

# **CHEMISTRY** A European Journal



# **Accepted Article** Title: Microporous nanotubes and nanospheres with iron-catechol sites: efficient Lewis acid catalyst and support for Ag nanoparticles in CO2 fixation reaction Authors: Arindam Modak, Piyali Bhanja, and Asim Bhaumik This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article. To be cited as: Chem. Eur. J. 10.1002/chem.201802319 Link to VoR: http://dx.doi.org/10.1002/chem.201802319 **Supported by** ACES



DOI: 10.1002/cctc.200((will be filled in by the editorial staff))

# Microporous nanotubes and nanospheres with iron-catechol sites: efficient Lewis acid catalyst and support for Ag nanoparticles in CO<sub>2</sub> fixation reaction

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Fe(III)-containing hyper-cross-linked microporous nanotubes (FeNT) and nanospheres (FeNS) have been synthesized through the reaction of catechol and dimethoxymethane in the presence of FeCl<sub>3</sub> or CF<sub>3</sub>SO<sub>3</sub>H. Both FeNT and FeNS demonstrate excellent catalytic activity in the Lewis acid catalysis (hydrolysis and regioselective methanolysis of styrene oxide) and tandem catalysis involving a sequential oxidation-cyclization process, which selectively converts benzyl alcohol to 2-phenyl benzimidazole. Apart from Lewis acidity, FeNT and FeNS also showed CO<sub>2</sub> uptake capacity of 2.6 and 2.2 mmol  $g^{-1}$ , respectively at 1 atm pressure and 273 K. Further, Ag

#### Introduction

Hyper-cross-linked polymers (HCPs) have received increasing research interest over the years as they possess high porosity, robust nanostructure combined with ease of their synthesis and diversity in selecting functional monomers.<sup>[1]</sup> Thus, HCPs provide an invaluable platform for new functional polymers, which are largely explored in gas storage, separation and catalysis.<sup>[2]</sup> Therefore, based on the knitting condensation-polymerization approach and by employing external linkers, a variety of high surface area metal-grafted organic polymers can be synthesized. Additionally, metal coordinated HCPs are highly flexible and robust in fixing metal complexes and/or small metallic nanoparticles (NPs) at the pore surfaces.<sup>[3]</sup> Hence, inorganic complexes and metallic NPs can be stabilized for prolonged use through this porous framework, in contrast to their prompt deactivation under homogeneous conditions. Further, due to the fast polymerization reactions, HCPs are mostly formed as an

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	Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.200xxxxxx

nanoparticles are successfully immobilized on the surfaces of FeNT and FeNS by liquid phase impregnation method to prepare Ag@FeNT and Ag@FeNS nanocomposites, which showed high catalytic activity for selective fixation of CO<sub>2</sub> to phenylacetylene to yield phenylpropiolic acid at 60 °C and 1 atm CO<sub>2</sub> pressure. Hence, Fe(III)-catechol containing hyper-cross-linked nanotubes and nanospheres have huge potential not only as Lewis acid catalysts but as an excellent support in immobilizing Ag nanoparticles for designing a robust catalyst for the carboxylation of terminal alkynes, which has wide scope in catalysis and environmental research.

agglomerated solid without any special morphologies i.e.; tubes/spheres. Thus, the development of HCPs with unique shape and structure is quite challenging. Few previous reports have demonstrated the synthesis of hollow tubular shaped HCPs,<sup>[4]</sup> which motivated us to explore the research on various reactive organic monomers, as chelating ligands that can easily coordinate with the reactive metal ions in solution phase. Among several chelating ligands, the "catechol" moiety act as a bidentate precursor for the stabilization of metal complexes.<sup>[5]</sup> Therefore, catechol functionalized high surface area porous support have huge potential in designing efficient heterogeneous catalysts. Although, there are few reports on porous polymers based on single site catechol supports or from tetra-arm alkynes and palladium catalysts,<sup>[6]</sup> these syntheses involved expensive catalyst preparation steps and the use of harmful reagents. Therefore, we target a catechol-based hyper-cross-linked polymer via cost-effective synthetic route.

On the other hand, ring opening of epoxides is an important route for designing compounds with versatile 1,2-type functional groups, like  $\beta$ -alkoxy alcohols, which are precursors for a broad range of pharmaceuticals.<sup>[7]</sup> Generally, homogeneous acid/base catalysts can effectively hydrolyze the epoxides to β-alkoxy alcohols, but the strength of acid/base is insignificant in controlling the regioselectivity of the product.<sup>[8]</sup> Thus, unwanted polymerization and/or mixture of products are formed during the epoxide ring opening. Although, several metal salts like Er(III), Sn(II), Al(III), In(III) are used to catalyze such reactions, but these are either toxic or less abundant, which restricts their catalytic potential.<sup>[9]</sup> Considering epoxide hydration at various (water:substrate, W/S) ratio, it is essential to control the reaction at low water concentration in order to avoid unwanted polymerization and byproduct formation in this reaction.<sup>[10]</sup> Similarly, Lewis acid catalyzed synthesis of benzimidazole has

huge scope in pharmaceutical research, since substituted benzimidazole are important building blocks for drugs having antiviral, antifungal, antiulcer, antihypertensive, antihistaminic, and anticancer properties.<sup>[11]</sup> However, one-step direct conversion of benzimidazole from benzyl alcohol and *o*-diaminobenzene often involves toxic oxidant together with expensive ruthenium<sup>[12]</sup> and iridium catalysts.<sup>[13]</sup> Hence, cost-effective design of nanocatalyst with desirable Lewis acidic sites at the surface is essential.

On the other hand,  $CO_2$  sequestration into value added fuels and chemicals are very demanding for the control and successful use of this greenhouse gas.<sup>[14]</sup> The conversion of atmospheric  $CO_2$  to enhance carbon chain products through C-C bond forming reactions are generally accomplished by using different catalysts with undefined particle morphologies.<sup>[15]</sup> Nanoparticles supported heterogeneous catalysts offer excellent advantages for costeffective synthesis of desired products, but the size and dispersion of NPs on the support often limit their catalytic performances.<sup>[16]</sup> NPs supported on HCPs<sup>[17]</sup> are found to be quite effective route in designing a robust and efficient heterogeneous catalyst. Hence, the development of more efficient and robust hyper-cross-linked porous polymer nanocatalyst based on catechol linker are highly demanding for  $CO_2$  fixation reactions.

Herein, we first report the synthesis of hyper-cross-linked polymers bearing iron-catechol moieties that can act as catalyst for ring opening of epoxides and tandem oxidation-cyclization reaction in one-step. Fe-catechol containing FeNT is quite efficient for the hydrolysis and methanolysis of epoxides at both low and high solvent concentration (2 to 20 M), which showed high conversion (100%) and selectivity (99%) for the desired products. Furthermore, this Fe-catechol based porous support can be decorated with Ag NPs for the fixation of  $CO_2$  in terminal alkynes to respective carboxylic acids under mild reaction conditions, suggesting the merit of these HCP supports in heterogeneous catalysis.

#### **Results and Discussion**

#### Synthesis and characterization of FeNT and FeNS



**Scheme 1.** Syntheses of iron-catechol based microporous hyper-cross-linked organic polymers having hollow nanotube and nanosphere morphologies.

Friedel-Craft condensation-polymerization between catechol and dimethoxymethane (FDA) has been carried out in the presence of different acid catalysts (FeCl<sub>3</sub> and CF<sub>3</sub>SO<sub>3</sub>H) as shown in Scheme 1. It is interesting to note that iron-catechol nanotubes are observed from conventional HCP synthesis by heating a mixture of catechol, FeCl<sub>3</sub> and FDA in a chlorinated solvent as dichloroethane. In this way, catechol moieties are insitu coordinated with iron sites in FeNT. On the other hand, when the synthesis is carried out in absence of FeCl<sub>3</sub> but by using CF<sub>3</sub>SO<sub>3</sub>H as catalyst, we observed metal free catechol nanosphere. This material was later post synthetically modified through the FeCl<sub>3</sub>/THF treatment to obtain FeNS material. Morphology of FeNT and FeNS are shown in Figure 1 (TEM) and Figure S1 (FESEM), which suggested that FeNT is composed of nanoparticles having micrometer long hollow tubes and their dimeter (~100 nm) is similar with other microporous nanotubes.<sup>[17,18]</sup> On the other hand FeNS consists of ~300-500 nm size nanospheres. Therefore, our synthetic strategy suggested the merit of knitting polymerization to obtain ironcatechol containing porous polymers with different nanoarchitectures over other complicated synthetic strategies for designing hyper-cross-linked polymers.[17a]



Figure 1. TEM images (a and b) FeNT and (c and d) FeNS; HRTEM images (e) FeNT, (f) FeNS.

It is pertinent to mention that the growth of nanotube like particle morphology of the material is dependent on various factors like molar concentrations of monomers and dimethoxymethane linker, catalyst (FeCl<sub>3</sub>), solvent (dichloroethane), reaction temperature, mechanical stirring, time etc.<sup>[4]</sup> As for example, when the synthesis was carried out in the absence of dimethoxymethane, resulting material did not show any nanotube like particle morphology (Figure S2).

Stability of FeNT and FeNS materials are investigated by TGA experiment. Figure 2a demonstrates the TGA plots, which suggested that these materials are stable upto 230 °C (wt loss c.a. ~20%) and this result agrees well with other microporous polymers.<sup>[1,19]</sup> From FT-IR spectra (Figure 2b) we see the presence of several bands for aromatic C=C (1600-1400 cm<sup>-1</sup>), C-O / C-C stretching (1400-1200 cm<sup>-1</sup>), C-H bending (1200-1000 cm<sup>-1</sup>), which are correlating with the phenyl groups of catechol. Again, we did not observe any characteristics band at ~1715 cm<sup>-1</sup> for ketone sites, suggesting that catechol is not oxidized to aromatic ketone. The broad band at 3400 cm<sup>-1</sup> is possibly arised from the hydrogen bonding in FeNT and FeNS. Moreover, from the FT-IR spectra we did not observe any band at 576 cm<sup>-1</sup> for  $\ensuremath{\mathsf{Fe-O}}$  stretching,  $\ensuremath{^{[20]}}$  which suggested the absence of iron oxide nanoparticles in the FeNT material before carbonization (Figure S3). However, upon carbonization CFeNT sample displayed this band due to Fe-o stretching. These result also agreed well with HRTEM images (Figure 1; e and f). Interestingly, the sharp -OH stretching of catechol at 3449 cm<sup>-1</sup> disappears for iron coordinated polymers and a broad stretching at 3468-3320 cm<sup>-1</sup> is observed, which could be because of free catechol as well as metal-coordinated catechol sites (Figure S3 and Figure 2b)



**Figure 2.** TGA profile of FeNT, FeNS and NS (a); FT-IR spectra of FeNT, FeNS and NS (b); solid state <sup>13</sup>C CP-MAS NMR of NS (c); powder X-ray diffraction patterns of FeNT, FeNS after soxhlet extraction (d); EPR spectra at 100 K (e) and Fe 2p XPS spectra of FeNT and FeNS (f).

<sup>13</sup>C CP-MAS-NMR spectrum is shown in Figure 2c, which suggested the presence of bands at 128.6 and 143 ppm, corresponding to aromatic carbon atoms of the catechol groups. Additionally, the crosslinking is evidenced from aliphatic signals at 26, 14, 44 ppm from several alkyl and alkoxy species.<sup>[19]</sup> Therefore, the <sup>13</sup>C NMR investigation revealed the successful polymerization of catechol units in FeNT and FeNS. Powder X-ray diffraction pattern of these materials are shown in Figure 2d, which suggested the formation of amorphous polymeric material

synthesized FeNS sample showed some peaks corresponding to some residual iron oxychloride impurity upon rigorous soxhlet extraction by refluxing in methanol could resulted amorphous FeNS material (Figure 2d) without any impurity phase. On the contrary, no diffraction peak corresponding to iron oxychloride was observed for the XRD pattern of FeNT. In order to investigate the coordination environment of iron present in FeNT and FeNS materials, we have carried out the EPR analyses and the results are shown in Figure 2e. At 100 K EPR measurement, FeNT showed distinguishable strong peaks corresponding to several g sites *i.e.* 8.2 and 4.6 values, suggesting the existence of high spin Fe(III) in distorted rhombic environment.<sup>[21]</sup> However, the EPR signal becomes weaker when the analysis temperature was raised to 298 K, which clearly indicated the formation of paramagnetic iron-catechol complex during the synthesis. Additionally, very small peak at g = 2.003 signified the less possibility for oxidation of catechol to o-semiquinone under the synthesis conditions. In contrast, the post synthesis impregnation with FeCl<sub>3</sub> in NS did not exhibit any EPR signal for Fe(III) sites, rather it showed a less significant signal at g = 3.4 on account of organic radicals, suggesting that the complexation characteristics of Fe(III) in FeNS is different than that of FeNT. Interestingly, when FeNT is digested by treating with 12N HCl, we could not observe any EPR signal, demonstrating that Fe(III) sites are indeed showed strong EPR in FeNT. Existence of Fe(III) has been further confirmed from XPS analysis, as shown in Figure 2f, where the presence of two Fe 2p peaks at binding energies 711 eV (Fe  $2p_{3/2}$ ) and 725 eV (Fe  $2p_{1/2}$ ) is seen.<sup>[22]</sup> It is pertinent to mention that Fe 2p in pure iron oxide showed peaks at 710 and 723.4 eV, corresponding to Fe2p<sub>3/2</sub> and Fe2p<sub>1/2</sub> respectively with additional strong satellite peaks at 713.7 eV (2p32) and 728.3 eV (2p1/2).[22] Although FeNT and FeNS showed two major Fe 2p peaks, at 728.3 eV (2p1/2) and 713.7 eV (2p3/2), but their corresponding satellite peaks are too weak to detect. However, Fe 2p XPS of the carbonized FeNT is characteristically more similar with iron oxide and distinctly different from FeNT (Section S1 and Figure S4). Therefore, the FT-IR, EPR and XPS analysis revealed the existence of iron(III) in FeNT and FeNS materials.

with a broad peak in the  $2\theta$ =15-30° range. Although the as-

#### Porosity and Surface area measurement



Figure 3. (a)  $N_2$  adsorption (closed circles) and desorption (open circles) isotherms of FeNT, FeNS and NS; (b) Pore size distribution from density functional theory (DFT) model; CO<sub>2</sub> adsorption isotherms of FeNT, FeNS and NS (c, d).

Porosity and surface areas of the FeNT, FeNS and NS materials are measured from  $N_{\rm 2}$  sorption analysis and these are shown in Figure 3a. All three materials showed high N<sub>2</sub> uptake at low  $P/P_0$  region (type I isotherm), corresponding to the presence of micropores.<sup>[23]</sup> In Table 1, we have summarized the physical parameters of these supported HCPs, which suggested that iron coordinated polymers have lower BET surface area than iron-free NS. The low surface area of FeNT and FeNS could be attributed to the presence of Fe(III) in the framework (higher atomic mass than carbon). DFT pore size distribution plots derived from these N<sub>2</sub> sorption isotherms are shown in Figure 3b, which suggested the presence of both micropores (< 2nm) and mesopores (2-6 nm). Nevertheless, all sorption isotherm shows hysteresis because of swelling characteristics of these soft polymeric frameworks.<sup>[24]</sup> The quantity of iron present in FeNT and FeNS materials are given in Table 1. Additionally, microporous nature of NS, FeNT and FeNS together with their good pore volumes have motivated us to measure their CO<sub>2</sub> uptake ability. Results are shown in Figure 3c and d, which suggested that NS has the highest CO<sub>2</sub> uptake ability (3.8 mmol g<sup>-1</sup>) over the FeNT (2.6 mmol g<sup>-1</sup>) and FeNS (2.2 mmol g<sup>-1</sup>) materials at 273 K and 1 atm pressure. This is because NS possess significantly large amount of free –OH sites as well as higher BET surface area and pore volume than Fe containing FeNT and FeNS materials. It is noteworthy to mention here that, these HCPs showed comparable CO<sub>2</sub> uptake capacity compared with other polymer tubes (CMPN-2; 1.8 mmol g<sup>-1</sup>),<sup>[25]</sup> conjugated polymers,<sup>[26]</sup> and other hydroxyl-rich microporous adsorbents,<sup>[27]</sup> suggesting their promising future in CO<sub>2</sub> sequestration. In Table S1 we compared CO<sub>2</sub> uptake ability of NS, FeNS and FeNT with other state-of-theart porous adsorbents like MOFs and COFs.

Table 1	. Physical	parameters	of FeNT,	NS and	FeNS as	s estimated	from BE	T analysis
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Name	S <sub>BET</sub> m <sup>2</sup> a <sup>-1</sup>	S <sub>Langmuir</sub> m <sup>2</sup> q <sup>-1</sup>	$V_{total}^{[a]}$ cm <sup>3</sup> q <sup>-1</sup>	V <sub>micro</sub> <sup>[b]</sup> cm <sup>3</sup> a <sup>-1</sup>	Micropore size	Fe amount
FeNT	400	547	0.45	0.1	0.9 -1.30	7.5
NS	545	734	0.35	0.2	0.5 -1.31	-
FeNS	352	475	0.22	0.12	0.5 -1.26	4.2

<sup>[a]</sup>Measured from N<sub>2</sub> sorption isotherm at 0.99 P/P<sub>0</sub>. <sup>[b]</sup>t-plot micropore volume calculated at 77 K from N<sub>2</sub> sorption isotherm. <sup>[c</sup> DFT micropore size distribution from N<sub>2</sub> sorption isotherm. <sup>[d]</sup>Calculated from ICP analysis.



#### Lewis acid catalysis of FeNT and FeNS

Figure 4. Kinetic studies for styrene oxide ring opening hydrolysis reaction catalyzed by FeNT (a) and FeNS (b); methanolysis reaction of styrene oxide by FeNT (c) and FeNS (d).

We have evaluated the potential of FeNT and FeNS as solid acid catalyst. In this context, we have investigated the hydrolysis/methanolysis reaction of styrene oxide as well as tandem oxidation-cyclization reaction. The ring opening hydrolysis and methanolysis of styrene oxide were carried out at 25 °C and at 60 °C, considering various H<sub>2</sub>O/substrate, as shown in Figures 4 a, b, c and d, respectively. The corresponding hydrolysis and methanolysis products were obtained in good to excellent yield, where selectivity for 1-phenylethane-1,2-diol was observed at 99% as the hydrolysis product. We observed the regioselective synthesis of 2-methoxy-2-phenylethanol as the major methanolysis product.

Apart from methanol, we also tried ring opening reactions in other solvents like ethanol, 2-propanol etc, where we found the reactivity decreases in the order: MeOH>EtOH>n-PrOH, with full conversion has been observed in methanol within 6 h, followed by 8 h in ethanol and 20 h in n-PrOH. This could be attributed to the higher steric effects as imparted by heavier alcohols.<sup>[28]</sup> It is noticeable that hydrolysis of styrene oxide showed faster kinetics when W/S is 20 at 25 °C, which later decreases with decreasing the H<sub>2</sub>O/substrate ratio. Since solvent plays an effective role in controlling this reaction, we then investigate the role of catalyst. For this reason, the blank experiment in the absence of FeNT and FeNS has been carried out and it showed no hydrolysis/methnolysis product even after 20 h at W/S 20. This result suggested that the reaction is truly catalytic in nature. As seen from Figure 4a and 4b, FeNT showed faster hydrolysis kinetics than FeNS that could be attributed to the coordinated Fe-catechol moieties in FeNT. Considering FeNT as catalyst, 95% conversion of styrene oxide is seen even at W/S = 2 and at 60 °C.

 
 Table 2. Tandem oxidation-cyclization of benzylalcohol with ophenylenediamine <sup>[a]</sup>



Entry	Catalyst	Additive	Solvent	Τ/	Time/	Yield <sup>[</sup>
				°C	h	<sup>b]</sup> %
1	FeNT	TBHP	CH <sub>3</sub> CN	60	24	70
2	FeNS	TBHP	CH <sub>3</sub> CN	60	24	55
3	-	TBHP	CH <sub>3</sub> CN	60	24	10
4	lr (2	-	mesityl	120	18	90
	wt%)		ene			
	/TiO <sub>2</sub> -					
	500 <sup>[32]</sup>					
5	Fe-	TBHP	CH₃CN	60	24	68
	PPOP <sup>[1</sup>					
	0]					

 $^{[a]}Reactions$  were carried out by 1.5 mmol benzyl alcohol, 0.5 mmol o-diaminobenzene, 0.004 mmol iron site and 70% TBHP (2.5 mmol, 1.5 mmol and 0.5 mmol) at an interval of 15 min, 12 h and 20 h

 $^{\rm [b]}\mbox{Confirmed from ^1H}$  and  $^{\rm 13}\mbox{C}$  NMR analysis, given in S5.

Similarly, methanolysis of styrene oxide at different MeOH/styrene oxide are given in Figures 4c and 4d, where the formation of 2-methoxy-2-phenylethanol is considered as the major regioisomer, seen from the results of liquid NMR (Figure S6). When MeOH/Styrene oxide is 5, FeNT shows 92% conversion of styrene oxide to 2-methoxy-2-phenylethanol at 60 °C and 21 h, whereas FeNS showed 84% conversion under same condition. Mechanistically it can be said that the formation of major regioisomer is dependent on the propensity of attack by  $H_2O$  or methanol to the less sterically hindered epoxide carbon which is activated by Lewis acid FeNS and FeNT. For this reason, styrene oxide shows faster hydrolysis rate compared with its methanolysis rate. Additionally, we also compare the catalytic activity of FeNT with other conventional catalysts, shown in Table S2.

Again, microporous FeNT and FeNS also contain physisorbed water (seen from TGA), which can influence the hydrolysis kinetics of styrene oxide. In order to investigate such effect, we used the catalyst after drying at 130 °C for 2 h in vacuum, which shows the non-existence of 1-phenylethane-1,2-diol as product, indicating that physisorbed water is less significant in this study. Nevertheless, Lewis acid sites are indeed essential for this reactions since no hydrolysis product is observed in absence of Fe(III). For heterogeneous catalysts that has been studied, Fe(III)-based mesoporous silica,[29] FeCl<sub>3</sub> supported on silica gel, [Error! Bookmark not defined.] [Fe(BTC)] (BTC: 1,3,5-benzenetricarboxylate) based metal-organic framework (MOF),<sup>[30]</sup> Fe-complex containing tridentate polymers.<sup>[31]</sup> showed comparable catalytic activity with FeNT and FeNS. It is noteworthy, the reaction without FeNT and FeNS but in presence of iron chloride solution did not give any reaction products while carrying out the reaction of styrene oxide and methanol at room temperature.



Figure 5. TEM (a), STEM (b) images of Ag@FeNT and Ag@FeNS respectively. Powder XRD (c) and XPS (d) patterns of Ag@FeNT and Ag@FeNS.

Additionally, the Lewis acidity of FeNT and FeNS were also explored in one-step synthesis of benzimidazole from benzyl alcohol and o-phenylenediamine and results are shown in Table 2. The catalytic data suggested that in the presence of TBHP as oxidant the Fe(III) sites of FeNT and FeNS are useful for oxidation of benzyl alcohol to benzaldehyde as intermediate, followed by cyclization with 0phenylenediamine.<sup>[32]</sup> FeNT shows 70% yield of benzimidazole at 60 °C, 24 h, which is milder than 135 °C reaction condition, reported by Reddy et al.[33] For oxidant free synthesis of benzimidazole, Tateyama et al. prepared Ir on TiO<sub>2</sub> support, which shows very high activity, but it requires high reaction temperature and complicated procedure for the catalyst activation with H<sub>2</sub> at 500 °C. On the contrary, few other porous polymers with iron sites are found useful for tandem cyclization under mild conditions, whereas other shows only oxidation catalysis.<sup>[34]</sup> Reusability of FeNT as Lewis acid catalyst was checked for ring opening reaction of styrene oxide, indicating that FeNT can be recycled for at least four consecutive cycles without much loss in yield and selectivity of 1-phenylethane-1,2-diol (Figure S7).

#### Ag nanoparticle loaded FeNT and FeNS as CO<sub>2</sub> conversion catalyst

Owing to significant Lewis acid property and high surface area of FeNT and FeNS, we believe these polymers might be an ideal platform for CO<sub>2</sub> conversion after loading with Ag NPs,<sup>[35]</sup> because CO<sub>2</sub> can be activated with Ag NPs and converted to carboxylic acids from alkynes.<sup>[36]</sup> However, there remains a strong challenge for efficient and cost-effective development of stable support materials, which to our knowledge is mainly limited to MOF-based supports. But the limitation of utilizing MOFs as stable support renders the full usefulness of HCPs as polymeric support of Ag NPs<sup>[37]</sup> for exploring CO<sub>2</sub> fixation with Ag@FeNT and Ag@FeNS. We characterized these two Ag catalysts by TEM, XRD and XPS analysis. As shown from TEM and STEM observation (Figure 5a and b), ~7-10 nm Ag NPs are homogeneously distributed on the support without any agglomeration. Various crystal planes [(111), (200), (220) and (331)] of Ag is clearly seen at

 $2\theta = 38^{\circ}, 44.2^{\circ}, 64.4^{\circ}$  and 77.4°, as evidenced from wide angle powder XRD from Figure 5c. Nevertheless, the mean size of Ag particles as observed from TEM analysis is correlated from the particle size (~7.8 nm), calculated from Debye-Scherer equation.[38]

Ag@FeNT / Ag@FeNS								
En try	Catalyst	T/ ℃	Base	PCO <sub>2</sub> / atm	Solvent	Yiel d <sup>[b]</sup> (%)		
1	Ag@FeNT	60	$Cs_2CO_3$	1	DMSO	70		
2	Ag@FeNS	60	$Cs_2CO_3$	1	CH <sub>3</sub> CN	62		
3	Ag@FeNT	60	K <sub>2</sub> CO <sub>3</sub>	1	DMSO	68		
4	Ag@FeNT	60	Cs <sub>2</sub> CO <sub>3</sub>	5	DMSO	89		
5	Ag@FeNT	25	$Cs_2CO_3$	1	DMSO	40		
6	Ag@FeNT	60	Cs <sub>2</sub> CO <sub>3</sub>	1	Dioxane	trac e		
7	FeNT	60	Cs <sub>2</sub> CO <sub>3</sub>	1	DMSO	-		
8	Ag/Al <sub>2</sub> O <sub>3</sub> <sup>[c]</sup>	50	Cs <sub>2</sub> CO <sub>3</sub>	40	DMSO	<10		
9	Ag/SiO <sub>2</sub> <sup>[d]</sup>	50	Cs <sub>2</sub> CO <sub>3</sub>	60	DMSO	48		
10	Ag/C <sup>[e]</sup>	50	Cs <sub>2</sub> CO <sub>3</sub>	40	DMSO	<5		
11	Ag@NT <sup>[f]</sup>	60	$Cs_2CO_3$	1	DMSO	50		
12	Ag@FeNT <sup>[</sup>	60	Cs <sub>2</sub> CO <sub>3</sub>	1	DMSO	52		

<sup>[a]</sup>Phenylacetylene (1.0 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1.5 mmol), 0.05 g Ag catalyst, 5 mL anhydrous DMSO after 15 h reaction. [b]Isolated product yield calculated from NMR. <sup>[c</sup> 5 wt% Ag in Al<sub>2</sub>O<sub>3</sub>. <sup>[d]</sup>20 wt% Ag in SiO<sub>2</sub>. <sup>[e]</sup>5 wt% Ag in carbon. <sup>[f]</sup>Catalyst is devoid of iron (Section 1, supporting information). <sup>[g]</sup>6.9 wt% Ag.

Different electronic state of Ag(0) are clearly seen from XPS result (Figure 5d), which means the existence of two bands corresponding to Ag3d3/2 and Ag3d5/2 of Ag nanoparticles. All these result justify the formation of Ag nanoparticles on FeNT and FeNS. Initially to explore the catalytic property of these two catalysts, we choose the carboxylation of a terminal alkyne phenylacetylene as the model reaction under the optimized conditions (60 °C, 1 atm CO2 and DMSO solvent for 15 h). This reaction produces phenylpropiolic acid in ~70% yield over Ag@FeNT, and ~62% yield over Ag@FeNS. The formation of phenylpropiolic acid from phenylacetylene was confirmed from NMR results (Figure S8 and S9). On the contrary, the non-catalyzed reaction showed only 2.5% yield of phenylpropiolic acid. When the reaction has been carried out with FeNT itself, it also showed very poor yield of phenylpropiolic acid. This investigation actually suggests the necessity of Ag(0) for activation and conversion of CO<sub>2</sub>. However, when Fe-sites are removed the catalytic activity of Ag@NT deceases considerably (entry 11), suggesting the Lewis acid sites as present in FeNT play significant role for this reaction and this is also observed for other supports.<sup>[39]</sup> In Table 3 we have summarized our catalytic results for the synthesis of phenylpropiolic acid. As seen from this table that unlike Ag deposited conventional supports, ironcatechol based porous support is indeed more reactive in activating CO<sub>2</sub> towards alkynes. This result suggested crucial role of Ag sites located in close proximity to the Lewis acidic iron-catechol sites. We also found that solvent plays crucial role in this CO<sub>2</sub> fixation reaction, where the product phenylpropiolic acid yield increases with increasing polarity of the solvent. DMSO was found to be the best solvent among all other solvents like CH<sub>3</sub>CN, THF, 1,4-dioxane, DMF. Among several bases, Cs<sub>2</sub>CO<sub>3</sub> showed high yield of the desired carboxylic acid, which could be because of its ability to



Figure 6. Recycling efficiency of Ag@FeNT for the carboxylation of phenylacetylene (1.0 mmol, 1.5 mmol Cs<sub>2</sub>CO<sub>3</sub>, 0.05 g Ag@FeNT catalyst, 5 mL anhydrous DMSO) under 1 atm CO2 pressure and kept at 60 °C for 15 h

deprotonate the terminal alkyne for accelerating the formation of silver acetylide intermediate. Strong polar solvents like DMSO favors in the dissolution of Cs<sub>2</sub>CO<sub>3.</sub> Therefore we saw that polar solvent and strong bases are mandatory in order to achieve successful fixation of CO2 onto the terminal alkynes.[40] On the other hand, small size Ag NPs (~7-10 nm) are crucial for the promotion of this reaction (size distribution of Ag, Figure S10).[41] Compared with FeNT, the BET surface area of Ag@FeNT appreciably decreases to 305 m<sup>2</sup> g<sup>-1</sup>, as obtained from the respective N<sub>2</sub> sorption isotherm (Figure S11). The total pore volume also decreases to 0.3 cm<sup>3</sup> g<sup>-1</sup>, which suggested that it might be possible for Ag NPs to occupy the cavity of the host framework. Since FeNT contains large mesopores and small micropores, therefore the size of Ag permits to occupy the mesoporous cavity of FeNT. When loading of Ag increases to 6.9 wt%, BET surface area slightly increases to 340 m<sup>2</sup> g<sup>-1</sup>, because the agglomerated Ag cannot occupy the pores, rather exists at the outer surface. This investigation demonstrates that optimum loading of Ag on FeNT support is necessary for this CO2 fixation reaction.[41] The merit of Ag@FeNT was further examined from its recyclability experiment (Figure 6). Product yields as shown in this figure after several cycles suggested that the Ag@FeNT catalyst can be recycled for at least four reaction cycles. After the fourth reaction cycle, almost 5% decrease in catalytic activity is observed possibly because of little agglomeration of Ag NPs at the surface of the polymeric nanotubes. Moreover, XPS analysis of recycled Ag@FeNT showed little shift of binding energy maximums (Ag3d<sub>5/2</sub>; 367.6 to 367.1) than fresh catalyst (Figure 5d). This can be due to the partial oxidation of Ag(0) during the reaction in DMSO. In order to investigate the probability of leaching of Ag to the reaction mixture, the liquid phase of the reaction mixture was collected by hot filtration

#### Conclusion

Iron(III) containing hyper-cross-linked microporous polymers with well-defined nanotube (FeNT) and nanosphere (FeNS) morphologies can be synthesized via acid catalyzed condensation-polymerization of catechol and dimethoxymethane in the presence of FeCl<sub>3</sub>. The resulting polymers exhibit high activity as Lewis acid catalyst. Furthermore, FeNT and FeNS can be utilized as support material for the successful immobilization of Ag NPs and the resulting materials act as efficient catalysts for the one-step selective fixation of CO2 onto terminal alkynes to the respective carboxylic acid. Nevertheless, the utility of catechol as functional moiety in building the porous support has huge potential in catalysis due to its strong binding affinity as chelating ligand for stabilization of inorganic metal ions and metallic nanoparticles. Utilizing catechol as cheap chemical, the bottom-up chemistry route for the synthesis of Fecontaining nanomaterials with 0 and 1D nanostructures reported herein has huge potential in designing bifunctional catalysts comprising both Lewis acidic and metal nanoparticles as active sites, which can be explored in other tandem organic reactions in future.

#### **Experimental Section**

#### Chemicals and reagents

All analytical grade reagents were used as received unless otherwise stated. Catechol, dimethoxymethane, dichloromethane, trifluorosulfonic acid, styrene oxide, benzylalcohol, phenylacetylene were purchased from Sigma-Aldrich Company, Ltd. (USA). For the  $CO_2$  fixation reaction,  $CO_2$  cylinder with high purity  $CO_2$  (99.99%) was used. All solvents and chemicals required for catalysis were brought from Merk and Spectrochem Pvt. Ltd.

#### Instrumentation

N2 adsorption-desorption isotherms are measured at -196 °C by using a Micromeritics ASAP2020 adsorption analyzer. Samples were degassed at 120 °C for 6 h before analysis. Pore size distribution was measured by using density functional theory (DFT) model using N2 at 77 K on carbon, slit pores. Thermogravimetry analysis (TGA) has been carried out by NETZSCH STA 449F3 analyzer starting from 30 to 800 °C with a heating rate of 10 °C  $min^{-1}$  in N<sub>2</sub>. X-ray photoelectron spectroscopic (XPS) data was recorded on a VG ESCALAB MK2 apparatus by using AlK $\alpha$  (h<sub> $\lambda$ </sub> = 1486.6 eV) as the excitation light source. Solid state  $^{13}\mbox{C}$  NMR spectra were obtained with a Bruker 500 MHz spectrometer equipped with a magic-angle spin probe using a 4 mm ZrO<sub>2</sub> rotor and the signals were referenced to glycine (C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>). Fourier transform infrared spectra (FT-IR) were recorded on a Nicolet Nexus 470 IR spectrometer (KBr pellets were prepared). Inductively coupled plasma (ICP) analysis was conducted on

PLASAMSPEC-II inductively coupled plasma atomic emission spectrometry (ICP-AES). Powder X-ray diffraction (PXRD) analysis has been carried out on a Rigaku D/Max2500 PC diffractometer with Cu K $\alpha$  radiation ( $\lambda$ =1.5418 Å) over the 2 $\theta$  range of 5-80° at a scan speed of 5° per min at room temperature. Bruker DPX-300 NMR spectrometer was used to measure the <sup>1</sup>H and <sup>13</sup>C NMR of the reaction products in liquid state. Particle sizes were determined from Nano Measurer 1.2 software.

#### Synthesis of FeNT

A 50 mL two-neck round bottom flask containing magnetic stirrer and reflux condenser was charged with 0.2 g (2 mmol) catechol, 0.6 g (4 mmol) FeCl<sub>3</sub> and 15 mL dichloroethane. The mixture was stirred and to it 0.34 mL (0.3 g, 4 mmol) dimethoxymethane was added to initiate the polymerization reaction and then heated in an oil bath at 80 °C for 20 h. At the end, the dark mixture was diluted with methanol and filtered. The solid residue was thoroughly washed with ethanol, THF, methanol and kept for 30 h under soxhlet extraction with refluxing methanol. Finally, the dark brown solid was dried under vacuum, which gives 80% yield of the product. CHN elemental analysis of FeNT suggested the presence of C = 39.7 %, O = 44.5 %, H = 4 %.

#### Synthesis of FeNS

In a 50 mL two-neck round bottom flask containing magnetic stirrer and reflux condensor, 0.2 g (2 mmol) catechol was dissolved in 15 mL dichloromethane. Then 0.6 g (8 mmol) dimethoxymethane was added slowly and stirred well for 30 min at room temperature (25 °C). Next. 0.003 mol (1.2 equivalent with catechol) trifluoromethanesulfonic acid (CF<sub>3</sub>SO<sub>3</sub>H) was added very slowly and continued the addition for 30 min. The whole mixture was kept under stirring at 25 °C for 1 h and then heated at 60 °C for 24 h. During the addition of CF<sub>3</sub>SO<sub>3</sub>H, the initial solution became reddish, which later turn to brown while prolonging the reaction time. The final product was collected by filtration and washed thoroughly with water, ethanol, THF, acetone and dried in vacuum. Yield of NS was 70%. For loading iron in NS, 0.1 g NS was dispersed in 15 mL THF and the whole mixture was stirred with 0.3 g FeCl<sub>3</sub> at 50 °C. After 24 h, the mixture was filtered and the residue was collected, washed with copious amount of water, ethanol, THF, acetone until the filtrate shows no color. The dark brown product has been collected and purified by rigorous soxhlet extraction for 72 h in refluxing methanol and this sample is designated as FeNS.

#### Synthesis of Ag@FeNT and Ag@FeNS

Ag nanoparticles were loaded onto FeNT and FeNS surface by NaBH<sub>4</sub> reduction method. For this, we at first prepare colloidal Ag NPs by mixing 100 mg AgNO<sub>3</sub> with 10 mL acetonitrile containing 0.5 mmol TRIS [2-Amino-2-(hydroxymethyl) propane-1,3-diol] and stirred for 5-10 min. Then, 10 mL NaBH<sub>4</sub> solution (0.8 mmol mL<sup>-1</sup>) in ethanol was added and stirred for additional 20 h and the resulting colloidal Ag NPs was stored at 4 °C. Next, 0.5 g FeNT/FeNS was dispersed in 10 mL of TRIS-stabilized Ag NPs and stirred for 12 h at 25 °C. The Ag loaded polymers were collected by centrifugation and washed with distilled water, ethanol until no Ag ions are detected in the filtrate. It was found that Ag@FeNT contains 3.4 wt% Ag and Ag@FeNS showed 3 wt% Ag loading, as estimated from inductively coupled plasma atomic emission spectroscopic (ICP-AES) analyses.

#### Ring opening reaction of Styrene oxide

For the epoxide ring opening reaction, the catalyst FeNT (10 mg =  $0.075 \mu$ mol Fe) was added into a solution of styrene oxide (0.25 g, 1 mmol) and water. The amount of water was adjusted according to various water/styrene oxide ratio (20, 5 etc.) and the solution was stirred at room temperature or at elevated temperature to get

the product. The progress of the reaction was monitored by a Agilent gas chromatography (GC) fitted with a J&W GC HP-5 capillary column (30 m x 0.32 mm x 0.25 mm) and FID detector. Similarly, methanolysis reactions were also studied at various methanol/styrene oxide ratio, while other conditions are same as used during hydrolysis reactions.

#### Tandem oxidation-cyclization reaction

To a 25 mL round-bottom flask, benzyl alcohol (1.5 mmol), odiaminobenzene (0.5 mmol), Fe-catalyst (FeNT/FeNS; 0.004 mmol Fe) were mixed in 5 mL acetonitrile followed by successive addition of 2.5 mmol, 1.5 mmol and 0.5 mmol TBHP (70% in water) at an interval of 15 min, 12 h and 20 h with continuous stirring of the mixture at 65 °C. At the end of the reaction (monitored by TLC), the reaction mixture was cooled to 25 °C and centrifuged to remove the catalyst. Finally, the solution was concentrated in vacuum and extracted with ethylacetate. The residue was purified by column chromatography on silica gel (*n*hexane/ethyl acetate) to obtain pure product in 60% yield.

#### CO<sub>2</sub> fixation to propiolic acid

All the reactions were carried out in a 15 mL stainless steel autoclave equipped with a magnetic stirrer. For a typical reaction, phenylacetylene (1.0 mmol), Cs<sub>2</sub>CO<sub>3</sub> (0.489 g, 1.5 mmol), 0.05 g Ag catalyst were taken in an autoclave along with 5 mL anhydrous DMSO. The autoclave was kept at 25 °C and purged with CO<sub>2</sub> for three times to remove air from inside the autoclave. Finally, CO<sub>2</sub> pressure was adjusted to (1-5) atm and the autoclave was kept in a preheated oil bath (60 °C). After several hour of reaction (10-12 h), the pressure was released slowly and the reaction mixture was cooled to 25 °C, followed by adding into 2(N) potassium carbonate solution (5 mL) under stirring for 30 min. The mixture was acidified to pH=1 by addition of conc. HCl, then extracted with ethyl acetate. The combined organic layers were washed with saturated brine solution, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and finally removed under low pressure to afford the isolated acid product. The product was identified and compared with authentic compound reported in literatures.

#### Acknowledgements

PB thanks CSIR, New Delhi for providing a senior research fellowship. AB thanks DST New Delhi for providing Indo-Egypt international project grant.

**Keywords:** Nanotubes; immobilization; Lewis acid catalysis; tandem catalysis; CO<sub>2</sub> fixation.

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Received: ((will be filled in by the editorial staff)) Published online: ((will be filled in by the editorial staff))

## Table of Content

### FULL PAPER



**Fe-catechol POP for acid catalysis and CO<sub>2</sub> fixation.** *Fe-catechol-based microporous polymers with different morphologies are synthesized under different synthesis conditions and they demonstrated efficient Lewis acid catalysis and support of Ag NPs for CO<sub>2</sub> fixation reaction for the carboxylation of terminal alkynes.*  Arindam Modak, \*<sup>[a,b]</sup> Piyali Bhanja and Asim Bhaumik\*<sup>[a]</sup>

Microporous nanotubes and nanospheres with ironcatechol sites: efficient Lewis acid catalyst and support for Ag nanoparticles in  $CO_2$  fixation reaction