300-330 nm clearly indicates absence of In_2O_3 extra-frame work species (octahedral Indium) [41] even at highest loading which is similar to XRD results [3435,42].

Fig. 10. UV spectra of (a) SBA-15 (b) In-SBA-15 (In/Si = 2/100) (c) In-SBA-15 (In/Si = 4/100) (d) In-SBA-15 (In/Si = 8/100)

The FTIR spectra of SBA-15 and indium loaded SBA-15 is shown in **Fig. 11**. The IR band at 1085 cm^{-1} and 1195 cm^{-1} are attributed to the asymmetric stretching vibration of framework Si–O–Si bridges [6]. The IR band at 960 cm^{-1} can be assigned for stretching vibration of Si–OH (surface silanol groups) and band at 817 cm^{-1} for Si–O–Si symmetric stretching. Just after metal loading the intensity of 960 cm^{-1} and 817 cm^{-1} is found to decrease, it indicates Si–O–In connectivity. Further higher metal loading doesn't show significant decrease in intensity of these bands. Possibly decrease of surface hydroxyl on higher loading will be compensated by extra surface hydroxyl generation during lower

valent dopent (In^{+3}) in higher valent silica matrix. The weak band at 1633 cm^{-1} and the broad band at 3500 cm^{-1} can be attributed to the combination of the stretching vibration of silanol groups or silanol “nests” with a cross hydrogen-bonding interactions and the H–O–H stretching mode of the physisorbed water [43].

Fig. 11. FTIR spectra of (a) SBA-15 (b) In-SBA-15 (In/Si = 2/100) (c) In-SBA-15 (In/Si = 4/100) (d) In-SBA-15 (In/Si = 8/100)

The ammonia temperature programmed desorption profile and amount of ammonia adsorbed of all three indium loaded SBA-15 samples are shown in **Fig. 12**. Catalyst samples have low temperature TPD profile (323-523 K) of weak acid site, intermediate temperature profile (523-773 K) for medium strength acid site and high temperature profile (773-1123 K) for stronger acid sites. It is found that the In-SBA-15 (In/Si=2/100) catalyst system has a fine tuning of weak and strong acid sites. With increasing indium loading medium sites acid strength are increased.

Fig.12. NH₃-TPD profile of different Catalysts

4. Catalytic activity results

The catalytic properties of bare and Indium doped SBA-15 specimens are studied for vapor phase Beckmann rearrangement reaction by varying different reaction parameters as different metallic loading, reaction temperature variation, different pretreatment time and temperature. The external mass transfer limitation and internal mass transfer limitation is calculated in each case by considering Mears criterion ($-r_A' \rho_b R \eta / k_c C_{Ab} < 0.15$) and Weisz-Prater criterion ($C_{WP} = -r_A' \rho_c R^2 / D_e C_{AS} < 1$) in each case (**Supporting Information**) [44].

The catalytic activities of the indium doped and bare SBA-15 materials towards the Beckmann rearrangement reaction are shown in **Table 3**. The bare SBA-15 results into 64% cyclohexanone oxime conversion and 79% ϵ -caprolactam selectivity. It indicates the inherent acidity present in the SBA-15 network which is capable of performing 1,2 alkyl shifts and lead to the ϵ -caprolactam formation [45,46,47]. After 4 hours of pretreatment in air at 673 K, In-SBA-15 (In/Si=2/100) catalyst shows superior performance towards the cyclohexanone oxime conversion (100%) and the ϵ -caprolactam selectivity (100%) at 623K reaction temperature with a space time yield (STY) value

1 114.4 mol h⁻¹ g_{cat}⁻¹. With increasing indium loading to In-SBA-15 (In/Si=4/100), both conversion and
2 selectivity are found to be decreased. Further metal loading In-SBA-15 (In/Si=8/100) reduces ϵ -
3 caprolactam selectivity. In all cases, no external as well as internal mass transfer limitation is found.

4 The effect of reaction temperature on the catalytic activity is studied over In-SBA-15
5 (In/Si=2/100) and shown in **Table 4**. At 573 K reaction temperature, no reaction takes place whereas
6 at higher temperature (673 K) 100% cyclohexanone oxime conversion is achieved but ϵ -caprolactam
7 selectivity is found very less. Many unwanted products are also present which may be due to the
8 decomposition products of ϵ -caprolactam at higher temperature [48]. It is observed that the best
9 activity with respect to cyclohexanone oxime conversion and ϵ -caprolactam selectivity for the 2% In-
10 SBA-15 is obtained at 623 K reaction temperature.

11 The effect of pretreatment on the cyclohexanone oxime conversion and ϵ -caprolactam selectivity
12 over In-SBA-15 (In/Si=2/100) are shown in **Table 5**. In the present study, the best catalytic activity is
13 found at 673 K pretreatment temperature and 623 K reaction temperature. A nice correlation is
14 observed in the case of catalytic activity with the pre-treatment temperature. Without pre-treatment,
15 lower catalytic activity is observed. Longer pretreatment time and higher pretreatment temperatures
16 are helpful to get completely dried catalyst surface. Therefore, a longer pre-treatment time (4 h) and
17 higher pre-treatment temperature (673 K) are favorable for obtaining optimum catalytic performance
18 in this present study. In all cases, no external as well as internal mass transfer limitation is found.

19 The catalytic activity of the In-SBA-15 (In/Si = 2/100) catalyst is evaluated for longer time on
20 stream (TOS) as shown in the **Table 6**. At longer reaction time up to 4 hours, the cyclohexanone
21 oxime conversion as well as ϵ -caprolactam selectivity is found to 100% in this study. Afterward there
22 is a slight decrease of both cyclohexanone conversion and ϵ -caprolactam selectivity in the present
23 case. On prolong time on stream study, catalytic active sites are possibly masked by oligomers which

1 results into decreasing cyclohexanone oxime conversion. During the rearrangement H₂O molecule is
2 formed which can compete with oxime intermediate and gives cyclohexanone as hydrated product. In
3 all cases, no external as well as internal mass transfer limitation is found.

4 The role of polar and non-polar solvent over the vapor phase reaction is studied over In-SBA-15
5 (In/Si=2/100) catalyst after 4h pretreatment at 673 K and 623 K reaction temperature. The catalytic
6 activity results are shown in **Table 7**. The non-polar solvents are generally found less suitable in most
7 of the earlier report on Beckmann rearrangement of cyclohexanone oxime reaction except the paper
8 presented by Xu et al. [49] In the present case, using non-polar solvent benzene, optimum
9 cyclohexanone oxime conversion and ϵ -caprolactam selectivity are obtained. In the case of methanol
10 and ethanol as solvent, no reaction took place. By using the polar solvent, catalytic activity is steeply
11 dropped down even those are observed over un-doped SBA-15. Cheng et al. [50] proposed that the
12 solvents blocked the active sites responsible for Beckmann rearrangement reaction due to the
13 competitive adsorption of polar solvents at catalyst acidic sites.

Table 3. Catalytic activity of and Indium doped SBA-15 towards Beckmann rearrangement reaction of cyclohexanone oxime

Catalyst	Pretreatment Temperature	TOS (min)	Cy-O Conv. (%)	Selectivity (%)			STY mol h ⁻¹ g _{cat} ⁻¹	Mass balance	Extenal Mass Transfer*	C _{wp}
				ϵ -Cap.	Cyc.	Aniline				
SBA-15	673 K	60	64.3	79.2	20.8	0	58.2	94.3	<0.15	<1
In-SBA-15 (In/Si=2/100)	673 K	60	100	100	0	0	114.4	>99	<0.15	<1
In-SBA-15 (In/Si=4/100)	673 K	60	85.5	91.2	8.6	0.2	89.2	97	<0.15	<1
In-SBA-15 (In/Si=8/100)	673 K	60	86.8	89.8	9.7	0.4	94.7	96	<0.15	<1

Reaction condition: Cyclohexanone oxime: benzene weight ratio is 1:11, feed flow rate =5 mL/h, catalyst wt. = 0.3 g, reaction temperature = 623 K, N₂ flow (U_f) = 30 ml/min, Pretreatment time: 4h; pressure = 1 atm, diameter of reactor = 1.5 cm, av. density of catalyst (ρ_c) = 1.05 x10³ Kg/m³ porosity (ϕ)= vol. of void space/(vol. of void + vol. of solid), bulk density of catalyst bed (ρ_b) = $\rho_c(1 - \phi)$, average particle diameter (d_p) = 500 x10⁻⁵, constriction factor (σ_c) = 1 (assuming uniform cylindrical pore), tortiosity (τ) = 1, *External MTL by Mears criterion (Fogler, p. 841; Mears, 1971), Internal MTL (C_{wp}) by Weisz-Prater criterion (Fogler, p. 839).

Table 4. Catalytic activity of Indium doped SBA-15 at different reaction temperature towards Beckmann rearrangement reaction of cyclohexanone oxime

Catalyst	Reaction Temperature	TOS (min)	Cy-O Conv. (%)	Selectivity (%)			STY mol h ⁻¹ g _{cat} ⁻¹	Mass balance	Extenal Mass Transfer*	C _{wp}
				ϵ -Cap.	Cyc.	Others				
In-SBA-15 (In/Si=2/100)	573 K	60	No reaction	-	-	-	-	-	-	-
In-SBA-15 (In/Si=2/100)	623 K	60	100	100	0	0	114.4	>99	<0.15	<1
In-SBA-15 (In/Si=4/100)	673 K	60	100	52.2	35	12.8	59.5	96	<0.15	<1

Reaction condition: Cyclohexanone oxime: benzene weight ratio is 1:11, feed flow rate =5 mL/h, catalyst wt. = 0.3 g, Pretreatment temperature = 673K, pretreatment time = 4h., N₂ flow (U_f) = 30 ml/min, pressure = 1 atm, diameter of reactor = 1.5 cm, av. density of catalyst (ρ_c) = 1.05 x10³ Kg/m³ porosity (ϕ)= vol. of void space/(vol. of void + vol. of solid), bulk density of catalyst bed (ρ_b) = $\rho_c(1 - \phi)$, average particle diameter (d_p) = 500 x10⁻⁵, constriction factor (σ_c) = 1 (assuming uniform cylindrical pore), tortiosity (τ) = 1, *External MTL by Mears criterion (Fogler, p. 841; Mears, 1971), Internal MTL (C_{wp}) by Weisz-Prater criterion (Fogler, p. 839).

Table 5. Catalytic activity of In-SBA-15 (In/Si=2/100) at different pretreatment temperature and pretreatment time towards Beckmann rearrangement reaction of cyclohexanone oxime

Catalyst	Pretreatment Temperature and Time	TOS (min)	Cy-O Conv. (%)	Selectivity (%)			STY mol h ⁻¹ g _{cat} ⁻¹	Mass balance	Extenal Mass Transfer*	C _{wp}
				ϵ -Cap.	Cyc.	Aniline				
In-SBA-15 (In/Si=2/100)	No Pretreatment	60	26.6	33.4	66.6	0	10.2	92.6	<0.15	<1
In-SBA-15 (In/Si=2/100)	673 K, 2 h	60	60	82	18	0	56.3	100	<0.15	<1
In-SBA-15 (In/Si=2/100)	673 K, 4 h	60	100	100	0	0	114.4	100	<0.15	<1

Reaction condition: Cyclohexanone oxime: benzene weight ratio is 1:11, feed flow rate =5 mL/h, catalyst wt. = 0.3 g, reaction temperature = 623 K, N₂ flow (U_f) = 30 ml/min, pressure = 1 atm, diameter of reactor = 1.5 cm, av. density of catalyst (ρ_c) = 1.05 x10³ Kg/m³ porosity (ϕ)= vol. of void space/(vol. of void + vol. of solid), bulk density of catalyst bed (ρ_b) = $\rho_c(1 - \phi)$, average particle diameter (d_p) = 500 x10⁻⁵, constriction factor (σ_c) = 1 (assuming uniform cylindrical pore), tortiosity (τ) = 1, *External MTL by Mears criterion (Fogler, p. 841; Mears, 1971), Internal MTL (C_{wp}) by Weisz-Prater criterion (Fogler, p. 839).

Table 6. Catalytic activity of In-SBA-15 at different time on stream (TOS) towards Beckmann rearrangement reaction of cyclohexanone oxime

Catalyst	Pretreatment Temperature and Time	TOS (min)	Cy-O Conv. (%)	Selectivity (%)			STY mol h ⁻¹ g _{cat} ⁻¹	Mass balance	Extenal Mass Transfer*	C _{wp}
				ϵ -Cap.	Cyc.	Aniline				
In-SBA-15 (In/Si=2/100)	673 K, 4 h	60	100	100	0	0	114.4	100	<0.15	<1
In-SBA-15 (In/Si=2/100)	673 K, 4 h	120	100	100	0	0	114.4	100	<0.15	<1
In-SBA-15 (In/Si=2/100)	673 K, 4 h	180	100	100	0	0	114.4	100	<0.15	<1
In-SBA-15 (In/Si=2/100)	673 K, 4 h	240	100	100	0	0	114.4	100	<0.15	<1
In-SBA-15 (In/Si=2/100)	673 K, 4 h	300	98	97.2	1.8	0	108.9	100	<0.15	<1
In-SBA-15 (In/Si=2/100)	673 K, 4 h	360	98.2	97	2	0	108.9	100	<0.15	<1

Reaction condition: Cyclohexanone oxime: benzene weight ratio is 1:11, feed flow rate =5 mL/h, catalyst wt. = 0.3 g, reaction temperature = 623 K, N₂ flow (U_f) = 30 ml/min, pressure = 1 atm, diameter of reactor = 1.5 cm, av. density of catalyst (ρ_c) = 1.05 x10³ Kg/m³ porosity (ϕ)= vol. of void space/(vol. of void + vol. of solid), bulk density of catalyst bed (ρ_b) = $\rho_c(1 - \phi)$, average particle diameter (d_p) = 500 x10⁻⁵, constriction factor (σ_c) = 1 (assuming uniform cylindrical pore), tortiosity (τ) = 1, *External MTL by Mears criterion (Fogler, p. 841; Mears, 1971), Internal MTL (C_{wp}) by Weisz-Prater criterion (Fogler, p. 839).

Table 7. Catalytic activity of In-SBA-15 in different solvent towards Beckmann rearrangement reaction of cyclohexanone oxime

Catalyst	Pretreatment Temperature and Time	Solvent	Cy-O Conv. (%)	Selectivity (%)			STY $\text{mol h}^{-1} \text{g}_{\text{cat}}^{-1}$	Mass balance	Extenal Mass Transfer*	C_{wp}
				ϵ -Cap.	Cyc.	Aniline				
In-SBA-15 (In/Si=2/100)	673 K, 4 h	Benzene	100	100	0	0	114.4	100	<0.15	<1
In-SBA-15 (In/Si=2/100)	673 K, 4 h	Methanol	0.8	36.7	63.2	0	0.3	100	<0.15	<1
In-SBA-15 (In/Si=2/100)	673 K, 4 h	Ethanol	No. Reaction	-	-	-	-	-	-	-

Reaction condition: Cyclohexanone oxime: benzene: ethanol: methanol weight ratio is 1: 11: 6.48: 4.5 (reactant: solvent mole ratio is 0.0088: 0.1408), feed flow rate =5 mL/h, catalyst wt. = 0.3 g, reaction temperature = 623 K, N_2 flow (U_f) = 30 ml/min, pressure = 1 atm, diameter of reactor = 1.5 cm, av. density of catalyst (ρ_c)= $1.05 \times 10^3 \text{ Kg/m}^3$ porosity (ϕ)= vol. of void space/(vol. of void + vol. of solid), bulk density of catalyst bed (ρ_b) = $\rho_c(1 - \phi)$, average particle diameter (d_p) = 500×10^{-5} , constriction factor (σ_c) = 1 (assuming uniform cylindrical pore), tortiosity (τ) = 1, *External MTL by Mears criterion (Fogler, p. 841; Mears, 1971), Internal MTL (C_{wp}) by Weisz-Prater criterion (Fogler, p. 839).

5. Discussion

The slope of SANS profile in high Q range indicates scattering from highly rough mesopore surface which is expected to originate from the presence of random-shaped micropores in the mesopore pore-wall. In the SANS profile of Indium doped samples additional scattering at high-Q as compared to the SBA-15 due to indium nano-particles was found. The increase in high-Q intensity in CO₂ probed in-situ SANS having pressure variation indicates the presence of densely adsorbed CO₂ in micropores. The non-monotonic variation of peak intensity with pressure at intermediate-Q range could be linked to the formation of the adsorbed liquid phase CO₂ along cylindrical pore wall. The increase in the low-Q intensity confirms densely adsorbed CO₂ proposition in the micropores which causes higher density of the porous grains. The scattering in the intermediate Q-range in SAXS profile evidenced the presence of hexagonal ordered mesopore. The perfectly hexagonal channels having pore like honeycomb pattern in lower indium loading sample can be visualized from HRTEM studies. Overall, from SANS, CO₂ probed in-situ SANS, SAXS profiles and HRTEM image it can be said that In-SBA-15 (In/Si = 2/100) material have hexagonal ordered channels enriched with both mesopores and micropores.

As evident by surface area and porosity results and Si-NMR results, it can be concluded that surface area, pore volume and pore diameter were increased till 4 mol % In-SBA-15 (In/Si = 4/100) due to expansion of silicates framework by incorporation of metal into silica wall. At highest loading In-SBA-15 (In/Si = 8/100), due to higher than optimum concentration of metal ion in gel mixture causes improper folding of template which give rise to low surface area, pore volume and pore diameter. Lattice parameter of sample followed the same trend as evident by SANS. Si–O–In connectivity and absence of In₂O₃ extra-framework species (octahedral indium) were confirmed by IR and UV-vis

spectra respectively. NH_3 -TPD results showed fine twining of weak acid site and strong acid sites with In-SBA-15 (In/Si=2/100). With increasing metal loading medium acid strength sites was found to be increased.

Indium system is chiefly known as Lewis acid center where chelation of carbonyl group to Lewis acid center can be easily found in literatures [51,52]. The chelation of nitrogen of oxime to Lewis acid center (metal exposed centers) can be expected that can promote ketone formation [53]. So, it can be expected that with increasing indium loading, medium acid strength sites or Lewis acidity was raised rendering lower ϵ -caprolactam selectivity. But in lower indium loading 2% In-SBA-15 (In/Si=2/100), only weak and strong acid sites are found. Weak acid sites are generally associated with weakly acidic silanol groups [54,55]. It indicates that in lower loading, metal are not much exposed on the surface but surrounded by silanol groups. It is also reported that acid strength of the surface hydroxyl groups are enhanced by Lewis acid sites [56]. It can be concluded that in lower indium loading chelation of oxygen of surface silanol to the indium Lewis acid centre may generate protons for possible cyclohexanone oxime rearrangement as shown in **Fig. 13**. Previously, it has been reported that indium showed a high selectivity at lower metal loading in the catalytic reactions such as Fiedel-Craft alkylation, acylation, Wagner-Meerwein rearrangement, and Diels-Alder reactions [8,9,10]. No activity with polar solvent can be claimed to blocking of these acid centers by polar solvents.

Fig. 13. Proposed reaction mechanism

6. Conclusion

The In-SBA-15 catalysts prepared by the sol-gel method are highly ordered 2D-hexagonal structure having well dispersed indium in the silica matrix. The presence of both mesopore and micropore is confirmed from in-situ SANS study. The lowest indium loaded SBA-15 has optimum ratio of weak and strong acid sites that can be claimed to optimum catalytic performance in term of high space time yield and stable activity on long time on stream. Based on characterization results and catalytic performance, it can be concluded that chelation of oxygen of surface silanol to the indium Lewis acid centre may generate protons for possible cyclohexanone oxime rearrangement.

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Fig. Captions

Fig. 1. The N₂ physisorption isotherms of (a) SBA-15 (b) In-SBA-15 (In/Si = 2/100) (c) In-SBA-15(In/Si=4/100) (d) In-SBA-15 (In/Si = 8/100)

Fig. 2. The ²⁹Si-NMR spectra of the In-SBA-15 samples

Fig. 3. Small angle X-ray scattering pattern of (a) SBA-15 (b) In-SBA-15 (In/Si = 2/100) (c) In-SBA-15(In/Si=4/100) (d) In-SBA-15 (In/Si = 8/100)

Fig. 4. SANS profile from SBA-15

Fig. 5. SANS profile from SBA-15 as a function of Indium doping

Fig. 6. The SANS profiles of SBA-15 at different pressures

Fig. 7. Variation of the scattering intensity in the different Q-range at different pressure

Fig. 8. FESEM image of (a) In-SBA-15 (In/Si = 2/100) (b) In-SBA-15 (In/Si = 4/100) (c) In-SBA-15 (In/Si = 8/100)

Fig. 9. HRTEM image of (a) In-SBA- 15 (In/Si = 2/100) with the incident electron beam perpendicular to the direction of channel b) In-SBA- 15 (In/Si = 2/100) with the incident electron beam parallel to the direction of main channels (c) In-SBA-15 (In/Si = 4/100) (d) In-SBA-15 (In/Si = 8/100). The inset image shows HRTEM images in 5nm range.

Fig. 10. UV spectra of (a) SBA-15 (b) In-SBA-15 (In/Si = 2/100) (c) In-SBA-15 (In/Si = 4/100) (d) In-SBA-15 (In/Si = 8/100)

Fig. 11. FTIR spectra of (a) SBA-15 (b) In-SBA-15 (In/Si = 2/100) (c) In-SBA-15 (In/Si = 4/100) (d) In-SBA-15 (In/Si = 8/100)

Fig. 12. NH₃-TPD profile of different catalyst

Fig. 13. Proposed reaction mechanism

Tables Captions

Table 1. The structural parameter of the SBA-15 with varying doping concentration

Table 2. The density and scattering length density of the bulk CO₂ at various pressures at 296 K on SBA-15

Table 3. Catalytic activity of and Indium doped SBA-15 towards Beckmann rearrangement reaction of cyclohexanone oxime

Table 4. Catalytic activity of Indium doped SBA-15 at different reaction temperature towards Beckmann rearrangement reaction of cyclohexanone oxime

Table 5. Catalytic activity of In-SBA-15 (In/Si=2/100) at different pretreatment time towards Beckmann rearrangement reaction of cyclohexanone oxime

Table 6. Catalytic activity of In-SBA-15 at different time on stream (TOS) towards Beckmann rearrangement reaction of cyclohexanone oxime

Table 7. Catalytic activity of In-SBA-15 in different solvent towards Beckmann rearrangement reaction of cyclohexanone oxime