RSC Advances

PAPER



Cite this: RSC Adv., 2016, 6, 76064

Received 20th May 2016 Accepted 3rd August 2016 DOI: 10.1039/c6ra13146h www.rsc.org/advances

1. Introduction

In recent years, extremely well dispersed metal oxides on solid supports are of great interest for current and future sustainable technologies such as their use as adsorbents,¹ in medical imaging,² chemical sensing,³ electronic devices⁴ *etc.* Among them, owing to the low price, rich abundance, environmentallyfriendly properties and remarkable catalytic performances, iron-based catalysts have received great attention in phenol hydroxylation,⁵ the Fenton reaction,⁶ Michael additions,⁷ isomerization⁸ *etc.* In addition, researchers found that the dispersity, microenvironment and surface interaction of iron oxides on the supports have a great influence on the catalytic performance in these reactions.

For enhancing the dispersity of catalytic active sites, new opportunities have gradually emerged since the discovery of mesoporous silica materials.⁹⁻¹¹ Mesoporous silica materials with various pore structures (*e.g.*, hexagonal, cubic, and lamella) are well-known for their high surface area, regular structure and



AL SOCIETY

View Article Online

View Journal | View Issue

Saifu Long,^a Shijian Zhou,^{ab} Fu Yang,^a Kangchao Lu,^a Tao Xi^a and Yan Kong*^a

Surface exposed catalytic active species are thought to be responsible for overall catalytic activity and selectivity. In this paper, controllable contents of iron oxides were *in situ* introduced into the inner surface of anionic surfactant-templated mesoporous silica (AMS) by the metal-modified anionic surfactant templating route, in which anionic micelles decorated with different amounts of Fe^{2+} were direct utilized to assemble with organosilicate. The characterization results demonstrated that, after thermal treatments, Fe_2O_3 species were *in situ* formed and highly-dispersed in the channels of AMS, and the pore size was accordingly tailored to the microporous level (<2 nm). In each AMS catalyst, Fe_2O_3 showed better dispersion and stability compared with the post-impregnated method. Moreover, the catalytic performances of phenol hydroxylation on the as-synthesized catalysts were significantly enhanced, and the optimal catalyst (Fe/Si = 3.5 wt%) gave a phenol conversion of 44.3% with a selectivity of 82.6% to dihydroxybenzene. By comparison with some reference mesoporous silica catalysts (0.15Fe/MCM-41 and 0.15Fe/SBA-15), the iron-based micropore-enriched silica catalyst (Fe/AMS) gave an obviously higher selectivity to dihydroxybenzene. Finally, the optimal catalyst was examined for at least 5 runs in phenol hydroxylation.

large pore volume, which are regarded as the best choice of support to disperse the active sites.12 In this case, to introduce the active sites in the mesoporous silica materials, some traditional synthesis methods including thermal decomposition,¹³ ultrasonic treatment,¹⁴ chemical vapor deposition¹⁵ and organic metal modification¹⁶ have been developed. Liu et al.¹⁷ introduced well-dispersed metal oxides into the pore of SBA-15 through incipient wetness impregnation and thermal transformation. Gu et al.18 reported that highly-dispersed copper species were successfully coated onto the inner surface of the rod-like mesoporous SBA-15 silica by using the hydrophobic core of a surfactant micelle as a carrier. However, there are still some disadvantages existed in these processes, such as uncontrolled growth, uneven distribution, low loading and complicated synthesis process, which would be detrimental to their practical application.

On the other hand, even with high surface areas and welldispersed catalytic active sites, the large pore size of mesoporous silica would make some large molecule byproducts form in the pore channels and then diffuse across the channels, leading to the low selectivity of target products.¹⁹ However, it is noticeable that microporous materials, such as TS-1,²⁰ Cu-ZSM-5, Fe-ZSM-5 (ref. 21) *etc.*, show better selectivity to the small molecule products, which should be attributed to the shape selectivity of microporous size.^{22,23} Nevertheless, microporous materials generally exhibit the reduced surface area, which could lead to the decreased number of exposed active sites.²⁴

^aState Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University, Nanjing 210009, China. E-mail: kongy36@njtech.edu.cn; Fax: +86-025-83587860; Tel: +86-025-83587860

^bJiangsu National Synergetic Innovation Center for Advanced Materials (SICAM), Nanjing Tech University, Nanjing 210009, Jiangsu, China

[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra13146h

Paper

Therefore, in order to obtain the relevant advantages of both mesoporous materials and microporous materials, great efforts have been devoted to modifying the pore surface of mesoporous materials based on its large surface area and pore channels.25 Gao et al.²⁶ prepared hierarchically porous ZSM-5/SBA-15 materials, which possessed a high density of active sites by confinement of sub-nanosized Pt particles within small-pore zeolites and exhibited high catalytic performance for the hydrogenation of 1,3-butadiene and cyclooctadiene at room temperature. However, the hierarchically porous materials possess a bimodal pore size distribution and complicated synthesis process, which would be unacceptable in practical application. Therefore, the simple method for the synthesis of silica catalysts with high surface area, micropore size distribution and well-dispersed catalytic active sites is still urgent for us to develop.

Herein, we made Fe^{2+} -modified anionic micelles as the new template for *in situ* inducing Fe^{2+} into the channel of AMS during the assemble process. The Fe_2O_3 species were directly formed and highly-dispersed inside the channels with a stable state by the thermal process, and the pore size was accordingly tailored into the microporous level (<2 nm). Subsequently, all the prepared samples were efficient characterized by UV-vis, FT-IR, H₂-TPR, XPS, XRD, N₂ adsorption and TEM. The catalytic performance and stability of catalysts were investigated by the reaction of phenol hydroxylation.

2. Experimental section

2.1. Materials

Sodium *N*-lauroylglutamate (Na-Nlg, >93%) was purchased from PengYuan (GuangZhou) Chemical Co., Ltd. Ferrous chloride tetrahydrate (FeCl₂·4H₂O) was purchased from Aladdin. 3-Aminopropyltriethoxysilane (APTES) was purchased from TCI(Shanghai) Development Co., Ltd. Sodium hydroxide (NaOH), phenol, hydrogen peroxide (H₂O₂, 30 wt%) and tetraethoxysilane (TEOS) were purchased from Sinopharm Chemical Reagent Co., Ltd. All the reagents except for H₂O₂ and Na-Nlg were analytical grade.

2.2. Preparation of catalysts

The typical synthesized process was depicted as follows: 3.70 g of Na-Nlg was dissolved in a mixed solution containing 230 mL of deionized water and 30 mL of NaOH solution (0.5 mol L⁻¹) under vigorous stirring at room temperature. The pH of resulting solution was adjusted to 8 with dilute hydrochloric acid (1 mol L⁻¹). Then, different molar amounts of FeCl₂·4H₂O were added in above obtained solutions, respectively. After that, 5.24 mL of APTES was added in the above mixture under vigorous stirring for 30 s to form a tawny suspension. Subsequently, 8.91 mL of TEOS was added into the suspension with continuous and intensive stirring for 10 min. Next, the resulting mixture was aged for 48 h at 42 °C. A final molar composition of mixture was 1.0 (Na-Nlg) : x (FeCl₂·4H₂O) : 3 (APTES) : 4 (TEOS) : 1750 (H₂O). The synthesized samples were centrifuged and washed with deionized water and ethanol for three times,

respectively. Finally, the obtained dried samples were calcined at 550 °C for 6 h in dry air stream with a heating rate of 1 °C min⁻¹. The final samples are designated as *x*Fe/AMS (where *x* represents the molar ratio of Fe²⁺/Na-Nlg, which is 0.05, 0.10, 0.15 and 0.20). The pure AMS was prepared based on the above similar procedure.

The comparative post-impregnated samples were prepared by the classical wet impregnation method.²⁷ In brief, 0.1 g of pre-synthesized pure AMS powder, MCM-41 powder and SBA-15 powder were respectively dispersed into the alcoholic solution of $FeCl_2 \cdot 4H_2O$ (2.53 wt%), and followed by rotary evaporation until complete dryness. The resultant various samples were then dried at 60 °C overnight and then calcined at 550 °C for 6 h in dry air stream with a heating rate of 1 °C min⁻¹. The obtained products were designed as 0.15Fe/AMS(p), 0.15Fe/MCM-41(p) and 0.15Fe/SBA-15(p), accordingly.

2.3. Characterizations

The UV-visible absorption (UV-vis) spectra of micelles were analyzed by a UV-vis spectrophotometer (BLV-GHX-V, Bilang Corporation, Shanghai, China).

Fourier transform infrared (FT-IR) spectra from the samples were recorded in the range of 400–4000 cm⁻¹, with powders dispersed on the pure KBr on Bruker VECTOR22 resolution (Bruker, Germany).

Diffused Reflection UV-vis (DRUV-vis) spectra of samples were obtained in the range of 200–800 nm by Lambda 950 spectrophotometer (PerkinElmer, Waltham, MA, USA).

Hydrogen temperature programmed reduction (H₂-TPR) measurements were performed utilizing a fixed-bed reactor under a flow of 10% H₂·Ar gas mixture and a heating rate of 10 $^{\circ}$ C min⁻¹ from room temperature to 750 $^{\circ}$ C. Before the TPR analysis, the carbonates and hydrates impurities were removed by flowing argon over the catalyst at a flow rate of 30 mL min⁻¹ at 300 $^{\circ}$ C for 1 h and the system was then cooled to room temperature. The amount of H₂ uptake during the reduction was measured continuously using a thermal conductivity detector (TCD).

The X-ray photoelectron spectra (XPS) were performed on a PHI 5000 Versa Probe X-ray photoelectron spectrometer equipped with Al K α radiation (1486.6 eV) (Ulvac-PHI, Chigasaki, Japan). The C 1s peak at 284.6 eV was used as the reference for binding energies.

The powder X-ray diffraction (XRD) patterns of the samples were collected with Smartlab TM 9 KW (Rigaku Corporation, Tokyo, Japan) equipped with a rotating anode and Cu K α radiation ($\lambda = 0.154178$ nm).

The N₂ (77.4 K) adsorption–desorption measurements were carried out with BELSORP-MINI volumetric adsorption analyzer (BEL Japan, Osaka, Japan) in a relative pressure range P/P_0 from 0.01 to 0.99. The annealed samples were outgassed in vacuum at 150 °C for 5 h before measurements. The specific surface areas and distribution of pore size were calculated using the Brunauer–Emmet–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively.

High-resolution transmission electron microscopy (HRTEM) images were recorded on a JEM-2010 EX microscope (JEOL, Tokyo, Japan), which was operated at an accelerating voltage of 200 kV. The samples were crushed in A.R. grade ethanol and the resulting suspension was allowed to dry on carbon film supported on copper grids.

Field emission scanning electron microscopy (FE-SEM) was performed on a Hitachi S4800 Field Emission Scanning Electron Microscopy (Hitachi, Tokyo, Japan).

The iron content in the samples was determined using a PE Optima 2000DV (PerkinElmer, Waltham, MA, USA) Inductively Coupling Plasma emission spectrometer (ICP). The samples were completely dissolved in hydrofluoric acid before analysis.

2.4. Catalysis tests

The phenol hydroxylation was carried out in 50 mL of threenecked round-bottom flask equipped with a magnetic stirrer and reflux condenser. The reaction mixture consists of 0.22 g of catalyst, 4.29 g of phenol, 0.36 g of sodium dodecyl sulfate and 2.1 mL of H₂O₂ (30 wt%), and the reaction was carried out under reflux at room temperature for 2 h. Then, the product distributions were analyzed by an HPLC 100 (Wufeng Scientific Instruments Co., Ltd, Shanghai, China). The conversion of reactant and selectivity of products were calculated by external standard method. In addition, the molar ratio of *n*(phenol)/ *n*(H₂O₂) is defined as follows:

n(phenol) = m/M = 4.29/94.11 = 0.045 where n, m and M refer to the molar number, the mass and the molecular weight of phenol, respectively.

 $n(H_2O_2) = \rho \times V \times wt\%/M = 1.13 \text{ g mL}^{-1} \times 2.1 \text{ mL} \times 30\%/$ 34.01 = 0.021 where *n*, ρ , *V*, wt% and *M* represent the density, the volume, the weight concentration and the molecular weight of H₂O₂, respectively.

The molar ratio of $n(H_2O_2)/n(\text{phenol})$ is about 2.

In order to investigate the recycling properties of 0.15Fe/AMS and 0.15Fe/AMS(p), the two catalysts were separated from the reaction mixture by centrifugation and used again in a fresh reaction respectively.

3. Results and discussion

3.1 Illustration for the synthetic method

The micropore-enriched silica composite with Fe₂O₃ inside the channel was prepared by a modified anionic micelle templating assemble route $(S^{T}X^{+}I^{-})$. Typically, in this pathway (Scheme 1), a novel anionic template Na-Nlg exhibits excellent chelating capability due to a large number of carboxyl functional groups and is able to self-assemble to form regular anionic micelles in the proper solutions. During the assemble process, Fe²⁺ would be anchored on the micelles by coordination with carboxyl groups as metal-modified micelle template (Na-Nlg, S⁻). In the following step, the head of metal-modified micelle template could match amino groups of the co-structure directing agent (CSDA) (APS, X^+). Then, silicate oligomers (I^-) deposited on CSDA matched functional micelles by the co-hydrolysis with CSDA. Finally, after calcination, Fe₂O₃ species were in situ formed and highly-dispersed inside the channels of AMS material. Obviously, the formation of metal-modified anionic template would be the key factor during this synthesis process.



Scheme 1 Metal-modified micelle templating method $(S^{-}X^{+}I^{-})$ for the synthesis of silica composite.



Fig. 1 UV-vis spectra and the digital photo (inset) of different solutions of (a) FeCl₂ solution, (b) NLG solution and (c) mixed solution of NLG and FeCl₂.

3.2 Characterizations for the interaction between Na-Nlg and Fe^{2+}

In order to verify the formation of metal-modified anionic micelle template, the chelating evidence of Fe^{2+} on anionic surfactant of Na-Nlg is examined by UV-vis spectroscopy. The UV-vis spectra and digital photos of different solutions of FeCl₂, Na-Nlg and their mixture are shown in Fig. 1. As compared with single FeCl₂ solution and single Na-Nlg solution, the mixture solution exhibits a newly emerging band centered at *ca.* 336 nm, which indicates the existence of interaction between Na-Nlg and Fe²⁺.²⁸ Furthermore, in the given digital photo, the mixture (c) displays an obvious change in contrast to the colorless single FeCl₂ solution (a) and single Na-Nlg solution (b), which strongly supports the coordination of Fe²⁺ on the Na-Nlg.

For further analyzing the interaction between introduced Fe^{2+} and surfactant of Nlg-Na, the FT-IR spectra of uncalcined As-pure AMS, uncalcined As-0.15Fe/AMS and 0.15Fe/AMS are also examined and shown in Fig. 2. As observed, for the sample of 0.15Fe/AMS, the peaks at *ca.* 1081 cm⁻¹ and 791 cm⁻¹ are attributed to the asymmetric and symmetric stretching

vibrations of Si–O–Si, respectively, while another absorbed peak at *ca.* 961 cm⁻¹ is typically corresponding to the stretching vibration of Si–OH surface groups, these bands are the feature absorption of silica. As for the uncalcined As-pure AMS and As-0.15Fe/AMS, several characteristic peaks appear at *ca.* 2923, 1588 and 1402 cm⁻¹ ascribed to –CH₂–, C=N and C–H of the surfactant. Moreover, as compared to the As-pure AMS, an obvious shift from 1558 cm⁻¹ to 1581 cm⁻¹ for the absorbed peak of C=N is observed in the sample of As-0.15Fe/AMS,²⁹ which is the strong evidence to favor the coordination of Fe²⁺ with the group of C=N on the amino acid head.

3.3. Characterizations for Fe₂O₃ state

Fig. 3 displays the wide-angle XRD patterns of series samples directly synthesized and post-impregnated sample of 0.15Fe/AMS(p). All the curves exhibit a broad diffraction peak from 20° to 30° ascribed to amorphous silica. Specifically, as for the post-impregnated sample of 0.15Fe/AMS(p), several diffraction peaks at 24°, 33°, 36°, 49°, 54°, 62° and 64° are detected and indexed to (012), (104), (110), (024), (116), (214) and (300) crystal faces of Fe₂O₃ (JCPDS 88-0315). However, no diffraction peak of Fe₂O₃ crystalline phase is detected in the curves of series *x*Fe/AMS samples, suggesting that high-dispersion and amorphous status of Fe₂O₃ in these samples.

For better understanding the nature and the coordination environment of iron species in different samples, Diffused Reflection UV-vis spectra (DRUV-vis) of *x*Fe/AMS were examined and their results are presented in Fig. 4. As observation, the curves of *x*Fe/AMS are divided into four sub-curves with maxima at *ca.* 218, 258, 360, and 503 nm. Typically, the absorption band at 218 nm is attributed to the characteristic absorption of silica. The second absorption band at 258 nm is associated with the d_{π} - p_{π} charge transfer (CT) between Fe and surface O of silica,³⁰ indicating that some iron atoms may directly link to siliceous matrix. The result should be due to the special templating method in which Fe²⁺ are enriched on the anionic micelles and then directly match structure directing agents or siliceous oligomers, resulting in the presence of surface-linked Fe species after calcination. For comparison, a DRUV-vis spectra of pure



Fig. 2 FT-IR spectra of 0.15Fe/AMS, As-pure AMS and As-0.15Fe/AMS.



Fig. 3 Wide-angle XRD patterns of xFe/AMS and 0.15Fe/AMS(p).

800



Fig. 4 DRUV-vis spectra of xFe/AMS and pure iron oxides.

iron oxides has been presented in Fig. 4. As expected, the curve shows little or no absorbance in the range 200-400 nm, which demonstrates the absence of surface-link Fe species. However, when the surface linked Fe atoms reach saturation, the excessive Fe atoms would aggregate into clusters or particles. In this case, the presence of other two absorption bands at ca. 360 nm

Table 1 State and relative distribution of iron species in xFe/AMS ^a									
Samples	$\operatorname{Fe}^{b}(\operatorname{wt\%})$	Surface-linked Fe		Fe ₂ O ₃ clusters		Fe ₂ O ₃ particle			
		% area	Fe (wt%)	% area	Fe (wt%)	% area	Fe (wt%)		
0.05Fe/AMS	0.92	12.5	0.12	75.7	0.69	11.8	0.11		
0.10Fe/AMS	1.62	15.1	0.24	75.4	1.22	10.4	0.16		
0.15Fe/AMS	2.53	13.4	0.34	78.1	2.01	8.5	0.18		
0.20Fe/AMS	2.89	13.3	0.38	73.7	2.12	13.0	0.36		

^{*a*} It is calculated from DRUV-vis spectra of *x*Fe/AMS. ^{*b*} It is determined by ICP-AES.

Paper



and 503 nm are attributed to octahedral Fe^{3+} in oligomeric Fe_2O_3 clusters and larger Fe_2O_3 particles, respectively, as can be seen in the spectra of pure iron oxides.³¹⁻³³ In order to analyze these results with great certainty, the further detailed information for the metal content and status distribution of different iron species are summarized in Table 1. As observed in Table 1, from the calculated results of relative percentage of band areas, the more incorporation of Fe_2O_3 does not lead to the consecutive enhancement of absorption of oligomeric Fe_2O_3 clusters, which indicates the saturation of Fe_2O_3 clusters on the pore wall. However, the dominated absorbed peak of oligomeric Fe_2O_3 clusters indicates that most of the Fe_2O_3 are well-dispersed on the pore wall with fine oligomeric Fe_2O_3 clusters.



Fig. 7 Low-angle XRD patterns of xFe/AMS and pure AMS.

In order to verify the chemical environments of iron oxide of *x*Fe/AMS and 0.15Fe/AMS(p), H₂-TPR experiments are performed and their results are displayed in Fig. 5. It is known that supported metal oxides on inert supports have a complicated reduction behavior due to difference of particle size, dispersity and surface interaction. In this case, the reduction profile of the iron species loaded on the support would be the result of the competition between two factors: the faster reduction of smaller size particles due to the increase in the surface/volume ratio, and the slower reduction of these smaller particles owing to the higher interaction with the support.³² As shown in Fig. 5, the curve of 0.15Fe/AMS(p) exhibits two reduction peaks with the maximum temperature at *ca.* 382 °C and 646 °C, which can be related to the Fe³⁺ \rightarrow Fe^{3+/2+} and Fe^{3+/2+} \rightarrow Fe⁰ processes, respectively.³⁴



Fig. 6 XPS spectra of the sample 0.15Fe/AMS: (a) Si 2p, (b) O 1s and (c) Fe 2p.



Fig. 8 N_2 adsorption/desorption isotherms (a) and pore size distribution (b) of xFe/AMS and pure AMS.

However, as for the directly synthesized samples, the reduction peaks attributed to $Fe^{3+} \rightarrow Fe^{3+/2+}$ move towards lower temperature of 361 °C. This lower reduction temperature should be attributed to the higher surface/volume ratio in the smaller metal particles,³⁵ indicating the presence of highly-dispersed Fe_2O_3 clusters in these samples. Moreover, it is interesting to note that the sample 0.05Fe/AMS shows a reduction peak at *ca.* 519 °C, which is assigned to the $Fe^{3+/2+} \rightarrow Fe^{2+}$ process. At low iron

View Article	Online
	Paper

content, the Fe²⁺ species are stabilized on the pore wall with high resistance to the reduction to metallic state.³² On the other hand, the enhanced intensity of reduction peak (Fe³⁺ \rightarrow Fe²⁺) suggests gradually increasing Fe₂O₃ clusters are embedded into the channel of mesoporous silica with the increase introduction of iron. Therefore, the TPR results further confirm high dispersion of Fe₂O₃ clusters in the channel of mesoporous silica, which is in good agreement with DRUV-vis results.

The surface composition and chemical state of 0.15Fe/AMS sample are further analyzed by XPS spectra. The Si 2p spectrum of 0.15Fe/AMS is shown in Fig. 6(a). This spectrum is composed of a single peak centered at ca. 103.1 eV, which is characteristic of silicates. The spectrum of O 1s of 0.15Fe/AMS (Fig. 6(b)) is also composed of a single peak centered at ca. 532.6 eV corresponding to oxygen in the SiO₂. While other peaks of oxygen attributed to iron oxides such as Fe₂O₃ (at ca. 530 eV) are not observed. The result is probably due to that their low signal is masked by the intense signal corresponding to the oxygen of the SiO2.36 The Fe 2p spectrum of 0.15Fe/AMS is shown in Fig. 6(c). The binding energy of Fe 2p_{3/2} at 711.9 eV, accompanied by a satellite peak at 720 eV, and the binding energy of $2p_{1/2}$ at 724.3 eV, are indicative of the presence of Fe³⁺ in iron oxide environment.³⁷ According to the literature, the binding energy value of pure iron oxide presents at 710.6 eV, but the binding energy value of Fe 2p_{3/2} of 0.15Fe/AMS shifts toward a higher value (711.9 eV), indicating that Fe₂O₃ have a strong interaction with silica wall.³⁸ Meanwhile, the presence of the peak at 715.9 eV between the peak of Fe $2p_{3/2}$ and its satellite peak could be attributed to Fe linked to surface O atoms on the silica wall,39 which is consistent with DRUV-vis result. To explain this phenomenon, as compared with Fe³⁺ in iron oxide environment, a decrease in the crystal field energy of the Fe³⁺ ions located at the surface should be the reason for the presence of this peak. Thus, with a decrease in the coordination, the surface-linked Fe³⁺ would be surrounded by a lower electron density, which requires the binding energy (715.9 eV) to be used to produce a photoelectron. Taken together, these results demonstrate Fe₂O₃ species are highly-dispersed and stabilized in the channel of silica in the form of clusters.

3.4. Characterizations for the structure of samples

The presence of Fe_2O_3 clusters on the pore walls of mesoporous silica would influence mesostructure ordering and pore size of

rade 2 rexterial parameters of all the samples								
Samples	Fe/Si ^a (wt%)	$S_{\mathrm{BET}}^{}b}\left(\mathrm{m}^2~\mathrm{g}^{-1} ight)$	$V_{\rm p} \left({\rm m}^3~{ m g}^{-1} ight)$	$D_{\rm p}^{\ c} ({\rm nm})$	a_0^d (nm)	$d_{100} ({\rm nm})$	$d_{\mathrm{w}}^{e}\left(\mathrm{nm} ight)$	
Pure AMS	_	312	0.32	3.29	5.42	4.69	2.13	
0.05Fe/AMS	0.92	518	0.23	1.72	4.21	3.65	2.49	
0.10Fe/AMS	1.62	499	0.20	1.72	4.25	3.68	2.53	
0.15Fe/AMS	2.53	434	0.19	1.72	4.29	3.72	2.57	
0.20Fe/AMS	2.89	399	0.15	1.67	4.56	3.95	2.89	
0.15Fe/AMS(p)	3.50	156	0.11	2.60	4.32	3.74	1.72	
0.15Fe/SBA-15(p)	3.50	490	1.39	5.40	10.00	8.66	4.60	
0.15Fe/MCM-41(p)	3.50	872	0.58	2.40	4.03	3.49	1.63	

^{*a*} It is determined by ICP-AES. ^{*b*} It is calculated by BET method. ^{*c*} It is calculated by BJH method using desorption data. ^{*d*} $a_0 = 2 \times d_{100}/\sqrt{3}$, which represents unit cell parameter. ^{*e*} $d_w = a_0 - D_p$, which represents pore wall thickness.

Table 2 Textural parameters of all the samples



Fig. 9 Representative TEM images of 0.15Fe/AMS (a) and EDX pattern of selected area (b).

*x*Fe/AMS samples. As observed in Fig. 7, pure AMS exhibits a (100) diffraction peak at $2\theta \approx 1.9^{\circ}$ with (110) and (200) diffraction peaks. The (100) diffraction peak for the pure AMS exhibits a stronger intensity and low angle of peak position, indicating the well-ordered mesostructure and large pore size of pure AMS. However, series of *x*Fe/AMS exhibit a weak intensity (100) diffraction peak at *ca.* $2\theta \approx 2.4^{\circ}$, which suggests the presence of mesostructure in *x*Fe/AMS. The result is due to that *x*Fe/AMS are prepared by modifying the pore surface of mesoporous AMS. Additionally, the intensity of (100) diffraction peak of *x*Fe/AMS is approximately invariable with the increase of iron content, indicating that the gradual formation of Fe₂O₃ clusters in the channel of mesoporous silica have little effect on the regularity of mesostructure.

The textural characteristics of the prepared samples are displayed in N₂-adsorption/desorption isotherms (Fig. 8(a)). As observed from the curve, the pure AMS shows the typical IV isotherm with an obvious capillary condensation step, indicating the mesostructure of pure AMS. However, the isotherms of *x*Fe/AMS samples exhibit type I-like curve, which are typical for microporous materials. Generally, a type I isotherm would have to level off below a relative pressure of about 0.1 for the materials to be exclusively microporous. However, the isotherms for xFe/AMS samples do not level off below the relative pressure of about 0.1, the samples are likely to exhibit an appreciable number of mesopores with pore sizes close to the micropore range.^{40,41} The presence of micropore is attributed to the coverage of Fe₂O₃ clusters on the pore walls of mesoporous silica. On the other hand, the more detailed textural parameters of samples are further summarized in Table 2. With the contents of irons increased from 0.05 to 0.20,

the specific surface areas for the samples decrease slightly from 518 to 399 m² g⁻¹, suggesting that iron species incorporated into the pore surface of mesoporous materials do not damage the mesostructure completely. In addition, it is very interesting that the specific surface areas of xFe/AMS is obviously higher than that of pure AMS, which may be due to the increase number of pores under the same pore volume. Besides, the pore size distribution in Fig. 8(b) shows that the most probable pore size of xFe/AMS is at ca. 1.70 nm and the more incorporation of Fe₂O₃ do not lead to the gradual drop of pore size, which is due to that the aggregated Fe_2O_3 particles migrate out of the channel of silica during the thermal treatment process. In addition, it is noticeable that pore wall thickness (d_w) increases from 2.13 nm to 2.89 nm with the increment of iron in the samples. It suggests that the increasing thickness may be assigned to the occupation of Fe_2O_3 species on the pore wall.

The structural characteristics of samples and distribution of iron species in the channel are further examined by highresolution transmission electron microscopy (TEM). The ordered and parallel channels are observed in the representative TEM images of 0.15Fe/AMS (Fig. 9(a)). The measured pore diameter from the TEM images is *ca.* 1.68 nm, which is close to N₂ adsorption/desorption results. This result reveals that the porous structure is not destroyed after *in situ* introducing Fe₂O₃ species. More importantly, visual Fe₂O₃ particles fail to be detected from TEM images, however, as shown in Fig. 9(b), the energy-dispersive X-ray (EDX) analysis suggests that 0.15Fe/AMS contains Si, O and Fe elements. In this case, Fe₂O₃ should be highly dispersed in the silica composite, which is consistent with XPS and N₂ adsorption/desorption results.



Fig. 10 (a) SEM image of 0.15Fe/AMS sample and the corresponding element mappings of the sample: (b) Si, (c) O, (d) Fe.

 Table 3
 The catalytic activities of all the samples for phenol hydroxylation^a

Samples	Pore size ^{b} (nm)	Fe/Si ^c (wt%)	$\mathrm{Fe}/\mathrm{Si}^d$ (wt%)	<i>X</i> (Ph) ^{<i>e</i>} /%	<i>S</i> (CAT) ^{<i>f</i>} /%	<i>S</i> (HQ) ^{<i>g</i>} /%	Ref.
0.05Fe/AMS	1.72	1.11	0.92	29.8	44.3	28.4	This work
0.1Fe/AMS	1.72	2.23	1.62	34.8	49.4	29.7	
0.15Fe/AMS	1.72	3.50	2.53	44.3	52.2	30.4	
0.20Fe/AMS	1.67	4.67	2.89	43.6	50.1	30.3	
$0.15 \text{Fe/MCM} - 41(p)^{h}$	2.40	3.50	2.52	38.6	32.8	18.6	
0.15Fe/SBA-15(p)	5.40	3.50	2.61	40.1	26.1	19.4	
0.15Fe/AMS(p)	2.60	3.50	2.50	36.7	31.4	19.6	
TS-1	0.54	_	_	29	50.2	49.8	44
Fe-ZSM-5	0.50	2.00	1.54	32.9	60.5	39.5	21

^{*a*} Reaction conditions: molar ratio, phenol/ $H_2O_2 \approx 2:1$, time, 2 h, reaction temperature, room temperature. ^{*b*} It is calculated by BJH method using desorption data. ^{*c*} The initial Fe/Si mass ratios in the synthesis gel. ^{*d*} Fe/Si mass ratios are determined by ICP-AES. ^{*e*} The conversion of phenol. ^{*f*} The selectivity of catechol. ^{*g*} The selectivity of hydroquinone. ^{*h*} The post synthesized sample.

To further understand the distribution of iron species on the surface of silica, elemental mapping from SEM measurement is conducted and the results are shown in Fig. 10. As observed, silica composite prepared by the metal-modified micelle templating method contains elements of Si, O, and Fe. Moreover, it is also clear that the iron element is uniformly dispersed on silica composite, which could confirm the high dispersion of iron species in the silica composite and is consistent with XPS and EDX results.

3.5. Catalytic tests

In the present work, the catalytic performance of *x*Fe/AMS is evaluated by direct oxidation of phenol at room temperature and the corresponding catalytic results are summarized in Table 3. According to recent reports,⁵ the pure AMS fails to show any activity and the bulk Fe₂O₃ performed poor activity in this reaction. While in Table 3, series samples of *x*Fe/AMS exhibit high conversion and selectivity, which indicates that highlydispersed Fe₂O₃ clusters could be more effective as an active site. In addition, by the gradually growth of the Fe/Si mass ratio from 0.92 to 2.89, the catalytic performances of 0.05Fe/AMS, 0.10Fe/AMS and 0.15Fe/AMS are improved correspondingly. According to the DRUV-vis and XPS results, this should be attributed to the increased number of exposed active sites in each catalyst. However, the catalyst of 0.20Fe/AMS gives a decreasing trend for catalytic activities. The result is due to



Scheme 2 Depiction for the phenol hydroxylation catalyzed by *x*Fe/AMS catalysts.

that extra Fe_2O_3 can accelerate the decomposition of H_2O_2 and yield high concentration of HO·, leading to the excessive oxidation.⁴² Therefore, the 0.15Fe/AMS is regarded as optimal catalyst in phenol hydroxylation, which exhibits high catalytic activities, giving the phenol conversion at 44.3% with selectivity of 82.6% to hydroquinone.

To better understanding the catalytic performances of xFe/AMS, catalytic performance of 0.15Fe/MCM-41(p), 0.15Fe/SBA-15(p), 0.15Fe/AMS(p), reported TS-1 and Fe-ZSM-5 are also investigated, and their catalytic results are summarized in Table 3. As observed in Table 3, as compared with 0.15Fe/MCM-41(p), 0.15Fe/SBA-15(p) and 0.15Fe/AMS(p), 0.15Fe/AMS shows

(a) 0.15Fe/AMS(p) 0.15Fe/AMS Phenol conversion (%) 50 40 30 20 10 0 1 2 3 4 5 **Recycling times** b 0.15Fe/AMS(p) 0.15Fe/AMS Fe contents (wt%) 3 2 0 1 2 3 5 **Recycling times**

Fig. 11 Recycling test of 0.15Fe/AMS and 0.15Fe/AMS(p): (a) the conversion of phenol and (b) mass ratios of Fe/Si.

Paper

a highest conversion and selectivity. Base on the results of textual properties, the high conversion should be due to the presence of highly-dispersed Fe₂O₃ clusters in 0.15Fe/AMS, which results from the metal-modified anionic surfactant templating route. On the other hand, it is worth noting that the order of pore size is Fe-ZSM-5 (0.5 nm) < TS-1 (0.54 nm) <0.15Fe/AMS (1.72 nm) < 0.15Fe/MCM-41(p) (2.40 nm) < 0.15Fe/ AMS(p) (2.60 nm) < 0.15Fe/SBA-15(p) (5.40 nm). And the molecular size of tar is much bigger than that of benzoquinone (0.54 nm) and dihydroxybenzene (0.56 nm). Therefore, for the microporous materials of Fe-ZSM-5 and TS-1, due to the shape selectivity,43 the relatively large molecule by-products of tar could hardly be formed in the channels, leading to the high selectivity of dihydroxybenzene. Similarly, compared with 0.15Fe/MCM-41(p), 0.15Fe/SBA-15(p) and 0.15Fe/AMS(p), the micropore-enriched 0.15Fe/AMS should exhibit a high selectivity of dihydroxybenzene. Nevertheless, even with high selectivity to dihydroxybenzene, the low surface area of Fe-ZSM-5 and TS-1 would lead to the decreased number of exposed active sites in the catalysts.²⁴ Besides, their extremely small micro-channel could hinder the reactant molecules diffusing across the channel. In contrast, the prepared micropore-enriched catalysts of xFe-AMS show larger pore channels, which can ensure that more of reactants diffuse into the channels. Therefore, compared with Fe-ZSM-5 and TS-1, xFe/AMS catalysts exhibit a high conversion in phenol hydroxylation.

In summary, as depicted in Scheme 2, the prepared micropore-enriched Fe/AMS catalysts show better dispersion of iron oxides, which would increase the number of exposed active sites. Moreover, the presence of more profitable pore channels of Fe/AMS catalysts could make more of reactants diffuse into the channels. Consequently, compared with other catalysts, micropore-enriched Fe/AMS catalysts exhibit a high conversion and selectivity in phenol hydroxylation.

In addition, to evaluate the catalytic stability of optimal catalyst, the 0.15Fe/AMS and 0.15Fe/AMS(p) catalysts are tested by running the reaction successively five times. As showed in Fig. 11 and Table S1,† after recycled in 5 times, 0.15Fe/AMS(p) exhibits the low iron concentration and catalytic performances. But for 0.15Fe/AMS catalyst, the iron concentration is still as high as 1.94 wt% and the catalytic phenol conversion is above 37.7%. This result should be attributed to the strong interact between Fe_2O_3 species and pore wall of mesoporous silica and is in accord with the above result.

4. Conclusions

In this work, controllable contents of surface iron oxides were *in situ* introduced into AMS by metal-modified anionic surfactant templating route. The structure properties, iron oxide status, chemical stability and catalytic properties of different catalysts for phenol hydroxylation have been studied. The results indicated that Fe_2O_3 species from template-induced method show better dispersion and stability compared to that of post-impregnated one. As unexpected, massive micropores (*ca.* 1.7 nm) were directly formed due to the occupation of irons species in mesochannel. In this case, the optimal 0.15Fe/AMS catalyst

exhibited highest catalytic activities in phenol hydroxylation, receiving the phenol conversion of 44.3% with hydroquinone selectivity of 82.6%. The extremely-dispersed catalytic active sites and massive micropores should be responsible for high catalytic activities. In addition, due to better chemical stability of the catalyst, 0.15Fe/AMS exhibited superior catalytic stability.

Acknowledgements

This work was supported by the National Natural Science Foundations of China (No. 21276125, 21476108, 20876077) and the Project of Priority Academic Program Development of Jiangsu Higher Education Institutions (PAPD).

Notes and references

- 1 J. Kou, C. Lu, W. Sun, L. Zhang and Z. Xu, ACS Sustainable Chem. Eng., 2015, 3, 3053-3061.
- 2 C. Corot, P. Robert, J. M. Idee and M. Port, *Adv. Drug Delivery Rev.*, 2006, **58**, 1471–1504.
- 3 X. Liu, R. Wang, T. Zhang, Y. He, J. Tu and X. Li, Sens. Actuators, B, 2010, 150, 442-448.
- 4 K. Zilberberg, J. Meyer and T. Riedl, *J. Mater. Chem. C*, 2013, **1**, 4796.
- 5 C. Wu, Y. Kong, F. Gao, Y. Wu, Y. Lu, J. Wang and L. Dong, *Microporous Mesoporous Mater.*, 2008, **113**, 163–170.
- 6 L. Guo, F. Chen, X. Fan, W. Cai and J. Zhang, *Appl. Catal., B*, 2010, **96**, 162–168.
- 7 S. Sobhani, M. Bazrafshan, A. A. Delluei and Z. P. Parizi, *Appl. Catal., A*, 2013, **454**, 145–151.
- 8 X. Xu, T. Liu, P. Xie, Y. Yue, C. Miao, W. Hua and Z. Gao, *Catal. Commun.*, 2014, 54, 77–80.
- 9 F. Yang, S. Gao, C. Xiong, S. Long, X. Li, T. Xi and Y. Kong, *RSC Adv.*, 2015, 5, 72099–72106.
- 10 H. Wang, X. Li, C. Xiong, S. Gao, J. Wang and Y. Kong, *ChemCatChem*, 2015, 7, 3855–3864.
- 11 J. Fan, X. Jiang, H. Min, D. Li, X. Ran, L. Zou, Y. Sun, W. Li, J. Yang, W. Teng, G. Li and D. Zhao, *J. Mater. Chem. A*, 2014, 2, 10654.
- 12 L. Chmielarz, P. Kuśtrowski, R. Dziembaj, P. Cool and E. F. Vansant, *Appl. Catal., B*, 2006, **62**, 369–380.
- 13 Y. Li, J. Sun, J. Wang, L. Zhang, L. Gao and X. Wu, *J. Porous Mater.*, 2011, **19**, 389–396.
- 14 S. Zhu, Z. Zhou, D. Zhang and H. Wang, *Microporous Mesoporous Mater.*, 2006, **95**, 257–264.
- 15 T. Hisatomi, M. Otani, K. Nakajima, K. Teramura, Y. Kako, D. Lu, T. Takata, J. N. Kondo and K. Domen, *Chem. Mater.*, 2010, **22**, 3854–3861.
- 16 A.-L. Radu, C. Damian, V. Fruth, T.-V. Iordache, A. Zaharia,
 H. Iovu and A. Sarbu, *Microporous Mesoporous Mater.*,
 2014, 198, 281–290.
- 17 C.-H. Liu, N.-C. Lai, S.-C. Liou, M.-W. Chu, C.-H. Chen and C.-M. Yang, *Microporous Mesoporous Mater.*, 2013, **179**, 40– 47.
- 18 J. Gu, Y. Huang, S. P. Elangovan, Y. Li, W. Zhao, I. Toshio, Y. Yamazaki and J. Shi, *J. Phys. Chem. C*, 2011, **115**, 21211– 21217.

- 19 S. Kulawong, S. Prayoonpokarach, A. Neramittagapong and J. Wittayakun, J. Ind. Eng. Chem., 2011, 17, 346–351.
- 20 T. Yokoi, P. Wu, Y. Guo and T. Tatsumi, *Catal. Commun.*, 2003, 4, 11–15.
- 21 A. L. Villa, C. A. Caro and C. M. d. Correa, *J. Mol. Catal. A: Chem.*, 2005, **228**, 233–240.
- 22 A. Thangaraj, R. Kumar and P. Ratnasamy, *J. Catal.*, 1991, 131, 294–297.
- 23 A. Tuel, S. Moussa-Khouzami, Y. B. Taarit and C. Naccache, *J. Mol. Catal. A: Chem.*, 1991, **68**, 45–52.
- 24 M. Kruk, T. Asefa, M. Jaroniec and G.-A. Ozin, *J. Am. Chem. Soc.*, 2002, **124**, 6383–6392.
- 25 L. Wu, Z. Li, D. Han, J. Wu and D. Zhang, *Fuel Process. Technol.*, 2015, **134**, 449–455.
- 26 D. Gao, A. Zheng, X. Zhang, H. Sun, X. Dai, Y. Yang, H. Wang, Y. Qin, S. Xu and A. Duan, *Nanoscale*, 2015, 7, 10918–10924.
- 27 M. A. Karakassides, D. Gournis, A. B. Bourlinos, P. N. Trikalitis and T. Bakas, *J. Mater. Chem.*, 2003, **13**, 871–876.
- 28 X. J. Lin, A. Z. Zhong, Y. B. Sun, X. Zhang, W. G. Song, R. W. Lu, A. M. Cao and L. J. Wan, *Chem. Commun.*, 2015, 51, 7482–7485.
- 29 K. Niu, D. Shi, W. Dong, M. Chen and Z. Ni, J. Colloid Interface Sci., 2011, 362, 74-80.
- 30 A. Gervasini, C. Messi, P. Carniti, A. Ponti, N. Ravasio and F. Zaccheria, J. Catal., 2009, 262, 224–234.
- 31 A. I. Carrillo, E. Serrano, R. Luque and J. García-Martínez, *Appl. Catal.*, A, 2013, 453, 383–390.

- 32 N. I. Cuello, V. R. Elías, C. E. Rodriguez Torres, M. E. Crivello, M. I. Oliva and G. A. Eimer, *Microporous Mesoporous Mater.*, 2015, 203, 106–115.
- 33 Q. Zhang, Y. Li, D. An and Y. Wang, Appl. Catal., A, 2009, 356, 103–111.
- 34 B. Coq, M. Mauvezin, G. Delahay and S. Kieger, J. Catal., 2000, 195, 298–303.
- 35 X. Shi, H. He and L. Xie, Chin. J. Catal., 2015, 36, 649-656.
- 36 A. De Stefanis, S. Kaciulis and L. Pandolfi, *Microporous Mesoporous Mater.*, 2007, **99**, 140–148.
- 37 J. L. Gu, X. Dong, S. P. Elangovan, Y. Li, W. Zhao, T. Iijima, Y. Yamazaki and J. L. Shi, *J. Solid State Chem.*, 2012, **186**, 208–216.
- 38 T. Yamashita and P. Hayes, *Appl. Surf. Sci.*, 2008, **254**, 2441–2449.
- 39 A. P. Grosvenor, B. A. Kobe, M. C. Biesinger and N. S. McIntyre, *Surf. Interface Anal.*, 2004, 36, 1564–1574.
- 40 Y.-D. Chiang, H.-Y. Lian, S.-Y. Leo, S.-G. Wang, Y. Yamauchi and K. C. W. Wu, *J. Phys. Chem. C*, 2011, **115**, 13158–13165.
- 41 H. Nan, Q. Cai, Q. Sun, J. Qi, Y. Liu, H. Zhou, Y. Yu, W. Shi, T. Wang, C. Xu and H. Li, *Microporous Mesoporous Mater.*, 2011, 142, 585–591.
- 42 X. Liang, R. Yang, G. Li and C. Hu, *Microporous Mesoporous Mater.*, 2013, **182**, 62–72.
- 43 T. Okuhara, Appl. Catal., A, 2003, 256, 213-224.
- 44 P.-Y. Chao, S.-T. Tsai, T.-C. Tsai, J. Mao and X.-W. Guo, *Top. Catal.*, 2009, **52**, 185–192.