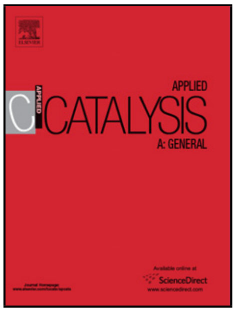


Title: Aerobic Baeyer-Villiger Oxidation of Cyclic Ketones
over Periodic mesoporous silica Cu/Fe/Ni/Co-HMS-X

Author: Sumbul Rahman Nagasuresh Enjamuri Ruth Gomes
Asim Bhaumik Debasis Sen S. Mazumdar Biswajit
Chowdhury

PII: S0926-860X(15)00160-X
DOI: http://dx.doi.org/doi:10.1016/j.apcata.2015.03.014
Reference: APCATA 15304

To appear in: *Applied Catalysis A: General*

Received date: 10-8-2014
Revised date: 14-1-2015
Accepted date: 13-3-2015

Please cite this article as: S. Rahman, N. Enjamuri, R. Gomes, A. Bhaumik, D. Sen, S. Mazumdar, B. Chowdhury, Aerobic Baeyer-Villiger Oxidation of Cyclic Ketones over Periodic mesoporous silica Cu/Fe/Ni/Co-HMS-X, *Applied Catalysis A, General* (2015), http://dx.doi.org/10.1016/j.apcata.2015.03.014

Highlights

Aerobic Baeyer-Villiger Oxidation of Cyclic Ketones over Periodic mesoporous silica Cu/Fe/Ni/Co-HMS-X

Sumbul Rahman[1], Nagasuresh Enjamuri[1], Ruth Gomes[2], Asim Bhaumik[2], Debasis Sen[3], J. K Pandey[4], S. Mazumdar[3] and Biswajit Chowdhury[1*]

1. Department of Applied Chemistry, Indian School of Mines, Dhanbad, India

2. Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

3. Solid State Physics Division, Bhabha Atomic Research Center (BARC), Mumbai, India

4. Respiratory protection lab, Central Institute of Mining and Fuel Research (CIMFR), Dhanbad, India

*Corresponding author: biswajit_chem2003@yahoo.com; Tel: (+91)-326-2235663; Fax: (+91)-326-2296563

- Co-HMS-X catalyst showed catalytic activity for baeyer villager oxidation reaction.
- Cu,Fe and Ni (0.25 mol%) are used as promoters in Co-HMS-X catalyst
- The highly active Ni-Co-HMS-X (Co/Ni = 20) had large number of acidic sites
- It could oxidise admantanone and cyclopntanone also with high conversion
- The selectivity was >99% in all the reactions

Aerobic Baeyer-Villiger Oxidation of Cyclic Ketones over Periodic mesoporous silica Cu/Fe/Ni/Co-HMS-X

Sumbul Rahman[1], Nagasuresh Enjamuri[1], Ruth Gomes[2], Asim Bhaumik[2], Debasis Sen[3], S. Mazumdar[3] and Biswajit Chowdhury[1*]

1. Department of Applied Chemistry, Indian School of Mines, Dhanbad, India
2. Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

3. Solid State Physics Division, Bhabha Atomic Research Center (BARC), Mumbai, India

*Corresponding author: biswajit_chem2003@yahoo.com; Tel: (+91)-326-2235663; Fax: (+91)-326-2296563

ABSTRACT

Baeyer-Villiger oxidation is important reaction in the organic synthesis for designing value added lactone/esters from the respective carbonyl compounds. Usually an active metal-containing material in the presence of peroxides catalyzes this reaction. Here highly ordered metal promoted periodic mesoporous silica with high surface area has been synthesized hydrothermally by the sol-gel method and thoroughly characterized by surface area and porosity measurements, SAXS, FESEM, HRTEM, FTIR, UV-Vis, NH_3-TPD and XRD techniques. Liquid phase Baeyer-Villiger oxidation of ketones to the corresponding esters have been carried out using molecular oxygen as an oxidant, benzaldehyde as the sacrificing agent over Co-HMS-X and M-Co-HMS-X (Metal = Ni, Fe, Cu) as catalysts. The obtained results demonstrate that among the three promoted catalyst i.e Ni-Co-HMS-X, Cu-Co-HMS-X and Fe-Co-HMS-X, Ni promoted catalyst is a promising and efficient catalyst with high catalytic activity (>99% cyclohexanone conversion and >99% ε-caprolactone selectivity) for the oxidation of cyclohexanone to ε-caprolactone. The high catalytic activity is attributed to the Ni on the wall of mesoporous silica along with cyclohexanone, which results in successful completion of the oxygen transfer step and generation of ε-caprolactone. Interesting information regarding cooperative role of cobalt and nickel towards catalytic activity is observed.

Keywords : mesoporous silica, reductant, molecular O_2, cyclohexanone, ε-caprolactone

1. Introduction

Aerobic oxidations of hydrocarbons with heterogeneous catalysts are quite attractive and challenging from an industrial viewpoint. The Baeyer-Villiger type oxidation is a valuable reaction to oxidize ketone to an ester directly [1]. Catalytic versions of the Baeyer-Villiger oxidation are particularly attractive for practical applications as described earlier.

Numerous efforts have been made to use oxygen and air as the oxidant in which reducing agents such as hydrogen have been sometimes utilized as a sacrificing agent. In presence of reducing reagent one oxygen atom from O_2 oxidizes the reactant, whereas the other is reduced as observed in literature. [2, 3] This type of reaction is similar to enzyme catalyzed reactions such as cytochrome P-450 monooxygenase reaction.

Different types of heterogeneous catalysts are employed for these Baeyer-Villiger oxidation reactions [4-6], such as microporous titanium silicate TS-1, supported ionic liquids and sulfonic acids, Sn-doped microporous and mesoporous materials, etc. Apart from this, heterogeneous base catalysts are also employed in this reaction and especially the amine functionalized mesoporous silica has attracted considerable interest in this context [7]. There are some advantages of mesoporous silicas over zeolites due to their larger pore opening and high surface area. However, the silica grafted with organic functional groups suffers from disadvantages of thermal stability and can only be utilized at relatively lower temperature. This limitation has motivated the researchers to explore the potential of mesoporous materials which have high thermal stability [8] [9] [10].

The cobalt based catalysts have been widely used for direct oxidation, epoxidation reactions using molecular O_2 as an oxidant [11].Quite recently we have found that gallium promoted Co containing hexagonal silica was effective for styrene epoxidation reaction using molecular O_2 [12]. This finding motivated us to explore the design catalyst consisting of mixed metal mesoporous silica for Bayer Villiger Oxidation reaction. To improve the activity for cobalt center by other metallic promoter e,g Cu, Fe and Ni have been widely studied towards several reaction e,g hydrodesulfurization (HDS). Herein, we report the Cu, Fe and Ni (0.25 mol %) promoted cobalt containing mesoporous silica (Co-HMS-X 5mol%) catalyst for Bayer-Villiger reaction taking cyclohexanone substrate using molecular O_2 as oxidant and benzaldehyde as sacrificial reductant. It is found that Ni promoted Co-HMS-X catalyst (Si:Co:Ni = 100:5:0.25) demonstrated >99% cyclohexanone conversion with >99% e-Caprolactone selectivity. The catalysts are characterized by several techniques i.e BET surface area and porosity measurements, SAXS, FESEM, HRTEM, UV-Vis, FTIR, XRD and NH_3-TPD techniques in order to elucidate the reason for high catalytic activity in presence of Co-Ni bimetallic center.

2. Experimental:

2.1. Materials and catalyst preparation

Hexagonally ordered periodic mesoporous silica Co-HMS-X was synthesized by using triblock copolymer as a template under acidic condition. In a typical synthesis Pluronic P123 (Aldrich, MW= 5800) (4 g) was dissolved in 144 mL distilled water and 7.4 g 35% HCl (Merck) by continuous stirring. After stirring for 4 h a clear solution was obtained and then 4 g n-butanol (Merck) was added to this solution and stirred for another1 h. Then tetraethyl orthosilicate (8.4 g) (TEOS, Acros) and aqueous solution of cobalt nitrate (0.81 g) (Aldrich) were added to this solution and stirred for 24 h at room temperature. The resulting gel composition of the mixture is P123 : H_2O : HCl : n-Butanol : TEOS :

$Co(NO_3)_2$, $6H_2O$: 0.017: 200: 5.4: 1.325: 1: 0.05-0.15 (molar ratio). To prepare the metal nitrate promoted Co-HMS-X catalyst, the gel composition is fixed at P123: H_2O: n-Butanol : TEOS : $Co(NO_3)_2$, $6H_2O$: $M(NO_3)_2$:: 0.017: 200: 5.4: 1.325: 1: 0.05-0.15: 0.0025 (M= Cu, Fe, Ni) molar ratio. After stirring, the mixture was taken in a closed polypropylene bottle and aged at 100^{o}C temperature for 24 h under static hydrothermal condition. Subsequently the material was filtered in hot condition without washing and then dried at 100^{o}C for 12 h in air. Finally the dried materials were calcined at 540^{o}C for 24 h [13]. The material obtained after calcination was labelled as Co-HMS-X and M-Co-HMS-X (M = Cu, Fe, Ni) respectively.

2.2. Catalyst characterization

2.2.1. BET Surface area and porosity measurement

The nitrogen adsorption-desorption isotherm of the sample were measured at liquid nitrogen temperature-196 ^{o}C with a Quantachrome NovaWin-3200e instrument. Pre-treatment of the samples were carried out at 300^{o}C for 3 h under high vacuum. Pore size distributions were calculated from the desorption branch of isotherms using Barrett-Joyner-Halenda (BJH) method.

2.2.2. Small angle X-ray scattering (SAXS)

Small-angle x-ray scattering (SAXS) measurements were performed using a laboratory based SAXS instrument with Cu K_α X-ray source. Variation of scattering intensity with wave vector transfer [$q=4\pi\sin(\theta)/\lambda$] was measured for the powder samples.

2.2.3. Field Emission Scanning Electron Microscope (FESEM)

Field emission scanning electron microscope (FESEM) was carried out using Supra 55, Carl (Zeiss, Germany) microscope. Sample was supported on lacey carbon and then coated with platinum prior to measurement.

2.2.4. High Resolution Transmission Electron Microscope (HRTEM)

The HRTEM investigation was done on JEOL JEM 2100 microscope operated at 200 KV acceleration voltage using lackey carbon coated Cu grid of 300 mess size.

2.2.5. Ultraviolet–visible spectroscopy (UV-Vis)

DRUV-Visible measurement was carried out by using Varian Cary 500 (Shimadzu) spectrophotometer. The spectra were recorded in the range 200-800 nm wavelength.

2.2.6. Fourier Transformation Infrared Spectroscopy (FT-IR)

The FT-IR measurements were carried out by using Perkin Elmer GX spectrophotometer. The spectra were recorded in the range 400-4000cm^{-1} using KBr pellet.

2.2.7. X-Ray Diffraction (XRD)

The powder X-ray diffraction studies of the calcined samples were performed on a Scintag Pad V X-ray diffractometer with analysis software and a Rigaku Ultima IV system.

2.2.8. Temperature Programmed Desorption (NH_3- TPD):

The temperature programmed desorption (TPD) of ammonia of the samples were done using a thermal conductivity detector (TCD) in a Micromeritics Chemisorb 2720 instrument. For the experiment, the samples were first degassed in flow of He at a flow rate of 30 ml/min for 2 hour at 100 ^{o} C. Then the samples were saturated with 10 % NH_3 in He at room temperature for 30 minutes. Then the excess NH_3 was removed by flow of He (flow rate 30 ml/min) for 45 minutes. Then the desorption of ammonia (carrier gas He) was studied by heating from room temperature to 700 ^{o} C at a temperature ramp of 10 ^{o} C/ min

2.3 Catalytic Test

Baeyer-Villiger oxidation of ketones (cyclopentanone, cyclohexanone, 2-adamantanone) was conducted in the liquid-phase by bubbling with oxygen in the reaction mixture. In a typical reaction procedure, 50 mg of catalyst (preactivated at 100 ^{o} C prior to use) was mixed with 10 mL of l,2-dichloroethane. 2 mmol of substrate (Acros 99.8%) and benzaldehyde (6mmol) were taken in a two neck 50 mL round bottle flask fitted with water condenser. The mixture was heated at 50 ^{o} C and molecular oxygen was bubbled into the mixture at a flow rate of 10 mL/min (maintained by Aalborg mass flow controller) for 2h under constant stirring at 540 rpm using Tarson spinot digital magnetic stirrer [14]. GC analysis of the sample was done using a gas chromatograph (CIC-India) fitted with SE-30 column. After the reaction, the catalyst was recovered, washed with acetone, dried in air, and used further for recycling experiments.

3. Results and Discussion

3.1. Textural characterization of the catalyst by BET Surface area and porosity measurement

The pore size distribution and N_2 physisorption isotherms of the catalyst are depicted in **Fig. 1** and textural results are summarized in **Table 1.** It is found that all materials has typical type IV adsorption/desorption isotherms with H1 hysteresis loop which is characteristic of typical mesoporous materials with 2D-hexagonal structure (**Fig. S1** supporting information). The steep rise of the isotherms at a relative partial pressure of 0.6–

0.8 is due to the capillary condensation of N_2. This indicates the uniformity of the pores as reported in literature [15]. The inset of **Fig. 1** shows the monomodal pore size distribution of the mesoporous HMS-X catalyst.

The specific surface areas (BET) of metal promoted Co-HMS-X increasees in the range from 674 m^2/g to 841 m^2/g. Addition of nickel in Co-HMS-X caused an increase in surface area which may be due to an increase in the pore size **(Table 1)** [16], [17]. The rate of hydrolysis and condensation of silicate precursor in presence of P123 template depends on the type of metal cation present in the solution [18] Among Co- HMS-X and Cu, Fe, Ni promoted Co-HMS-X materials, Ni-Co-HMS-X has the highest surface area i.e. 841 m^2g^{-1} in comparison with other catalysts.

3.2. Structural Characterization of the catalyst by Small Angle X-ray Scattering (SAXS)

The SAXS patterns of various catalysts are shown in **Fig. 2.** A highly long range ordered mesoporous silica structure is evident from SAXS studies. Each sample exhibits an intense diffraction peak corresponding to the (10) plane at 0.64 nm^{-1}, typical characteristic of HMS material [19, 20]. The intensity of the reflection corresponding to the (1 0), (1 1) and (2 0) planes decrease after the cobalt doping in HMS-X as compared with the undoped siliceous HMS-X. The peak position remained almost constant for Co-HMS-X with respect to HMS-X which proves that the hexagonal ordered structure of mesoporous silica remains unchanged even after cobalt incorporation. Addition of promoters Fe and Ni) do not change the original hexagonal structure of the HMS-X catalyst. The peak intensity corresponding to (10), (11) and (20) planes decreases for Cu-Co-(HMS-X) catalyst, which is due to deterioration of the long range order strengthening the results obtained from N_2 physisorption studies [21].

3.3. Morphological study of the catalyst by FESEM characterization

To further investigate the morphology and textural property of the M-Co-HMS-X catalyst the catalysts are characterized FESEM techniques. The FESEM images (**Fig. 3**) of the catalyst show that the material has wormlike morphology with minimal aggregation [22]. The morphology of Co-HMS-X (5 mol%) after the addition of promoters (e.g. Cu, Fe and Ni) were remained similar for all the catalysts.

The powder XRD patterns in the high angle region of $10^o < 2\theta < 60^o$ for all the samples are given in **Fig. S2** (supporting information). The wide-angle patterns show a broad diffraction peak at $2\ \theta = 23^\circ$, which is of amorphous silica. It is seen that there are no diffraction lines due to crystalline Co_2O_3 reflections even after adding some metal promoters. The XRD investigation of the samples was unable to detect cobalt oxide phase which indicates the high dispersion of cobalt oxide to the silica surface. [17]

3.4 Chemical characterization of the catalyst by UV-vis spectroscopy and FTIR spectroscopy

Electronic spectroscopy in UV–Vis region is considered as an effective technique for studying the local coordination environment and electronic state of isolated transition metal ions as well as aggregated transition metal oxides. The M-Co-HMS-X catalysts were further investigated by the UV–vis spectroscopy as shown in **Fig. S3** (supporting information**)**. The absorbance in the range of 500–700 nm is characteristic of Co (II) in an isolated state, which can be unambiguously assigned to the ${}^4A_2(F)\rightarrow{}^4T_1(P)$ transition of tetrahedral coordinated Co(II) ions incorporated in the framework of HMS-X mesoporous silica [23, 24]. The blue color of the catalyst is also a fingerprint of tetrahedral $Co(II)O_4$ sites. [2]

The FTIR spectra of HMS-X, Co-HMS-X and three different metal (Cu, Fe and Ni) promoted Co-HMS-X material are shown in **Fig. 4**. The bands at 1085 cm^{-1} and 1195 cm^{-1} are attributed to the asymmetric stretching vibration of framework Si-O-Si bridges. The peak at 817 cm^{-1} is attributed to Si-O-Si symmetric stretching [13]. The gradual decrease of peak intensity at 817 cm^{-1} may be due to the successive formation of Si-O-Co moiety. The band at 960 cm^{-1} has been interpreted for stretching vibration of Si-OH and Si-O $^{\delta-}$groups. As found in literature the peak ascribed in the region 960 cm^{-1} can be considered as an evidence of the isomorphous substitution of Si by Co metal ions i,e as Si–O-Co connectivity [25]. This peak is also widely used to characterize the presence of transition metal atoms near the silica framework as the stretching Si–O vibration mode perturbed by the neighbouring metal ions. The bands appeared around 3500 cm^{-1} and 1633 cm^{-1} can be attributed to O-H and H-O-H stretching respectively [26]. FTIR spectra showed no changes in the vibration band after the addition of promoters like (Cu, Fe and Ni) in doped mesoporous Co-HMS-X matrix [12].

3.5. NH_3-TP Characterization

The changes of surface acidic properties of all the four catalysts studied were investigated by temperature programmed desorption of ammonia (NH_3-TPD) which is shown in **Fig.5**. The TPD profile in terms of temperature of NH_3 desorption and volumes of desorbed NH_3 are shown in **Fig. 6.** While comparing the TPD profiles of Co HMS-X and (Cu, Fe and Ni) promoted Co-HMS-X mesoporous silicas it is found that nickel incorporation increases the density strong acid sites in the Co-HMS-X material [13]. It is also reported in literature that desorption at higher temperature region is due to the chemisorptions of ammonia on stronger acid sites [12]. On the contrary the addition of Cu and Fe in Co-HMS-X produced only a limited change in the acidic sites [27].

4. Baeyer-Villiger oxidation of ketones

4.1 Catalytic Performance of Materials

The catalytic activity of the doped silica materials **(Table 1)** for the Baeyer-Villiger type oxidation was examined by performing the aerobic oxidation of cyclohexanone to ε-caprolactone in the presence of benzaldehyde as reductant. The HMS-X it has got quite high surface area but it showed no activity towards B-V oxidation reaction. In the case of cobalt doped HMS-X showed activity towards B-V oxidation reaction and it continued even after adding promoters like Cu, Fe and Ni also.

Table 2 summarizes the cyclohexanone oxidation in different reaction conditions (e.g. solvent, reaction temperature, duration of reaction, molecular O_2 flows etc). In order to investigate the effect of the solvents on the reaction, cyclohexanone was oxidized with molecular O_2 in presence of several solvents e,g DCE, Acetonitrile, 1-4 dioxane, toluene and DMF and the results are summarized in **Table 2**. Among several solvent DCE afforded the highest conversion whereas acetonitrile was the secondary optimal solvent with 64.8% conversion of cyclohexanone. Although in both the examined solvents the product selectivity remains >99%, but in presence of DCE the conversion over 90% was obtained. On the other hand other solvents like1-4 dioxane, toluene and DMF showed unfavorable effect in this oxidation reaction. In the following experiments, we chose DCE as the organic medium to perform the oxidation reaction as reported in literature. [28]

The Baeyer-Villiger oxidation reactions were carried out at different temperatures to investigate the influence of reaction temperature on the, cyclohexanone conversion and product distribution. The effect of the reaction temperature is summarized in **Tables 2**. It shows that solvent the conversion increased as the reaction temperature was increased from 20 to 70 ^{o} C in DCE solvent. Being a triplet (two unpaired electrons in ground state), molecular oxygen is un-reactive toward organic molecules at low temperatures. The reaction of dioxygen with the single state of organic substrates is spin-forbidden [29]. The increase in reaction temperature from 20 to 50 ^{o} C results a significant increase in the conversion but increasing the reaction temperature from 50 to 70 ^{o} C leads to a decrease in the conversion. The product selectivity is higher than 99% throughout the temperature range 20 to 70° C As reported in the literature [30], at higher temperature rate are probably determined by the diffusion of reactants to the active sites. It seems that an appropriate reaction temperature is favourable to the formation of ε-caprolactone for this reaction [12, 15].

Table 2 shows that cyclohexanone conversion increases with the reaction time from 30 min to 120 min in a fast rate i.e. 36% to 96.3% but activity decreases beyond 120 min of reaction. From the results and literature reports it can be said that catalytic system is capable of giving good result in short time on stream. [1-9]

The influence of flow rate of O_2 on the oxidation of cyclohexanone over Co- HMS-X at 50^{o}C has also been carried out**.** The cyclohexanone conversion was 84% when flow rate was 5 mL/min, and then slowly increased to 93.6% with the rise of flow rate of O_2 to 10 mL/min. The conversion is decreased or remained constant when the flow rate of O_2 was 15 mL/min which may be due to the over oxidation of the substrate as reported in the literature. [31].

In the present study the oxidation reaction is also performed without using benzaldehyde (**Table 3).**It is observed that no reaction takes place which established the role of aldehydes to activate the dioxygen [32]. **Table 3** summarizes the cyclohexanone oxdation over Co-HMS-X in the presence of different aldehydes like benzaldehyde, acetaldehyde and anisaldehyde. Benzaldehyde showed the best performance in the tested aldehyde so far where over 90% conversions are achieved. The acetaldehyde and anisaldehyde free radicals are unstable where as in case of benzaldehyde free radical it is quite stable due to the resonance effect. The free radical generated in anisaldehyde is unstable due to +R effect of CH_3 group present in the molecule.

To establish that reaction is truly heterogeneous in nature, the reaction is carried out for 30 min in presence of catalyst and again it continued for 90 mins after removing the catalyst (**Table 3**). While comparing these results with the experiment where the complete reaction is performed with catalyst (**Table 2**), it can be said that after 30 min the conversion is almost same in both the cases. When the reaction is performed in presence of catalyst the conversion is reached over 90%, but in case of without catalyst the activity is reached up to 63% only. From the given results it can be concluded that catalyst plays a very pivotal role in this reaction.

Cyclohexanone, cyclopentanone, and 2-adamantanone were oxidized under the same reaction conditions (**Table 3)**, Among the cyclic ketones, the six member cyclic ketone was more efficiently oxidized than cyclopentanone. This reaction behavior could be explained in terms of steric hindrance. The oxidation of 2-adamantanone also yielded their corresponding lactones in high yields but it was comparatively lower than those of other five member and six member ketone. This may be due to the bulkiness of the substituent functional group which creates the steric hindrance [33]. The stereochemistry and reactivity seem to follow the tendency reported in literature for the Baeyer-Villiger type oxidation. Although the reaction rate depends on the chemical structure of ketones, it can be concluded that the Co-HMS-X catalysts can oxidize various ketones to corresponding lactones or esters under such mild reaction conditions [4].

4.2 Recycling studies

The catalyst recyclability is one of the important parameter to commercialize the catalyst. Recycling tests were carried out by repeating the catalytic reaction after separating the catalyst powder from the reactants and products. **Table 3** shows the catalytic activities of the Co-HMS-X catalyst after each recycling test. There was a marginal decrease observed in conversion may be due to the loss of catalyst during filtration and drying. This suggests that stability of this catalyst is good enough to work continuously in the present reaction condition.

The cyclohexanone conversion and ε-caprolactone yields are improved significantly with higher selectivity around 99%, with the addition of very little amount of promoter into the framework, i.e. as low as 0.25mol %. The Ni-Co-HMS-X catalyst showed the highest conversion of 100%, The conversion values from these experiments are given in **Table 1** with the N_2 physisorption data. The result suggests that the catalytic activity for the cyclohexanone oxidation shows a good correlation with the BET surface area. The ionic radius of Ni^{+2} is smallest i.e 69 pm in comparison to Fe^{+2} and Cu^{+2}. So because of its small size it easily enters in the framework and increases the surface area of the catalyst i.e ($841 m^2 g^{-1}$). With increase in surface area, the catalyst has more exposed surface to adsorb and protect the radical species from the inhibition. The NH_3 TPD results also supported the results of catalyst activity. Ni promoted Co-HMS-X catalyst has highest acidity which is responsible for its high activity. Therefore doped silica materials seem to have a particular advantage compared with the other undoped silica materials.

5. Reaction mechanism

It is quite important to understand the reaction mechanism of the Baeyer-Villiger type oxidation catalyzed by silica materials. The generally accepted reaction scheme for the O_2/aldehyde oxidation system consists of two reaction steps: (a) peracid formation from the aldehyde and O_2 and (b) the oxidation of the reactant by the peracid [34, 35].

We hereby propose a reaction mechanism in **Fig. 7** for the oxidation of ketones by the O_2/aldehyde system catalyzed by HMS-X silica materials. The oxidation process starts from the autoxidation of aldehyde to form the peroxy acid, and the produced peroxy acid can readily enable the Baeyer-Villiger oxidation of ketone. The initiation reaction of this autoxidation could be the formation of carbonyl radical from aldehyde and O_2. This initiation probably occurs without any catalyst. The chain propagation reactions, the insertion of O_2 into the carbonyl radical to form the peroxy radical species, and the formation of the peracid species by the reaction between the peroxy radical and aldehyde increase the concentration of peracid. , As long as sufficient amount of radicals exist in the system, this chain propagation reaction would be much faster than the initiation reaction; therefore, the majority of the aldehyde is consumed by the propagation rather than initiation under the reaction conditions. However, if a large amount of ketone was supplied into the system, this chain propagation reaction was inhibited by ketone. Probably the alpha hydrogen atom of the ketone was abstracted by the radical species, and the chain reactions were inhibited.

We assume that the main role of the silica materials in this oxidation system is to adsorb and protect the radical species from the inhibition. Even if the majority of radical species were killed by the inhibitor, the catalyst surface can supply active radical species. In other words, the catalyst surface can act as a buffer for the radical species, which are necessary for the chain propagation reactions. The radical species formed by the initiation reaction would be readily adsorbed on the catalyst surface, and the concentration of the radical species becomes quite low at the early stage of the reaction.

6. Conclusions

In summary, a high surface area hexagonal mesoporous silica catalyst M-Co-HMS-X (M = Fe, Cu, Ni) was prepared by sol-gel procedure and shown to act as a highly active catalyst for the aerobic Baeyer-Villiger oxidation of ketones with almost 100% conversion and high selectivity. It has been revealed that Ni promoted Co-HMS-X catalyst had high catalytic activity towards the Baeyer-Villiger type oxidation reaction. The higher acidic site density in the case of Ni promoted Co-HMS-X catalyst as observed from NH_3-TPD results was responsible for the enhanced catalytic activity. The catalyst recycling tests suggest that the durability of the catalyst is quite moderate in the tested reaction conditions. The mechanistic study has revealed that the peroxycarboxylic acid is the important intermediate, and the silica based catalyst contributes to high aldehyde efficiency by buffering the radical species, which are essential for the chain propagation reactions. The activity of Co-HMS-X catalysts in the present investigation are superior to other mesoporous catalyst and the activity of mesoporous materials may be attributed to the interwoven two-dimensional pore system of the materials which favors mass-transfer kinetics for the diffusion of large and bulky molecules such as 2-adamantanone. To our knowledge, such catalysis by doped silica materials is quite new and highly selective in comparison to the catalyst system reported so far. The present finding would contribute to the establishment of environmentally friendly oxidation systems.

Acknowledgments

SR would like to acknowledge UGC (F-39-802/2010 (SR), Govt of India for research fellowship. BC and EN would like to acknowledge DST (SR/F1/PC-10/2012 for funding.

References

[1] Y. Nabae, H. Rokubuichi, M. Mikuni, Y. Kuang, T. Hayakawa and M. Kakimoto, ACS Catal., 3 (2013) 230-236.

[2] E.Y. Jeong, M. B. Ansari, and S. E. Park, ACS Catal., 1 (2011) 855–863.

[3] A. Corma, L. T. Nemeth, M. Renz & S. Valencia, Nature , 412 (2001) 424-425.

[4] T. Kawabata, N. Fujisaki, T. Shishido, K. Nomura,T. Sano, K. Takehira. J. Mol. Catal. A: Chem. 253 (2006) 279-289.

[5] C. J. Sanchidria, J. M. Hidalgo, R. Llamas, J. R. Ruiz, Appl. Catal. A: Gen, 312 (2006) 86-94.

[6] I. Nowak. A. Feliczak, I. Nekoksova, J. Cejka, Appl. Catal. A: Gen. 321 (2007) 40 -48.

[7] X. Dong, D. Wang, K. Li, Y. Zhen, H. Hua, G. Xue, Mater. Res., 57 (2014) 210-220.

[8] M. Paul, N. Pal, J. Mondal , M. Sasidharan and A. Bhaumik, Chem. Eng. Sci. 71 (2012) 564-572.

[9] A. Chrobok, Tetrahedron 66 (2010) 2940-2943.

[10] B. Dutta, S. Jana, S. Bhunia, H. Honda, S. Koner, Appl. Catal. A: Gen. 382 (2010) 90-98.

[11] Q. Tang, Q. Zhang, H. Wu, Y. Wang, J. Catal. 230 (2005) 384-397.

[12] S. Rahman, C. Santra, R. Kumar, J. Bahadur, A. Sultana, R. Schweins, D. Sen, Sudip Maity, S. Mazumdar, B. Chowdhury, Appl. Catal. A: Gen. 482 (2014) 61-68

[13] S. Mandal, C. Santra, R. Kumar, M. Pramanik, S. Rahman, A. Bhaumik, S. Maity,D. Sen, B. Chowdhury, RSC Adv. 4 (2014) 845-854.

[14] H. Subramanian, E.G. Nettleton, S. Budhi, R. T. Koodali, J. Mol. Catal. A: Chem. 330 (2010) 66-72.

[15] H. Cui, Y. Zhanga, Z. Qiua, L. Zhaoa, Y. Zhua, Appl. Catal. B: Environ. 101 (2010) 45-3.

[16] M. Lualdia, G. D. Carlob, S. Logdberga, S. Jaras, M. Boutonneta,V. L. Parolac, L. F. Liotta, G. M. Ingob, A. M. Veneziac. Appl. Catal. A: Gen. 443- 444 (2012) 76-86.

[17] P. Bhangea, D. S. Bhange, S. Pradhan and V. Ramaswamy. Appl. Catal. A: Gen. 400 (2011) 176-184.

[18] G. J. de, A. A. Soler- Illia and C. Sanchez, New J. Chem., 24, (2000), 493-499

[19] X. L. Yang, W. L. Dai, H. Chen, J. H. Xu, Y. Cao, H. Li, K. Fan, Appl. Catal. A: Gen.

283 (2005) 1-8.

[20] D. Sen, S. Mazumder, J. S. Melo, Arshad Khan, S. Bhattyacharya, S. F. D Souza, Langmuir, 25 (2009) 6690-6695.

[21] P. A. Robles-Dutenhefner, K. A. da Silva Rocha, E. M. B. Sousa, E. V. Gusevskaya, J. Catal. 265 (2009) 72-79.

[22] J. Taghavimoghaddam, G. P. Knowles, and A. L. Chaffee, J. Mol. Catal. A: Chem. 379 (2013) 277- 286.

[23] H. Ma, J. Xu, C. Chen, Q. Zhang, J. Ning, H. Miao, L. Zhou, X. Li, Catal. Lett. 113 (2007) 104-108.

[24] S. Farhadi, J. Safabakhsh, P. Zaringhadam, J. Nano Chem. 3 (2013) 69.

[25] T. Tsoncheva, L. Ivanova, J. Rosenholm, M. Linden, Appl. Catal B: Environ. 89 (2009) 365-374.

[26] M. S. Morey, S. O'Brien, S. Schwarz and G. D. Stucky, Chem. Mater. 12 (2000) 898-911.

[27] A.M. Veneziaa, G. Di Carlob, L.F. Liotta, G. Pantaleoa, M. Kantcheva, Appl. Catal. B: Environ. 106 (2011) 529-539.

[28] T. Kawabata , Y. Ohishi , S. Itsuki, N. Fujisaki, T. Shishido , K. Takaki , Q. Zhang, Y. Wang, K. Takehira , J. Mol. Catal. A: Chem. 236 (2005) 99-106.

[29] H.Y. Lan, X. T. Zhou, H. B. Ji, Tetrahedron 69 (2013) 4241-4246.

[30] Q. Tang, Q. Zhang, H. Wu, Y. Wang, J. Catal. 230 (2005) 384-397.

[31] D. Jiang, T. Mallat, D.M. Meier, A. Urakawa, A. Baiker, J. Catal. 270 (2010) 26-33.

[32] (a) T. Yamada, T. Takai, O. Rhode, T. Mukaiyama, Bull. Chem. Soc. Jpn. 64 (1991) 2109-2117; (b) T. Takai, E. Hata, T. Yamada, T. Mukaiyama, Bull. Chem. Soc. Jpn. 64 (1991) 2513-2518. (c) B. B.Wentzel, P. L. Alsters, M. C. Feiters, M. J. R. Nolte, J. Org. Chem. 69 (2004) 453-3464. (d) T, X. Zhou, H. Q. Tang, B. H. Ji, Tetrahedron Lett. 50 (2009) 6601-6605. (j) T. Yamada, K. Imagawa, T. Nagata, T. Mukaiyama, Chem. Lett. 21 (1992) 2231-2234.

[33] J. R. Ruiz, C. J. Sanchidrian, R. Llamas. Tetrahedron 62 (2006) 11697-11703.

[34] S. Murahashi, Y. Oda, T. Naota, Tetrahedron Lett. 33 (1992) 7557.

[35] R. Giannandrea, P. Mastrorilli, F. C. Nobile, P. G. Suranna, J. Mol. Catal. 94 (1994).

Figure Captions

Fig.1 Surface area & pore size (inset) of the catalyst.

Fig. 2 SAXS image of the catalyst.

Fig. 3 FESEM images of the catalyst, **1(a)** & **(b)** Co-HMS-X (5 mol%), **2 (a)** & **(b)** Cu-Co-HMS-X (Co/Cu=20), **3 (a)** & **(b)** Fe-Co-HMS-X (Co/Fe=20), **4 (a)** & **(b)** Ni-Co-HMS-X(Co/Cu=20).

Fig.4. FTIR spectra of the catalysts.

Fig. 5. NH_3-TPD of the catalyst.

Fig. 6. NH_3-TPD profile of the catalyst.

Fig. 7. Reaction mechanism of the ketone oxidation by the O_2/ aldehyde system catalyzed by silica material HMS-X.

Table Captions

Table1. Catalytic Results of Baeyer-Villiger Oxidation of Cyclohexanone Using Molecular Oxygen by Various Catalysts.

Table 2: Catalytic Results of Baeyer-Villiger Oxidation of Cyclohexanone using Co-HMS-X as a catalyst.

Table 2: Catalytic Results of Baeyer-Villiger Oxidation of Cyclohexanone using Co-HMS-X as a catalyst.

Tables

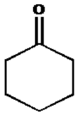
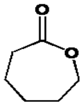
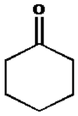
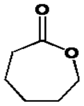
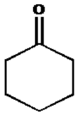
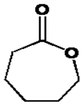
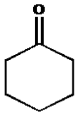
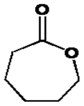
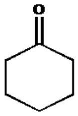
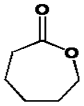
Table1. Catalytic Results of Baeyer-Villiger Oxidation of Cyclohexanone Using Molecular Oxygen by Various Catalysts

Catalyst	Conversion (%)	Selectivity (%)	Surface Area (m^2g^{-1})	Pore Size (nm)	Pore Volume (ccg^{-1})
HMS-X	-	-	702	6.0	9.23
Co-HMS-X (5 mol%)	93.6	100	674	5.4	8.87
Cu-Co-HMS-X (Co/Cu=20)	77.4	100	727	5.9	1.01
Fe-Co-HMS-X (Co/Fe=20)	94.6	100	759	6.3	1.02
Ni-Co-HMS-X (Co/Ni=20)	100	100	841	5.9	1.07
No catalyst	54.0	100	-	-	-
#Co-HMS-X (5 mol%)	14.4	100	525	5.9	0.70

Reaction conditions: DCE solvent, 10 mL; Cyclohexanone, 2 mmol; Benzaldehyde, 6 mmol, catalyst, 100 mg; O_2, 10 mL/min; reaction time, 2 h; reaction temperature, 50 ◦C; tridecane used as an internal standard.

(1,4 Dioxane is used as alcohol in place of n-Butanol)

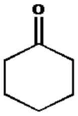
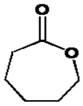
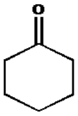
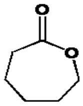
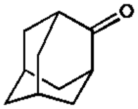
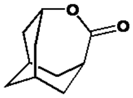
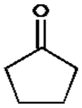
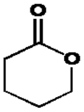
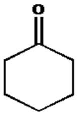
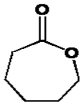
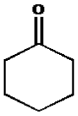
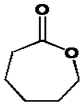
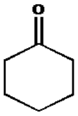
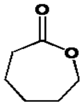
Table 2: Catalytic Results of Baeyer-Villiger Oxidation of Cyclohexanone using Co-HMS-X as a catalyst

Substrate	Product	Different parameter	Conversion (%)	Selectivity (%)
		DCE	93.6	>99
		Acetonitrile	64.8	>99
		1-4 Dioxane	-	-
		Toluene	-	-
		DMF	-	-
		20 ^{o}C	9.0	>99
		30^{o}C	61.2	>99
		40 ^{o}C	75.5	>99
		50 ^{o}C	93.6	>99
		60 ^{o}C	81.0	>99
		70 ^{o}C	56.2	>99
		30min	36.0	>99
		60min	59.5	>99
		90min	67.6	>99
		120min	93.6	>99
		150min	91.9	>99
		180min	84.7	>99
		210min	86.7	>99
		#30min	33.6	>99
		#Catalyst removed	61.2	>99
		5mL/min	84.7	>99
		10mL/min	93.6	>99
		15mL/min	93.0	>99

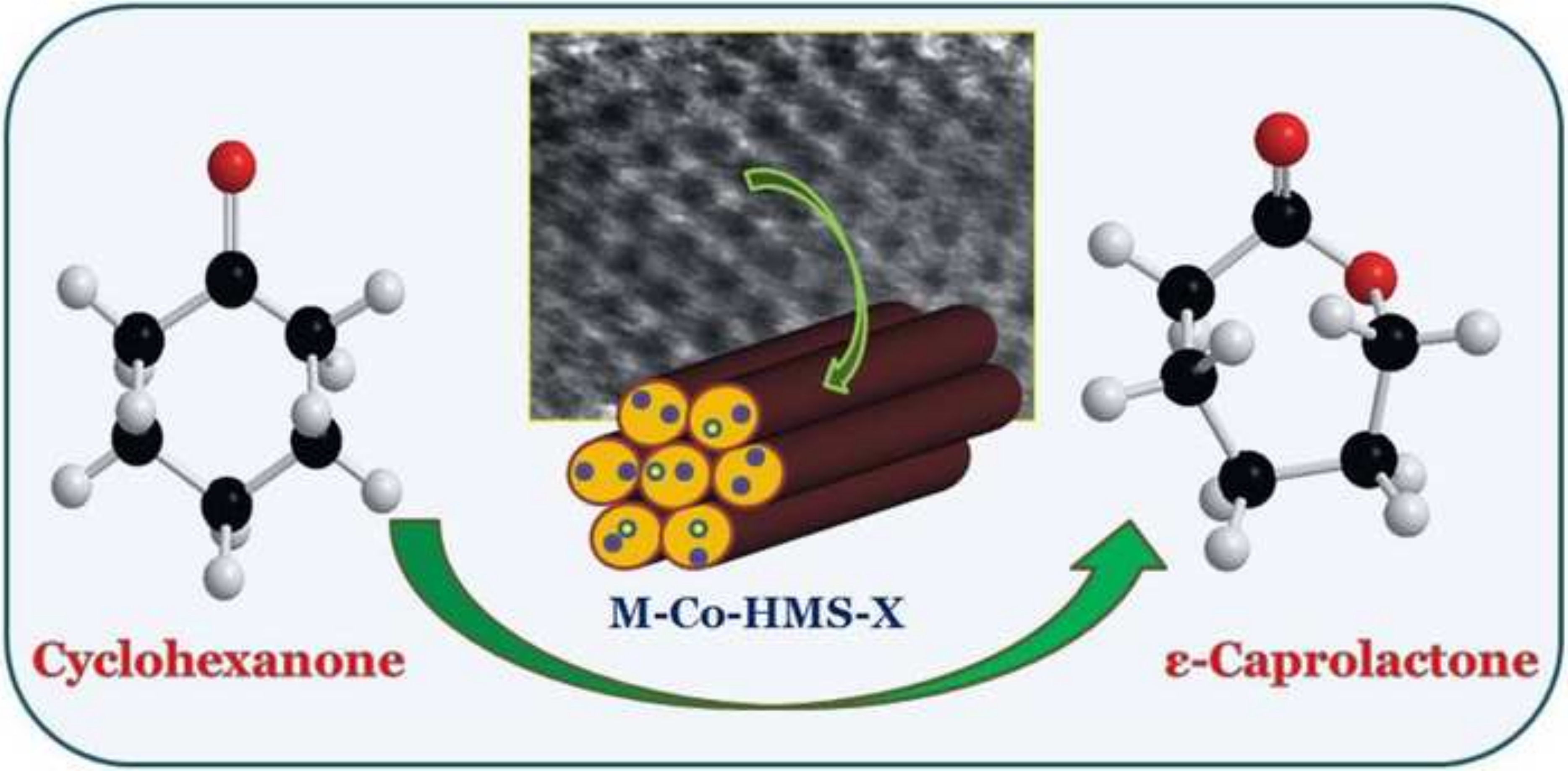
Reaction conditions: DCE solvent, 10 mL; Cyclohexanone, 2 mmol; Benzaldehyde, 6 mmol, catalyst, 100 mg; O$_2$, 10 mL/min; reaction time, 2 h; reaction temperature, 50 ◦C; tridecane used as an internal standard.

After 30min run product is collected and catalyst is removed by centrifugation, again the reaction mixture is kept for reaction for 90 min.

Table 3: Catalytic Results of Baeyer-Villiger Oxidation of Cyclohexanone using Co-HMS-X as a catalyst

Substrate	Product	Different parameter	Conversion (%)	Selectivity (%)
		Without reductant	-	-
		Benzaldehyde Acetaldehyde Anisaldehyde	93.6 - -	>99 -
		-	80.1	>99
		-	83.8	>99
		1st Recycling	90.9	>99
		2nd Recycling	87.7	>99
		3rd Recycling	87.1	>99

Reaction conditions: DCE solvent, 10 mL; Cyclohexanone, 2 mmol; Benzaldehyde, 6 mmol, catalyst, 100 mg; O_2, 10 mL/min; reaction time, 2 h; reaction temperature, 50 ◦C; tridecane used as an internal standard.


M-Co-HMS-X
Cyclohexanone
ε-Caprolactone

Figures

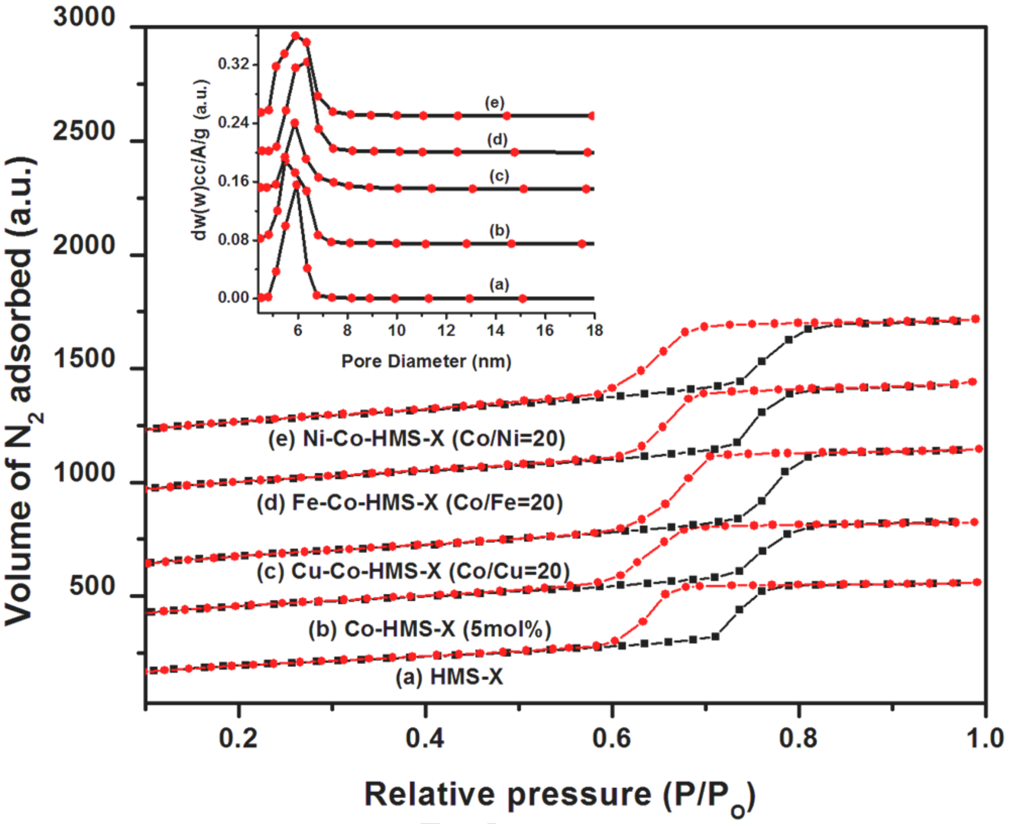


Fig. 1

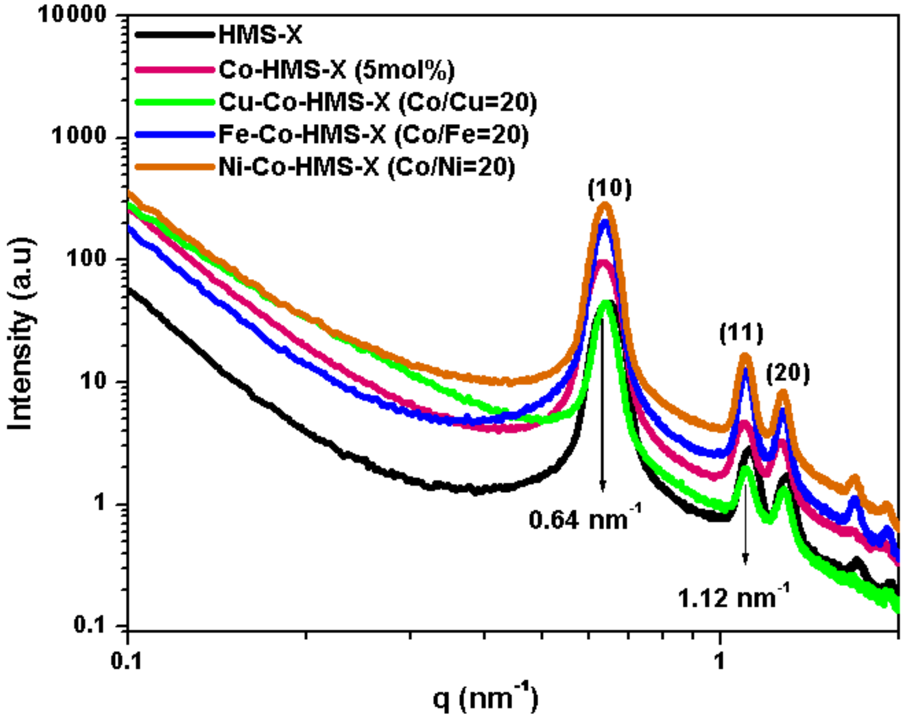

HMS-X
Co-HMS-X (5mol%)
Cu-Co-HMS-X (Co/Cu=20)
Fe-Co-HMS-X (Co/Fe=20)
Ni-Co-HMS-X (Co/Ni=20)
(10)
(11)
(20)
0.64 nm^{-1}
1.12 nm^{-1}
Intensity (a.u)
q (nm^{-1})
10000
1000
100
10
1
0.1
0.1
1

Fig. 2

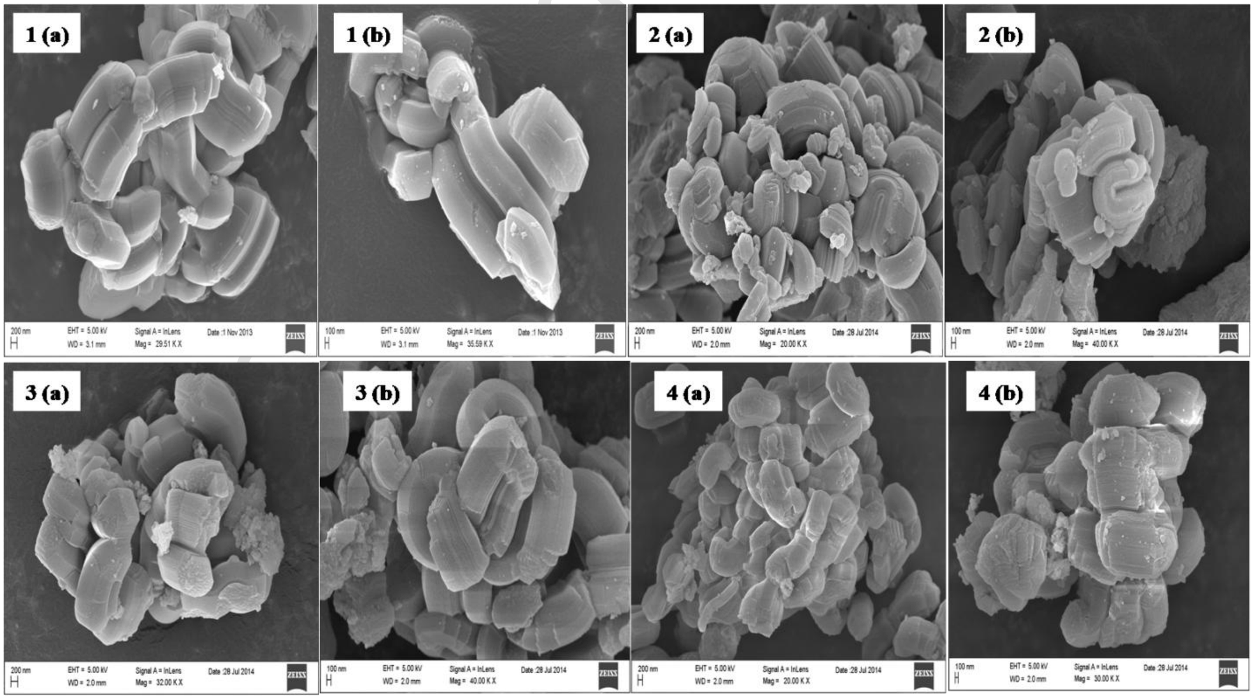

1 (a)
1 (b)
2 (a)
2 (b)
3 (a)
3 (b)
4 (a)
4 (b)

Fig. 3

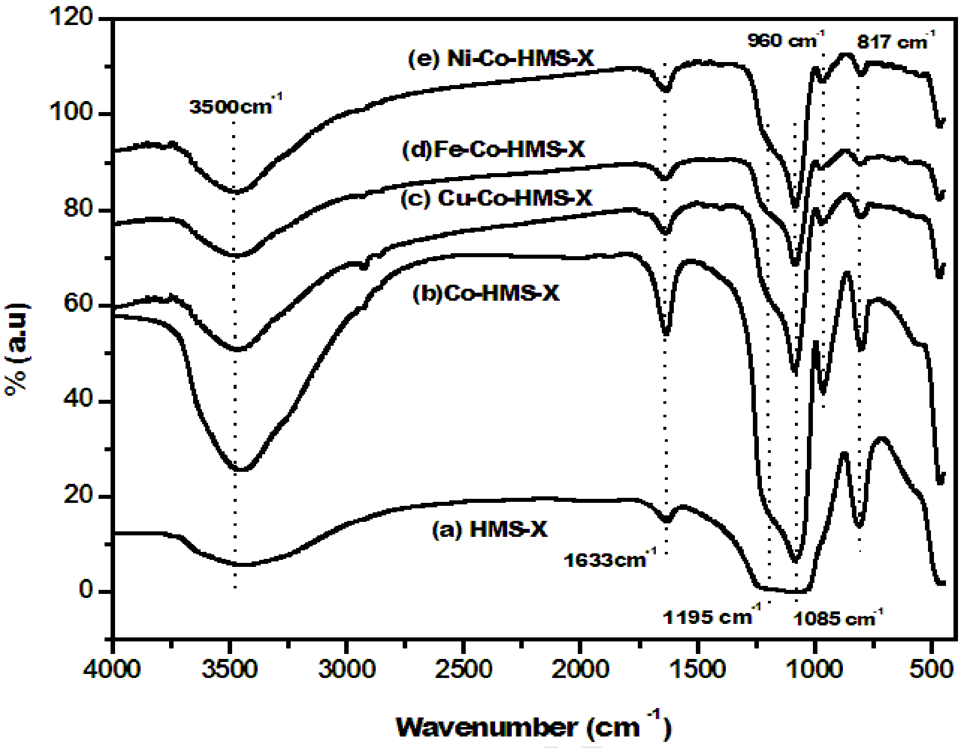

120
100
80
60
40
20
0
% (a.u)
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm^{-1})
(e) Ni-Co-HMS-X
(d)Fe-Co-HMS-X
(c) Cu-Co-HMS-X
(b)Co-HMS-X
(a) HMS-X
3500cm^{-1}
960 cm^{-1}
817 cm^{-1}
1633cm^{-1}
1195 cm^{-1}
1085 cm^{-1}

Fig.4

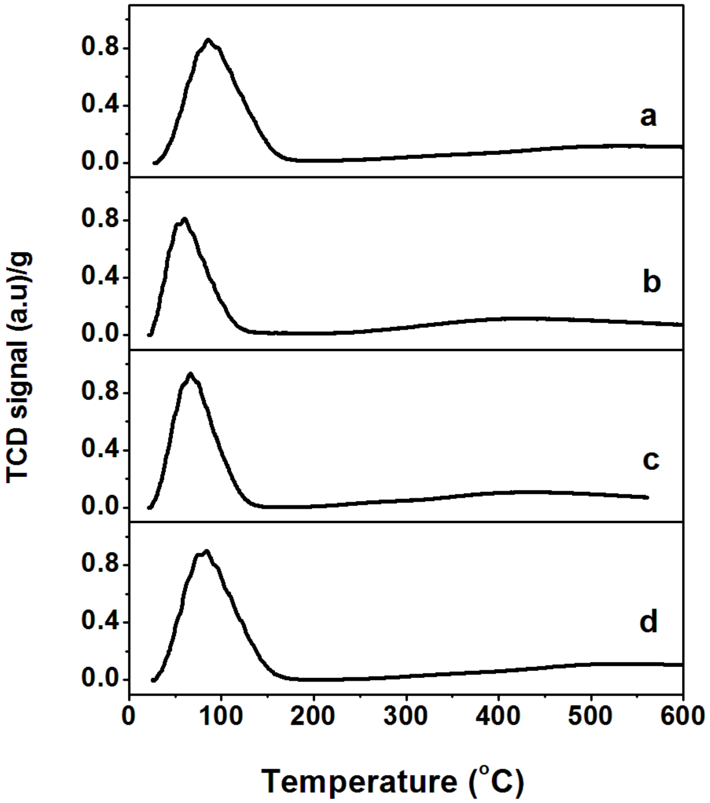

0.8
0.4
0.0
a
b
c
d
TCD signal (a.u)/g
0
100
200
300
400
500
600
Temperature (°C)

Fig. 5

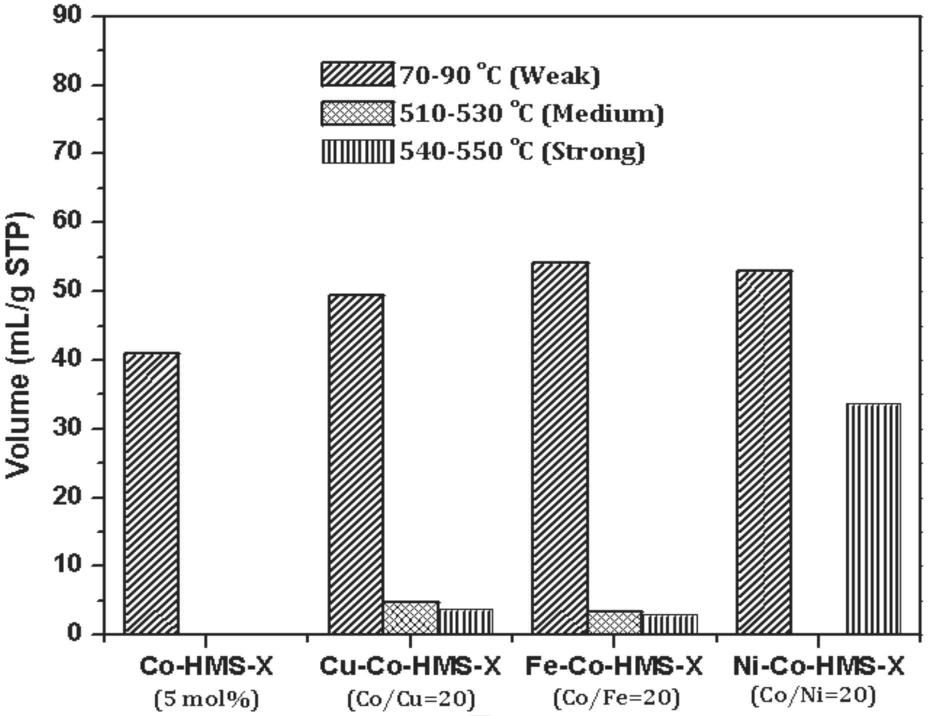

Volume (mL/g STP)
90
80
70
60
50
40
30
20
10
0
70-90 °C (Weak)
510-530 °C (Medium)
540-550 °C (Strong)
Co-HMS-X
(5 mol%)
Cu-Co-HMS-X
(Co/Cu=20)
Fe-Co-HMS-X
(Co/Fe=20)
Ni-Co-HMS-X
(Co/Ni=20)

Fig. 6

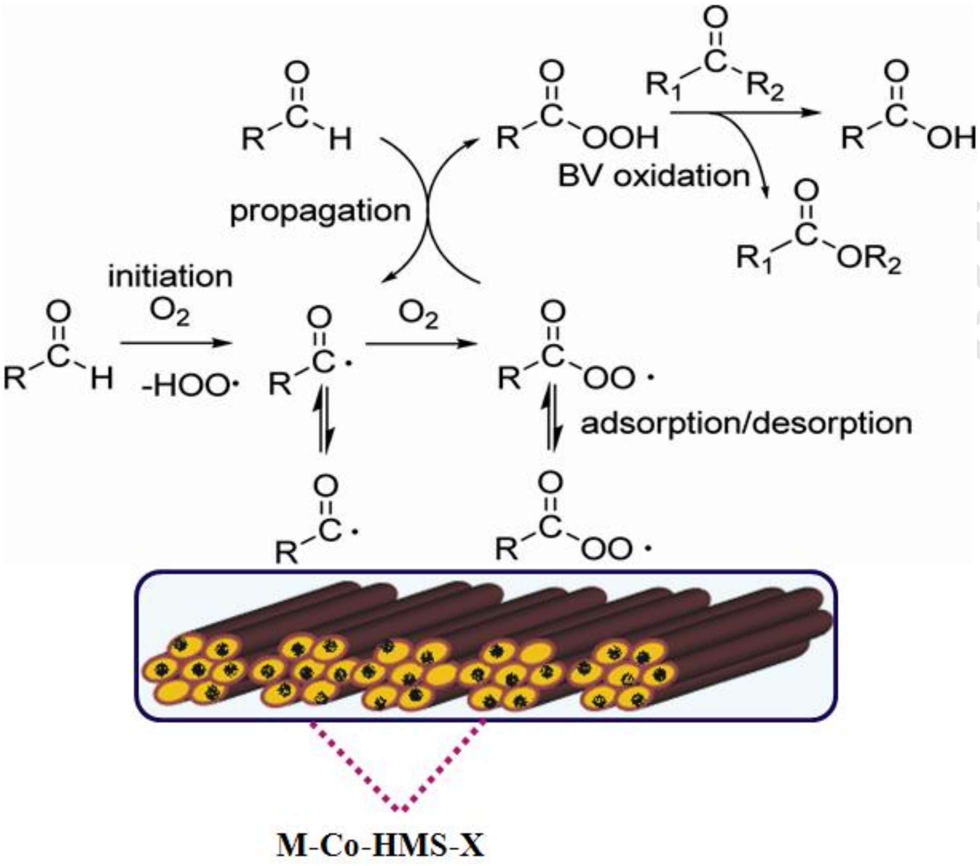

propagation
BV oxidation
initiation
O_2
-HOO·
O_2
adsorption/desorption
M-Co-HMS-X

Fig. 7