

View Article Online View Journal

# **RSC Advances**

This article can be cited before page numbers have been issued, to do this please use: C. Dai, A. Zhang, M. Liu, J. Li, F. Song, C. Song and X. Guo, *RSC Adv.*, 2016, DOI: 10.1039/C5RA26009D.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/advances

# Journal Name

## **RSCPublishing**

## ARTICLE

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012, Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

Published on 18 January 2016. Downloaded by University of York on 21/01/2016 12:03:05.

# Facile one-step synthesis of hierarchical porous carbon monoliths as superior support of Fe-based catalyst for CO<sub>2</sub> hydrogenation

Chengyi Dai,<sup>a</sup> Anfeng Zhang,<sup>a</sup> Min Liu,<sup>a</sup> Junjie Li,<sup>a</sup> Fangyu Song,<sup>a</sup> Chunshan Song<sup>a,b</sup>\* and Xinwen Guo<sup>a</sup>\*

A versatile strategy involving one-step desilication of coke-deposited spent zeolite catalyst was successfully developed to prepare hierarchical porous carbon monoliths (HPCMs). Such a strategy avoids the use of hard or soft templates and carbon source, eliminates high temperature carbonization, simultaneously, minimizes the emissions from processing spent catalysts. The resulting carbon exhibits a controlled morphology such as three-dimensional network, hollow sphere or nanosheets, a high degree of graphitization and multi-level porous structure. Its mesopore (2-50 nm) surface area can reach 522 m<sup>2</sup>/g and both mesopore and macropore (50-350 nm) volumes are more than 1.0 cm<sup>3</sup>/g. Such hierarchical porous carbon was found to be a superior support for minimizing the nanoparticle size and enhancing the synergism of Fe-K catalyst for promoting CO<sub>2</sub> hydrogenation. Using such catalyst results in increased the conversion of carbon dioxide and enhanced selectivity of high value olefins ( $C_{2.4}^{-}$ ) and long-chain hydrocarbons ( $C_{5}^{+}$ ).

## **1** Introduction

Porous carbon materials can offer superior physical and chemical properties, such as thermal conductivity, chemical stability, electric conductivity and low density, leading to their extensive use in batteries, supercapacitors, gas storage and as processes.1-4 supports for many important catalytic Conventional carbon materials, such as activated carbon (AC), are synthesized by carbonization and chemical (e.g.  $KOH^{5}$ ) activation of organic precursors, such as coal, wood, fruit shell, and polymers.<sup>6, 7</sup> These carbon materials normally have micropores with high surface area. However, the narrow channels limit the diffusion of molecules to access the active site in the micropores. Recently, hierarchical porous carbon materials have been synthesized using (a) hard templates  $\frac{8-10}{2}$ through impregnation, carbonization, and template removal, or (b) soft templates<sup>11-13</sup> through condensation and carbonization. These methods overcome the limitation of micropores but suffer from complicated procedures and high costs. Therefore, finding an efficient and low cost strategy to synthesize hierarchical porous carbon is of great importance.<sup>14</sup>

ZSM-5 type zeolites offer a strong and tunable acidity, excellent shape selectivity and good hydrothermal stability, leading to their widely use in petrochemical fields.<sup>15, 16</sup> In the catalytic process, such as methanol to propylene (MTP) reaction, the acid sites on the outer surface can lead to the

formation of coke with high degree of graphitization, which could cause the catalyst deactivation.<sup>17-19</sup> With the rapid development of the chemical industry, large amounts of spent zeolite catalysts are produced every year. However, most of them are disposed of in landfills, which could lead to a serious environmental problem and a large waste of valuable materials.<sup>20</sup>

Herein, an efficient and low cost strategy involving one-step desilication of coke-deposited spent zeolite catalyst was successfully developed to prepare hierarchical porous carbon monoliths (HPCMs). Such strategy avoids the use of hard or soft template and carbon source, eliminates high temperature carbonization under inert atmosphere, and simultaneously, decreases the emission of spent zeolite catalyst. The resulting hierarchical carbon has been found to be a superior support of FeK for minimizing the nanoparticle size and enhancing the Fe-K synergism for promoting catalytic CO<sub>2</sub> hydrogenation reaction, especially for increased conversion of carbon dioxide and enhanced selectivity of high value olefins ( $C_{2.4}^{=}$ ) and long-chain hydrocarbons ( $C_5^{+}$ ).

#### 2 Experimental

# 2.1 Synthesis of hierarchical porous carbon monoliths (HPCMs)

In this work, we selected three kinds of conventional highsilica ZSM-5 shaped catalyst, which were denoted as CAT-1, CAT-2 and CAT-3, respectively. The MTP reaction was performed at 500 °C in a fixed-bed reactor under atmospheric pressure. The WHSV for methanol was 3.0  $h^{-1}$  with a MeOH/H<sub>2</sub>O molar ratio of 1: 1. After fully deactivated in the MTP reaction, the three kind of spent catalysts were selected as carbon source. The zeolite was removed using a mixture of hydrofluoric acid (10% in water). After 24 h, the obtained monolithic carbon was washed with water several times and dried overnight at 100 °C. The monolithic carbons obtained from CAT-1, CAT-2 and CAT-3 was denoted as HPCMs-1, HPCM-2 and HPCMs-3, respectively.

#### 2.2 Synthesis of HPCMs supported catalysts

The samples of commercial activated carbon (AC) and HPCMs-1 were used as the support materials. The Fe-based catalyst was prepared by the incipient wetness impregnation method using ethanol aqueous solutions (95 wt%) of Iron(III) acetylacetonate (Fe(acac)<sub>3</sub>) and potassium nitrate (KNO<sub>3</sub>). The catalyst was obtained after drying at 100 °C overnight followed by calcination in N<sub>2</sub> at 500 °C for 3 h to decompose iron and potassium precursors, for which the heating rate was 2 °C min<sup>-1</sup>. The real Fe and K loading on the HPCMs-1 are 11.4 and 5.7 wt %, respectively, as measured by energy dispersive X-ray (Fig. S1).

#### 2.3 Characterization

Published on 18 January 2016. Downloaded by University of York on 21/01/2016 12:03:05.

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Smartlab diffract meter using nickel-filtered CuK $\alpha$  X-ray source at a scanning rate of 0.02° over the range between 5° and 80°. The crystallite phases were identified by comparing the diffraction patterns with the data of the Joint Committee on Powder Standards (JCPDS).

Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were taken on a JEM-2100F instrument (JEOL Company) with an acceleration voltage of 200 kV. The samples for TEM analysis were prepared by dipping the copper grids into the ethanol solutions of the samples and drying at ambient conditions.

Scanning electron microscopy (SEM) images were obtained on a Hitachi S-5500 instrument with an acceleration voltage of 3 kV.

Thermo gravimetric analysis (TGA) was performed on an SDT Q600 (TA Instruments, USA) in the temperature range of 25-800 °C under air or N<sub>2</sub> at a heating rate of 10 °C min<sup>-1</sup>.

Ar isotherms at -186 °C were measured in a Quantachrome autosorb-iQ<sub>2</sub> gas adsorption analyzer. Prior to the measurement, the samples were degassed in vacuum ( $p/p_0 < 10^{-7}$ ) at 300 °C for 10 h. The Brunauer-Emmett-Teller (BET) method was applied to calculate the total surface area, while the micro-meso porous size distribution was determined from Ar adsorption isotherm by quenched solid density functional theory (QSDFT).

The meso- and macro- porosity of the samples were measured by a mercury porosimeter (AUTOPORE IV 9500,

Micromeritics, USA) with two low-pressure stations plus one high-pressure station and a maximum pressure of 33,000 psia.

X-ray photoelectron spectroscopy (XPS) was conducted on an ESCALAB 250 (Thermo VG Corporation) using Mg K $\alpha$ radiation (1253.6 eV, 15 kV, 10 mA, 150 W). The recorded spectra were fitted by a least square procedure to a product of Gaussian–Lorentzian functions. The concentration of each element was calculated from the area of the corresponding peak. Raman spectra were collected using a Nicolet Almega XR Raman system with a 532 nm excitation laser from Thermo Fisher Scientific Inc.

H<sub>2</sub>-TPR measurements were carried out with ChemBET Pulsar TPR/TPD equipment (Quantachrome, USA) to analyse the reducibility of the calcined catalysts. Prior to the reduction, the calcined sample (0.10g) was placed in a quartz tube in the interior of a controlled oven. The sample was flushed with high purity argon at 300 °C for 8 h to remove water and other contaminants then cooled down to room temperature. A gas mixture containing 5 vol% H<sub>2</sub> in Ar was passed through the sample at a total flow rate of 30 ml min<sup>-1</sup> with a heating rate at 10 °C min<sup>-1</sup> up to 900 °C. A cooling trap was placed between the sample and the detector for removal of released water formed during the reduction process.

#### 2.4 Catalytic testing

The catalytic hydrogenation of carbon dioxide was carried out in a pressurized fixed-bed flow reactor where a weighted 1 g catalyst was pretreated by reduction with pure H<sub>2</sub> at 500 °C overnight. After the reduction, the feed gas was changed to the mixture of carbon dioxide and hydrogen under the reaction conditions of n (H<sub>2</sub>)/n (CO<sub>2</sub>) =3 (molar ratio); P=3 MPa; T=400 °C and the space velocity was 3600 mlg<sup>-1</sup>h<sup>-1</sup>.

The products were analyzed on-line by a gas chromatograph (FULI GC 97). Carbon monoxide, carbon dioxide and methane were analyzed on a carbon molecular sieve column with a thermal conductivity detector (TCD) while methane and  $C_2$ - $C_8$  hydrocarbons were analyzed with a flame ionization detector (FID) with a HayeSep Q column. Chromatograms were correlated through methane and product selectivity was determined based on carbon.

#### **3** Results and discussion

#### 3.1 Material synthesis and characterization

The schematic of HPCMs synthesis is shown in Fig. 1a. For ZSM-5 zeolite, during the MTP reaction process, the carbon species are mostly polycyclic aromatics. Due to the limitation of micropores, carbon deposits often exist on the surface of the zeolite, leading to severe diffusion restrictions and fast deactivation of catalyst. Although the activity can be enhanced by the calcination treatment, the catalyst activity and stability are difficult to achieve the level of fresh catalyst. Thus, after several regeneration treatments, the catalyst is no longer able to meet industrial requirements, and this kind of catalyst is called spent catalyst. We used spent catalyst as carbon source, after Published on 18 January 2016. Downloaded by University of York on 21/01/2016 12:03:05.

one-step zeolite removal using hydrofluoric acid, the HPCMs were obtained. Fig. 1b shows the image of fresh catalyst, which is cylinder with height of 2 mm and diameter of 1-10 mm. The spent catalyst and HPCMs maintained the macro-morphology of the fresh catalyst, while the yield of HPCMs depends on the coke content of spent catalyst. For spent CAT-1, the content of coke with weight loss temperature greater than 400 °C is 21 wt% (Fig. 2a). After zeolite movement, the yield of HPCMs-1 is about 20 wt%, similar with the coke content of spent CAT-1. The TG and DTG curves (Fig. 2b) show that the weight loss of HPCMs-1 under N<sub>2</sub> at 800 °C was only 6 wt%, indicate the low content of oxygen or volatile substances in HPCM-1. The TG curves of it under air confirm that the zeolite could removal completely via hydrofluoric acid treatment.



Fig. 1 (a) Schematic of the HPCMs synthesis; image of fresh catalyst (b), spent catalyst (c) and HPCMs (d)



Fig. 2 TG and DTG curves of (a) spent CAT-1 under air, (b) HPCMs-1 under air and  $\mathsf{N}_2$ 

Fig. 3 shows the SEM and TEM images of the fresh catalyst and HPCMs. Due to the coke often deposit on the surface of ZSM-5, after zeolite remove treatment, the morphology of HPCMs will reverse copy the morphology of zeolite. For example, if the morphology of zeolite is aggregate (Fig. 3a), sphere (Fig. 3d) or rectangle (Fig. 3g), the HPCMs with reticular (Fig. 3b), hollow (Fig. 3e) or sheet (Fig. 3h) morphology will be obtained.



Fig. 3 SEM (a, b, d, e, g, h) and TEM (c, f, i) images of CAT-1 (a), CAT-2 (d), CAT-3 (g) and HPCMs-1 (b, c), HPCMs-2 (e, f), HPCMs-3 (h, i).



Fig. 4 Ar adsorption and desorption isotherms at -186  $^{\circ}$ C (a), micro-meso pore size distribution (b), Hg intrusion curve (c) and macro pore size distribution (d) of HPCMs-1. The micro-meso porous size distribution was determined from Ar adsorption isotherm by quenched solid density functional theory (QSDFT), and the macroporous distribution was determined from Hg intrusion curve.

To determine the pore structure of HPCMs, Ar adsorption and desorption isotherms and Hg intrusion curve were measured. For HPCMs-1, the Ar adsorption and desorption isotherms show type III / IV (macropore/mesopore) characteristies (Fig. 4a). The increase in adsorption amount at  $p/p_0$  (0.6-0.9) indicates the existence of mesopores, from which calculated mesoporous (2-50 nm) volume is 0.53 cm<sup>3</sup>g<sup>-1</sup> (Table 1). The further Ar uptake at high  $p/p_0$  (0.9-1.0) demonstrates the existence of macropores. To exactly determine the macroporous structure of HPCMs-1, Hg intrusion curve was Published on 18 January 2016. Downloaded by University of York on 21/01/2016 12:03:05.

measured (Fig. 4	4c), from	which	calculated	macroporous	(50-
350 nm) volume	was 1.39	$cm^3g^{-1}$ .	Fig. 4b and	d 4d show the	

Sample Code	S <sub>micro</sub> <sup>[a]</sup> [m <sup>2</sup> g <sup>-1</sup> ]	S <sub>BET</sub> <sup>[b]</sup> [m <sup>2</sup> g <sup>-1</sup> ]	V <sub>micro</sub> <sup>[a]</sup> [cm <sup>3</sup> g <sup>-1</sup> ]	V <sub>meso</sub> <sup>[a]</sup> [cm <sup>3</sup> g <sup>-1</sup> ]	V <sub>macro</sub> <sup>[a]</sup> [cm <sup>3</sup> g <sup>-1</sup> ]	V <sub>pore</sub> <sup>[c]</sup> [cm <sup>3</sup> g <sup>-1</sup> ]
HPCMs-1	0	218	0	$0.53(0.51^{d})$	$0.94(1.39^{d})$	1.47
HPCMs-2	0	557	0	1.01	1.07	2.08
HPCMs-3	0	253	0	0.59	0.60	1.19
HPCMs-1-650	47	301	0.02	0.45	0.90	1.37
HPCMs-1-750	479	724	0.16	0.60	0.94	1.70
HPCMs-1-850	481	941	0.18	0.72	0.87	1.77

[a] QSDFT method, micropore (d<2 nm), mesopore (2 nm<d<50 nm) and macropore (d>50 nm) [b] BET method, [c] p/p<sub>0</sub>=0.99, [d] measured from Hg intrusion, mesopore (24 nm<d<50 nm) and macropore (50 nm<d<350 nm)

micro-meso pore size distribution determined from Ar adsorption isotherm and the macropore distribution was determined from Hg intrusion curve, respectively. In addition, the pore structure of HPCMs-2 and HPCMs-3 were also determined by Ar adsorption-desorption technique, (Fig. 5) indicate all of the three HPCMs were meso-macro porous materials without micropores.



Fig. 5 Ar adsorption and desorption isotherms at -186  $^\circ C$  (a, c) and micro-meso pore size distribution (b, d) of HPCMs-2 (a, b) and HPCMs-3 (c, d).



Fig. 6 Ar adsorption and desorption isotherms at -186  $^{\circ}$ C (a) and micro-meso pore size distributions (b) of HPCMs-1 after KOH activation at 650, 750 and 850  $^{\circ}$ C for 3 h, respectively, KOH/HPMS-1=2:1 (weight ratio). The micro-meso pore size distribution was determined from Ar adsorption isotherm by quenched solid density functional theory (QSDFT).

The effect of KOH activation was also estimated. Ar adsorption and desorption isotherms at -186 °C and pore size distributions of HPCMs-1 after KOH activation are shown in Fig. 6a and 6b. With the rising temperature from 650 to 850 °C, the adsorption isotherms change from type III/IV to combined type I / III / IV (micropore/macropore/mesopore). Compared with HPCM-1, the BET surface area of HPCMs-1-850 increased from 218 m<sup>2</sup>g<sup>-1</sup> to 941 m<sup>2</sup>g<sup>-1</sup>, mainly of micropores area growth. The micropore volume was also increased from 0 to 0.18 cm<sup>3</sup>g<sup>-1</sup>. That because during the KOH activation, gases such as CO2 and CO were generated, resulting in the formation of micropores,<sup>21</sup> meanwhile the mesopore and macropore were still retained after KOH activation, and finally obtained micromeso-macro porous carbon monoliths as shown in Fig. 6b.

To determine the chemical structure of HPCMs-1, XRD pattern, Raman spectrum and XPS spectra were measured. Before the removal of zeolite, the five characteristic diffraction peaks of MFI topology at 7.8°, 8.8°, 23.0°, 23,9°, and 24.4° clearly indicate the phase of ZSM-5 (Fig. S2, JCPDS: 44-0003). After remove zeolite, Fig. 7a shows the typical XRD patterns of HPCMs-1, the diffraction peaks of MFI topology disappear. The broad XRD peak at 2-Theta value of 24.5° was attributed to the (002) reflection of the graphitic-type lattice and the corresponding interlayer spacing (0.36 nm) is slightly larger than that of natural graphite (0.34 nm), which represents welldeveloped graphitization.<sup>22, 23</sup> The interlayer spacing could also be measured from HRTEM image (Fig. 7a inset, Fig. S3), which in agreement with the XRD result. The weak XRD peak at 2-Theta of 43.5° was attributed to the (101) reflection of carbon structure.

The Raman spectrum of HPCMs-1 is shown in Fig. 7b. The peak positions of the D and G bands are 1340 and 1587 cm<sup>-1</sup>, respectively. The D band is a common feature of disordered carbons, while the G band is related to a graphitic carbon phase with an SP<sup>2</sup> electronic configuration.<sup>24</sup> The radio of these two bands ( $I_D/I_G$ ) is 0.93:1, reflecting the partial graphitization of the carbons in the HPCMs. The XPS spectrum of HPCMs-1 is shown in Fig. 7c. According to the XPS data, atomic percentages of C (96.0 at%) and O (4.0 at%) can be determined. The high-resolution C<sub>18</sub> XPS spectrum showed a dominant

Published on 18 January 2016. Downloaded by University of York on 21/01/2016 12:03:05.

Journal Name

peak at 284.5 eV and two small peaks at 285.9 and 288.4 eV (Fig. 7d). The peak at 284.5 eV corresponds to the SP<sup>2</sup>-hybridized graphitic carbon, while the peaks at 285.9 and 288.4 eV are attributed to C-OH and C=O configurations, respectively.<sup>25</sup>



Fig. 7 XRD pattern (a), Raman spectrum (b), XPS survey (c) and high-resolution C1s XPS spectra (d) of HPCMs-1 (inset a: HRTEM image of HPCMs-1. inset c: chart showing the percentages of carbon and oxygen according to XPS data)

# **3.2 HPMCs as the support of Fe-based catalyst for the hydrogenation of carbon dioxide**

Fig. 8a and 8b-d show TEM images of Fe-K/AC and Fe-K/HPCMs-1, for the commercial activated carbon (AC) as support, the metal oxide particles are of 17 nm mean size, whereas using HPMCs-1 as support, the mean size of metal oxide particles decrease to about 9 nm. The lattice spaces are measured to be 2.5 and 3.0 Å (Fig. 8d), which matches the values of the d-spacing of Fe<sub>3</sub>O<sub>4</sub> (311) and Fe<sub>3</sub>O<sub>4</sub> (220), respectively (JCPDS: 65-3107). Fig. S4 shows carbon (yellow), iron (red) and potassium (green) element mapping images of Fe-K/AC (a, b, c, d) and 15Fe10K/HPCMs-1 (e, f, g, h), respectively. Compared with Fe-K/AC, the iron and potassium in the sample of HPMCs-1 exhibit more uniform distribution, which is conducive to enhancing the promotion and improves the activity of the catalyst.

The decrease of particle size of metal oxide supported on the HPMCs-1 was also demonstrated by XRD patterns in Fig. 8e. For the fresh catalysts, the XRD patterns exhibited the characteristic diffraction peaks of Fe<sub>3</sub>O<sub>4</sub> (JCPDS: 65-3107) at  $30.1^{\circ}$ ,  $35.5^{\circ}$ ,  $43.2^{\circ}$ ,  $53.5^{\circ}$ ,  $56.9^{\circ}$  and  $62.6^{\circ}$ . The Fe/AC shows a sharp (311) peak, indicating the large particle size of Fe<sub>3</sub>O<sub>4</sub>. When the potassium was introduced in the catalyst, the peaks of Fe<sub>3</sub>O<sub>4</sub> became broader, indicate the introduction of potassium is interaction to the enhancement of iron disperse, which is attributed to the interaction of iron and potassium. The wide diffraction peaks of Fe-K/HPCMs-1 suggest that Fe<sub>3</sub>O<sub>4</sub> particle size is much smaller than on sample Fe-K/AC, which is consistent with the TEM and element mapping results.

The reduction behavior of catalysts was studied by H<sub>2</sub>-TPR. As shown in Fig. 8f, for the Fe-K supported on the AC, the reduction temperature of metal oxide is lower than the monometal loading samples. That is because the Fe-K catalyst has a higher metal dispersion, which has been proved by TEM images and XRD patterns. Thus, the catalyst Fe-K/HPCMs has the lowest reduction temperature, this result suggests that the catalyst Fe-K/HPCMs had the highest degree of reduction after reduction with pure H<sub>2</sub> at 500 °C overnight.



Fig. 8 TEM (a, b, c) and HRTEM (d) images of Fe-K/AC (a) and Fe-K/HPCMs-1 (b, c, d), respectively; (e) XRD patterns of Fe/AC (e-1), Fe-K/AC (e-2) and Fe-K/HPCMs-1 (e-3); (f)  $H_2$  TPR profiles of Fe/AC (f-1), K/AC (f-2), Fe-K/AC (f-3) and Fe-K/HPCMs-1 (f-4). The insets in (a) and (b) show the particle size distributions of metal oxide based on measurements of approximately 100 nanoparticles by TEM.

Table 2 shows the catalytic performances of the carbon supported Fe-based catalysts for CO<sub>2</sub> hydrogenation. For monometal Fe catalyst (Fe/AC), the conversion of CO<sub>2</sub> was very low (5.6 %) because of the weak adsorption of iron species to carbon oxide. For monometal K catalyst (K/AC), the conversion of CO<sub>2</sub> was increase to 15.6, however, due to its weak activation ability to hydrogen, the selectivity of CO is very high (93.6%), mainly occurred reversed-water-gas-shift reaction. When the potassium was introduced in the iron-based catalyst (Fe-K/AC), the synergistic effect of iron and potassium simultaneously enhances the activation of hydrogen and adsorption of carbon dioxide,<sup>26, 27</sup> increasing the conversion of carbon dioxide to 27.0%. However, because of the uneven distribution of iron and potassium, the selectivity of hydrocarbon has not been improved. As expected, the use of

HPCMs-1 as the support significantly increased the conversion of CO<sub>2</sub> to 33.4%, decreased the selectivity of CO to 38.9% as well as increased the selectivity of high value  $C_{2.4}^{=}$  and  $C_5^{+}$  hydrocarbons to 18.0% and 18.1%, respectively. Characterization and catalytic performance results show that the HPCMs is a superior support of FeK for minimizing the nanoparticle size and enhancing the Fe-K interaction for promoting catalytic performance of CO<sub>2</sub> hydrogenation.

Table 2 CO<sub>2</sub> conversion and selectivity of Fe/AC, K/AC, Fe-K/AC and Fe-K/ HPCMs-1, respectively. Reaction conditions: n (H<sub>2</sub>)/n (CO<sub>2</sub>) =3 (molar ratio); P=3 MPa; T=400  $^{\circ}$ C and the space velocity was 3600 mlg<sup>-1</sup>h<sup>-1</sup>, time on stream 5h.

	$CO_2$	Selectivity (%)				
Catalyst	Conv. (%)	СО	$\mathrm{CH}_4$	C <sub>2-4</sub> =	C <sub>2-4</sub> <sup>0</sup>	$C_5^+$
Fe/AC	5.6	66.3	24.6	0.4	8.7	0
K/AC	15.6	93.6	4.6	0.1	1.7	0
Fe-K/AC	27.0	92.5	4.2	0.6	2.4	0.3
Fe-K/ HPCMs-1	33.4	38.9	13.5	18.0	11.5	18.1

## **4** Conclusions

Published on 18 January 2016. Downloaded by University of York on 21/01/2016 12:03:05.

In this work, hierarchical porous carbon monoliths have been successfully synthesized by an efficient and low cost strategy from coke-deposited spent zeolite catalyst. The resulting carbon exhibits a controlled morphology, a high degree of graphitization and a meso-macro porous structure. Such hierarchical porous carbon was found to be a superior support of FeK for minimizing the nanoparticle size and enhancing the Fe-K interaction for promoting catalytic performance of  $CO_2$  hydrogenation.

The present strategy in this work can be used for preparing a wide range of synthetic hierarchical porous carbon materials, because the spent catalyst with specific channels and morphologies can be selected to obtain the carbon material we need. For example, some spent zeolite catalysts with a large micro-pore size (e.g. Y or Beta) may be used to synthesize microporous carbon material with high surface area.

## Acknowledgements

The authors thank the financial support from the National Natural Science Foundation of China (21306018, 21503029, 21503027) and the Fundamental Research Funds for the Central Universities (DUT15ZD236, DUT15RC(3)027).

### Notes and references

a State Key Laboratory of Fine Chemicals, PSU-DUT Joint Center for Energy Research, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, P. R. China. Fax: +86-0411-84986134; Tel: +86-0411-84986133, +86-0411-84986134; E-mail: guoxw@dlut.edu.cn b EMS Energy Institute, PSU-DUT Joint Center for Energy Research, Department of Energy & Mineral Engineering, and Department of Chemical Engineering Pennsylvania State University, University Park, Pennsylvania 16802, United States. Fax: 814-865-3573; Tel: 814-863-4466; E-mail: csong@psu.edu.

 $\dagger$ Electronic Supplementary Information (ESI) available: [HRTEM image of HPCMs-1, Raman spectra of HPCMs-1 after thermal treatment at different temperatures under N<sub>2</sub>].

- C. Liang, Z. Li and S. Dai, Angew. Chem. Int. Ed, 2008, 47, 3696-3717.
- S. Wang, C. Han, J. Wang, J. Deng, M. Zhu, J. Yao, H. Li and Y. Wang, Chem. Mater., 2014, 26, 6872-6877.
- B. Zhu, K. Li, J. Liu, H. Liu, C. Sun, C. E. Snape and Z. Guo, J. Mater. Chem. A, 2014, 2, 5481-5489.
- M. Park, J. Ryu, Y. Kim and J. Cho, Energy Environ. Sci., 2014, 7, 3727-3735.
- M. Li, C. Liu, H. Cao, H. Zhao, Y. Zhang and Z. Fan, J. Mater. Chem. A, 2014, 2, 14844.
- L. Zhou, H. Cao, S. Zhu, L. Hou and C. Yuan, Green Chem., 2015, 17, 2373-2382.
- L. Zhu, Q. Gao, Y. Tan, W. Tian, J. Xu, K. Yang and C. Yang, Microporous and Mesoporous Mater., 2015, 210, 1-9.
- W. Nickel, M. Oschatz, M. v. d. Lehr, M. Leistner, G.-P. Hao, P. Adelhelm, P. Müller, B. M. Smarsly and S. Kaskel, J. Mater. Chem. A, 2014, 2, 12703.
- P. Strubel, S. Thieme, T. Biemelt, A. Helmer, M. Oschatz, J. Brückner, H. Althues and S. Kaskel, Adv. Funct. Mater., 2015, 25, 287-297.
- L. Song, L. Li, X. Gao, J. Zhao, T. Lu and Z. Liu, J. Mater. Chem. A, 2015, 3, 6862-6872.
- 11. S. D. C. Liang, J. Am. Chem. Soc., 2006, **128**, 5316-5317.
- C. Liang, K. Hong, G. A. Guiochon, J. W. Mays and S. Dai, Angew. Chem. Int. Ed, 2004, 43, 5785-5789.
- S. Tanaka, N. Nishiyama, Y. Egashira and K. Ueyama, Chem. Commun., 2005, 2125-2127.
- A. D. Roberts, S. Wang, X. Li and H. Zhang, J. Mater. Chem. A, 2014, 2, 17787-17796.
- Z. Qin, L. Lakiss, L. Tosheva, J.-P. Gilson, A. Vicente, C. Fernandez and V. Valtchev, Adv. Funct. Mater., 2014, 24, 257-264.
- S. Mitchell, N. L. Michels, K. Kunze and J. Perez-Ramirez, Nature Chem., 2012, 4, 825-831.
- S. Müller, Y. Liu, M. Vishnuvarthan, X. Sun, A. C. van Veen, G. L. Haller, M. Sanchez-Sanchez and J. A. Lercher, J. Catal., 2015, 325, 48-59.
- F. Schmidt, C. Hoffmann, F. Giordanino, S. Bordiga, P. Simon, W. Carrillo-Cabrera and S. Kaskel, J. Catal., 2013, 307, 238-245.
- L. R. Aramburo, S. Teketel, S. Svelle, S. R. Bare, B. Arstad, H. W. Zandbergen, U. Olsbye, F. M. F. de Groot and B. M. Weckhuysen, J. Catal., 2013, 307, 185-193.
- Q. Zhang, S. Hu, L. Zhang, Z. Wu, Y. Gong and T. Dou, Green Chem., 2014, 16, 77-81.
- T. Mitome, Y. Iwai, Y. Uchida, Y. Egashira, M. Matsuura, K. Maekawa and N. Nishiyama, J. Mater. Chem. A, 2014, 2, 10104.
- H. Peng, G. Ma, K. Sun, J. Mu and Z. Lei, J. Mater. Chem. A, 2014, 2, 17297-17301.

## Page 7 of 8

Published on 18 January 2016. Downloaded by University of York on 21/01/2016 12:03:05.

Journal Name

- 23. S. Tao, Y. Wang, D. Shi, Y. An, J. Qiu, Y. Zhao, Y. Cao and X. Zhang, J. Mater. Chem. A, 2014, **2**, 12785.
- 24. X. Meng, H. Cui, J. Dong, J. Zheng, Y. Zhu, Z. Wang, J. Zhang, S. Jia, J. Zhao and Z. Zhu, J. Mater. Chem. A, 2013, 1, 9469.
- P. Chen, L.-K. Wang, G. Wang, M.-R. Gao, J. Ge, W.-J. Yuan, Y.-H. Shen, A.-J. Xie and S.-H. Yu, Energy Environ. Sci., 2014, 7, 4095-4103.
- R. Satthawong, N. Koizumi, C. Song and P. Prasassarakich, J. CO2 Utilization, 2013, 3-4, 102-106.
- C. Dai, A. Zhang, L. Li, K. Hou, F. Ding, J. Li, D. Mu, C. Song, M. Liu and X. Guo, Chem. Mater., 2013, 25, 4197-4205.

**RSC Advances Accepted Manuscript** 



A versatile strategy involving one-step desilication of coke-deposited spent zeolite catalyst was successfully developed to prepare hierarchical porous carbon monoliths (HPCMs).