# Selective Oxidation of Glycerol to Glyceric Acid in Base-Free Aqueous Solution at Room Temperature Catalyzed by Platinum Supported on Carbon Activated with Potassium Hydroxide

Hua Tan,\*<sup>[a]</sup> Omar E. Tall,<sup>[a]</sup> Zhaohui Liu,<sup>[b]</sup> Nini Wei,<sup>[c]</sup> Tahir Yapici,<sup>[a]</sup> Tong Zhan,<sup>[d]</sup> Mohamed Nejib Hedhill,<sup>[c]</sup> and Yu Han<sup>[b]</sup>

Pt supported on KOH-activated mesoporous carbon (K-AMC) was used to catalyze glycerol oxidation under base-free conditions at room temperature. To study the relationship between the carbon surface chemistry and the catalytic performance of the K-AMC-based Pt catalysts, different levels of surface oxygen functional groups (SOFGs) on the AMC supports were induced by thermal treatment at different temperatures under inert or  $H_2$  gas. A strong effect of the surface chemistry was

Introduction

The transformation of biomass into transportation fuels and valuable chemicals has attracted considerable attention in recent years because of the requirement for the sustainable development for our society.<sup>[1–7]</sup> Glycerol (GLY) is a renewable feedstock for the manufacture of various value-added chemicals because it is the major byproduct of the production of biodiesel by the transesterification of biomass with alcohols.<sup>[8]</sup> So far, many processes have been developed to transform GLY into different intermediates for chemical production.<sup>[9–12]</sup> Among these processes, the selective oxidation of glycerol has been investigated widely to produce various valuable oxygenated derivatives, such as glyceric acid (GA), dihydroxyacetone (DHA), lactic acid (LA), and tartronic acid (TA).<sup>[13–16]</sup> In particular, GA is well known for its benefits in medicine and skincare

[a]	Dr. H. Tan, Dr. O. E. Tall, Dr. T. Yapici
	King Abdullah University of Science and Technology Thuwal, 23955-6900 (Saudi Arabia) E-mail: hua.tan@kaust.edu.sa
[b]	Z. Liu, Prof. Y. Han Advanced Membranes and Porous Materials Center King Abdullah University of Science and Technology Thuwal, 23955-6900 (Saudi Arabia)
[c]	N. Wei, Dr. M. N. Hedhill Nano imaging lab King Abdullah University of Science and Technology Thuwal, 23955-6900 (Saudi Arabia)
[d]	T. Zhan Water Desalination and Reuse Research Center King Abdullah University of Science and Technology Thuwal, 23955-6900 (Saudi Arabia)
	Supporting Information for this article can be found under http:// dx.doi.org/10.1002/cctc.201600052.

observed on AMC-supported Pt catalysts for glycerol oxidation. The presence of carboxylic acid groups impedes the adsorption of glycerol, which leads to the reduction of catalytic activity, whereas the presence of high-desorption-temperature SOFGs, such as phenol, ether, and carbonyl/quinone groups, provide hydrophilicity to the carbon surface that improves the adsorption of glycerol molecules on Pt metal surface, which is beneficial for the catalytic activity.

 $treatment^{[17]}$  and is an important intermediate for further oxidation products, such as TA and mesoxalic acid.  $^{[18]}$ 

Carbon materials, such as activated carbon (AC), carbon blacks, and carbon nanotubes, are used as supports for noblemetal catalysts for GLY oxidation and other catalytic reactions because of their unique properties, such as high surface area, stability, and relative inertness in highly acidic and basic media.<sup>[19-22]</sup> However, the surface chemistry of carbon supports has a great impact on the catalytic activity of the supported metal catalysts.<sup>[23-25]</sup> For example, Xu et al. reported a strong effect of the surface chemistry of carbon on Au/AC catalysts for acetylene hydrochlorination. The catalytic performance, which includes activity and stability, of the Au/AC catalyst improved with the increase of the amount of surface oxygencontaining groups, especially phenol, ether, and carbonyl groups.<sup>[26]</sup> Wan et al. clarified that carbon nanotubes that contain more carbonyl/quinone and less carboxyl groups favor 2,5-furandicarboxylic acid formation by enhancing the adsorption of the reactant and reaction intermediates on AuPd supported on carbon nanotubes catalysts for the oxidation of 5hydroxymethylfurfural under base-free conditions.[27] More specifically, a strong effect of the activated carbon surface chemistry has been reported and discussed by Rodrigues et al. on the activity of Au/AC catalysts for glycerol oxidation under basic conditions.<sup>[28]</sup>

Currently, for the reduction of the extra acidification step and environmental concerns, GLY oxidation has been advanced to be conducted under base-free conditions to produce pure carboxylic acid instead of its salt form.<sup>[29–32]</sup> However, under base-free conditions, supported Au catalysts were totally inactive for GY oxidation, whereas supported Pt catalysts showed better catalytic activity.<sup>[21]</sup> Therefore, we studied the impact of the surface chemistry of carbon on carbon-supported Pt catalysts for GLY oxidation under base-free conditions.

A wet oxidation method was used to modify the carbon materials because it not only introduces surface oxygen functional groups (SOFGs) on the carbon surface but also alters the surface hydrophobic/hydrophilic balance.[33] The wet oxidation of carbon materials is performed typically in oxidizing solutions, such as HNO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, or KOH. However, although HNO<sub>3</sub> can introduce a large amount of SOFGs on the carbon surface, it can also reduce the specific surface area and porosity.<sup>[34]</sup> Furthermore, H<sub>2</sub>O<sub>2</sub> can be used to generate SOFGs but it is very toxic and can damage the mesostructures of the carbon materials severely.<sup>[35]</sup> KOH is a better activation agent because it can introduce a large amount of SOFGs on the carbon surface without affecting the mesostructures.<sup>[36]</sup> Therefore, in this work KOH-activated mesoporous carbon (K-AMC) was chosen as a support for Pt catalysts. After wet oxidation with KOH, the surface chemistry of K-AMC was varied by applying a thermal treatment at different temperatures, which did not affect their textural properties significantly. The wetness impregnation method was used to prepare Pt catalysts supported on the carbons activated differently. The relationship between the surface chemistry of the carbon supports and the catalytic performance of Pt catalysts was investigated for GLY oxidation under base-free conditions, and the role of the SOFGs is also discussed.

# **Results and Discussion**

### **Catalyst characterization**

The mesoporous carbon was prepared by a colloidal silica nanocasting route. The nitrogen sorption isotherm of the pristine carbon shows type IV curves with an H2-type hysteresis loop characteristic of typical mesoporous materials. The Barrett–Joyner–Halenda (BJH) pore size peak was centered at around 14.3 nm, which is slightly larger than the average diameter of the primary nanoparticles of Ludox SM-30 because of the presence of coalesced colloidal aggregates. In addition, the low-pressure N<sub>2</sub> uptake indicates the presence of some micropores on the pore walls, which could be the result of the release of volatile fragments during the pyrolysis (Figure S1). The mesoporous structure is confirmed by TEM (Figure S2), which reveals that the pristine carbon contains spherical mesopores that are distributed randomly and interconnected. N<sub>2</sub> sorption

was also measured on K-AMC. The detailed pore parameters of the pristine carbon and K-AMC are listed in Table 1 for comparison. These results show that the KOH activation increases the BET surface area and the micropore and total pore volume and enlarges the size of mesopores slightly to 18.7 nm. These results indicate that the mesoporous structure of pristine carbon is relatively preserved. However, the pore microstructures and surface chemistry are influenced significantly by the activation parameters and carbon sources.

It is well known that thermal treatment of activated carbon materials under inert atmosphere is an important way to study the effect of surface chemistry on carbon-supported metal catalysts because different levels of SOFGs on the carbon surface could be created without altering their textual structures great-ly.<sup>[26,28]</sup> Thermal treatment at 600 and 900 °C did not cause drastic changes to the textual properties of K-AMC (Table 1). The increase in the micropore volume and surface area after thermal treatment is probably because of the removal of some low-temperature-desorbed SOFGs that block the micropores.<sup>[37]</sup>

Elemental analysis was conducted for all the carbon samples. The elemental compositions for all the carbon samples are shown in Table S1. The oxygen content increased significantly from 4.48% for pristine carbon to 16.11% for K-AMC, which confirmed the introduction of a large amount of SOFGs on the carbon surface by KOH activation. After thermal treatment at 600 and 900 °C the oxygen content decreased to 10.21 and 3.11%, respectively. To determine the quantity and nature of SOFGs, temperature-programmed desorption (TPD) MS was performed to characterize the surface chemistry of all the carbon samples in this work. According to the peak-fitting method proposed previously,<sup>[26, 38, 39]</sup> the CO<sub>2</sub> curves could be deconvoluted into three peaks, which are carboxylic acid, carboxylic anhydride, and lactone, whereas the CO TPD-MS profiles were deconvoluted into four peaks, which correspond to carboxylic anhydride, phenol, ether, and carbonyl/quinone from low to high desorption temperature. The obtained CO and CO<sub>2</sub> TPD-MS profiles of the different carbon samples are shown in Figures 1 and 2, respectively. In accordance with previous studies, the released CO<sub>2</sub> resulted from the decomposition of carboxylic acid at low temperature (150–450  $^\circ$ C) and lactone at high temperature (600-800 °C); the decomposition of carboxylic anhydride gave both CO<sub>2</sub> and CO in the temperature range of 400–650  $^\circ\text{C}.$  CO was also generated from the decomposition of phenol (600–800  $^\circ\text{C}),$  ether (600–800  $^\circ\text{C}),$  and carbonyl/quinone (750–1000 °C).<sup>[40]</sup> The amount and desorption temperatures of the different SOFGs are summarized in

Table 1. Textual properties and chemical nature of pristine carbon, K-AMC, K-AMC-600, and K-AMC-900.										
Carbon samples	$S_{\text{BET}}$ [m <sup>2</sup> g <sup>-1</sup> ]	$S_{\rm micro}$ [m <sup>2</sup> g <sup>-1</sup> ]	$S_{\text{external}}$ [m <sup>2</sup> g <sup>-1</sup> ]	$V_{total}$ [cm <sup>3</sup> g <sup>-1</sup> ]	$V_{ m micro}$ [cm <sup>3</sup> g <sup>-1</sup> ]	D <sub>влн</sub> [nm]	C <sub>total</sub>	XPS result O <sub>total</sub>	s O <sub>total</sub> /C <sub>total</sub>	
pristine carbon	631.9	321.0	310.9	1.46	0.13	14.3	94.58	5.42	0.057	
K-AMC	1190.5	830.7	359.8	1.46	0.35	18.7	82.99	17.01	0.205	
K-AMC-600	1366.8	1006.7	360.1	1.47	0.42	19.0	86.89	13.11	0.151	
K-AMC-900	1265.6	966.8	298.8	1.42	0.39	21.4	96.39	3.61	0.037	
$S_{err}$ BET surface area: $S_{min}$ : t-plot micropore area: $S_{min}$ : t-plot external surface area: $V_{min}$ : total pore volume: $V_{min}$ : micropore volume: $D_{em}$ : BJH pore										

 $S_{\text{BET}}$ : BET surface area;  $S_{\text{micro}}$ : *t*-plot micropore area;  $S_{\text{external}}$ : *t*-plot external surface area;  $V_{\text{total}}$ : total pore volume;  $V_{\text{micro}}$ : micropore volume;  $D_{\text{BJH}}$ : BJH pore size from the adsorption branch.





Figure 1. Results of the deconvolution of  $CO_2$  TPD-MS spectra of pristine carbon, K-AMC, K-AMC-600, and K-AMC-900 using a multiple Gaussian function.

Tables 2 and 3. The pristine carbon shows a low amount of SOFGs on its surface. After KOH activation, all types of SOFGs increased on the K-AMC sample drastically, especially the SOFGs that release CO. After thermal treatment at 600 °C under N<sub>2</sub>, most of the low-desorption-temperature SOFGs on K-AMC-600, such as carboxylic acid, carboxylic anhydride, and some of the high-desorption-temperature SOFGs, such as lactone and phenol groups, were diminished strongly. However, the phenol, ether, and carbonyl/quinone groups were still present. Surprisingly, the quantity of carbonyl/quinone groups in-



**CHEMCATCHEM** 

Full Papers

**Figure 2.** Results of the deconvolution of CO TPD-MS spectra of pristine carbon, K-AMC, K-AMC-600, and K-AMC-900 using a multiple Gaussian function.

creased slightly, probably because the released CO<sub>2</sub> during thermal treatment was readsorbed on the carbon surface and transformed into highly stable SOFGs.<sup>[28,41]</sup> After thermal treatment at 900 °C under N<sub>2</sub>, almost all the SOFGs decreased drastically.

The surface atomic compositions obtained by XPS analysis of pristine carbon, K-AMC, K-AMC-600, and K-AMC-900 are also presented in Table 1. The surface of all the carbon samples contains mainly carbon and oxygen atoms, and no potassium was detected. This indicates that the washing procedure was

<b>Table 2.</b> Amount and decomposition temperature of different SOFGs and the total amount of SOFGs obtained by the deconvolution of the CO <sub>2</sub> TPD-MS spectra of different carbon supports.										
Samples	Samples Quantity [μmol/g] of oxygen-containing groups and their desorption temperature (7) [°C]									
	Carboxylic ar	nhydride (peak a)	Phenol (p	eak b)	Ether (pe	ak c)	Quinone/ca	rbonyl (peak d)	Total quantity	
	Quantity	Т	Quantity	Т	Quantity	Т	Quantity	Т		
pristine carbon	15	531	37	632	120	778	87	881	258	
K-AMC	159	560	247	673	398	784	433	887	1237	
K-AMC-600	97	540	184	647	348	782	463	873	1092	
K-AMC-900	33	548	44	639	71	776	102	877	250	
HNO₃-AMC	147	517	398	621	217	756	247	867	1009	
HNO <sub>3</sub> -AMC-600	70	525	217	643	234	762	284	867	805	
K-AMC-400-H <sub>2</sub>	73	554	168	644	326	792	437	864	1004	
K-AMC-700-H <sub>2</sub>	24	567	41	658	61	779	88	871	214	

Table 3. Amount and decomposition temperature of different SOFGs and total amount of SOFGs obtained by the deconvolution of the CO TPD-MS spectra of different carbon supports.

Samples		Quan	itity [µmol/g] of oxygei	n-containing groups an	d desorption temper	ature (T) [°C]	
	Carboxyl	(peak a)	Carboxylic ar	nhydride (peak b)	Lactone (	peak c)	Total quantity
	Quantity	Т	Quantity	Т	Quantity	Т	
pristine carbon	113	318	116	428	45	618	274
K-AMC	443	312	267	425	179	592	889
K-AMC-600	76	334	117	427	94	614	287
K-AMC-900	43	337	66	434	39	646	148
HNO3-AMC	454	275	382	402	145	602	981
HNO <sub>3</sub> -AMC-600	82	279	106	396	70	604	258
K-AMC-400-H <sub>2</sub>	57	346	76	422	80	615	213
K-AMC-700-H <sub>2</sub>	20	327	14	445	17	628	51

ChemCatChem 2016, 8, 1699-1707



efficient (Figure S3). The ratio of total oxygen to total carbon, which represents the degree of surface oxidation (Table 1), shows that the oxygen content increases dramatically from 5.42 to 17.01% for pristine carbon after KOH activation and then decreases to 13.11 and 3.61% for K-AMC-600 and K-AMC-900, respectively. These results are consistent with those of elemental analysis.

High-resolution O1s X-ray photoelectron spectroscopy (XPS) spectra of all the carbon samples are shown in Figure 3. The spectra can be deconvoluted into four peaks with binding energies (BEs) at 530.7, 532.1, 533.3, and 535.3 eV, which correspond to oxygen in carbonyl/quinone groups (C=O), oxygen in



**Figure 3.** XPS spectra of the O1s core-level in pristine carbon, K-AMC, K-AMC-600, and K-AMC-900 samples: 1) oxygen in C=O groups; 2) oxygen atoms in hydroxyl or ether groups; 3) oxygen in anhydride, lactone, or carboxylic acid groups; 4) chemisorbed  $O_2$  or water.

hydroxyl or ethers, oxygen in anhydride, lactone, or carboxylic acids, and chemisorbed oxygen or water.<sup>[42]</sup> The relative distribution of the SOFGs from the O1s spectra were calculated and are listed in Table 4. KOH activation increases the oxygen atomic concentration of all types of SOFGs on the carbon surface. The thermal treatment at 600 °C mainly removes the low-desorption-temperature SOFGs, especially carboxylic acid, whereas the oxygen atomic concentration of the high-desorption-temperature carbonyl/quinone groups increased, consistent with the corresponding TPD-MS spectra. If the K-AMC sample was treated thermally at 900 °C, the oxygen atomic concentration of all types of SOFGs decreased to a level lower than that of the pristine carbon sample.

<b>Table 4.</b> XPS results: surface composition for pristine carbon, K-AMC,K-AMC-600, and K-AMC-900.									
Samples Surface oxygen atomic concentration [%]									
	530.7 eV	532.1 eV	533.3 eV	535.3 eV					
	(peak 1)	(peak 2)	(peak 3)	(peak 4)					
pristine carbon	1.99	2.73	0.70	0					
K-AMC	5.97	7.18	3.04	0.82					
K-AMC-600	6.65	5.45	1.01	0					
K-AMC-900	2.13	1.41	0.07	0					

The carbon-supported Pt catalysts were prepared by the wetness impregnation reduction method. Currently, it is well accepted that the presence of SOFGs decreases the hydrophobicity of the carbon surface, which makes it more accessible to the Pt precursor, thus the presence of SOFGs is beneficial to obtain highly dispersed Pt particles on the carbon supports.<sup>[43, 44]</sup> The TEM images illustrated in Figure 4 show that



Figure 4. TEM images of a) Pt/pristine carbon, b) Pt/K-AMC, c) Pt/K-AMC-600, and d) Pt/K-AMC-900.

the average size of Pt nanoparticles on pristine carbon is  $\approx 3\text{--}$ 4 nm, and some nanoparticle clusters are noted on the carbon surface. If the pristine carbon was activated by KOH, highly dispersed Pt nanoparticles with a size of around 2 nm were created on the K-AMC support. This shows how well SOFGs facilitate the Pt precursor adsorption, which leads to the higher dispersion of Pt nanoparticles on the carbon surface. The highresolution XPS spectrum for the Pt4f core level (Figure S4) shows that the BE of the  $Pt4f_{7/2}$  component on Pt/K-AMC is at 71.1 eV, which corresponds to pure metallic Pt.<sup>[45]</sup> Interestingly, highly dispersed Pt nanoparticles with a size of around 2 nm were also observed on K-AMC-600 despite the loss of some types of SOFGs (mainly carboxylic acid). If most of the SOFGs were removed from the carbon surface after thermal treatment at 900 °C, the Pt nanoparticles became polydisperse, and the average size increased to around 5-6 nm. This phenomenon indicates that the presence of some high-desorption-temperature SOFGs, such as phenol, ether, and carbonyl/quinone groups, helps to form highly dispersed Pt nanoparticles on the K-AMC-600 support.

XRD patterns of Pt/pristine carbon, Pt/K-AMC, Pt/K-AMC-600, and Pt/K-AMC-900 are shown in Figure 5. Two broad peaks centered at  $2\theta = 25$  and  $44^{\circ}$  were observed in the XRD pattern of pristine carbon. These two peaks could be attributed to the (002) plane of the graphitic structure and the (100) plane of disordered amorphous carbon, respectively. The XRD pattern

ChemCatChem 2016, 8, 1699-1707

www.chemcatchem.org



Figure 5. XRD patterns of Pt/pristine carbon, Pt/K-AMC, Pt/K-AMC-600, and Pt/K-AMC-900.

of Pt/pristine carbon also exhibits reflections of the (111), (200), and (220) planes at  $2\theta = 39.6$ , 46.5, and 67.7°, respectively. These peaks are characteristic of the face-centered cubic structure of Pt nanoparticles. However, these three peaks do not appear in the XRD patterns of Pt/K-AMC and Pt/K-AMC-600 because the Pt nanoparticles are too small and highly dispersed on the supports. The particle size of Pt/pristine carbon and Pt/K-AMC-900 catalysts calculated by the Scherrer formula are 4.1 and 5.8 nm, respectively, which is consistent with the TEM results.

### Catalytic activity measurements

The activities of GLY oxidation over carbon-supported Pt catalysts at room temperature under base-free conditions are summarized in Table 5. The Pt metal loadings for all the catalysts, which are close to the theoretical value (2 wt%), are listed in Table S1. The Pt/pristine carbon catalyst showed catalytic activity (9.7%) to oxidize GLY to GA at room temperature under base-free conditions. After KOH activation, the GLY conversion increased significantly to 33.4%, and the selectivity to GA increased from 49.8 to 68.5%. This increase could be because of the introduction of a large amount of SOFGs on the K-AMC support, first, because the SOFGs bring more hydrophilicity to the activated carbon surface, which enables GLA molecules to adsorb better on the surface of K-AMC; second, because the presence of SOFGs on the carbon surface favors a homogeneous Pt precursor distribution, which leads to the high dispersion of small Pt nanoparticles on the K-AMC support. As reported previously, only if the particle size of Pt is smaller than 6 nm, the selective oxidation of GLY could be performed successfully under base-free conditions. The turnover frequency of GLY increases to a maximum at a mean Pt particle size of 2.5 nm followed by a decline with a further increase in size.<sup>[46]</sup> After the thermal treatment of K-AMC at 600 °C, although the sizes of the Pt nanoparticles are similar to that of Pt/K-AMC, the GLY conversion and GA selectivity on Pt/K-AMC-600 increase to 67.6% and 78.3%, respectively. From the TPD-MS results of the K-AMC and K-AMC-600 supports, a considerable loss is noticed in the low-desorption-temperature SOFGs, mainly in the carboxylic acid groups, whereas the high-desorption-temperature SOFGs such as phenol, ether, and carbonyl/ quinone groups are maintained relatively well on the carbon surface. According to Yuan et al.,<sup>[47]</sup> the carboxylic acid groups could impede the adsorption of acidic GLY on the carbon surface, thus the removal of carboxylic acid groups leads to the enhancement of the GLY oxidation activity of Pt/K-AMC-600.

After the K-AMC support was treated thermally at 900 °C, all types of SOFGs were almost lost. According to Menendez et al., carbon supports annealed at high temperature have basic properties.<sup>[48]</sup> The basic character is mainly caused by the Lewis base sites located in the  $\pi$ -electron-rich regions within the basal planes of the graphitic microcrystals away from the edges.<sup>[48]</sup> It is suggested that the carbon surface basicity is associated essentially with the absence of SOFGs, which are predominantly acidic in nature.<sup>[49,50]</sup> Other studies on basic materials, such as hydrotalcite, MgO, and N-doped carbon nanotubes, as supports for Pt catalysts reported the effective catalysis of GLY oxidation under base-free conditions.<sup>[29,30,32,47]</sup> Thus it is accepted that the increase in surface basicity could lead to an enhanced catalytic activity.

The GLY conversion on Pt/K-AMC-900 (48.9%) is much higher than that on Pt/pristine carbon (9.7%). The Pt size effect and the loss of high-desorption-temperature SOFGs cannot explain the discrepancy in the catalytic activities on both catalysts because the Pt particle size in Pt/K-AMC-900 is

Table 5. Catalytic performance of different carbon-supported Pt catalysts in GLY oxidation under base-free conditions. <sup>[a]</sup>										
Conversion [%]			CMB [%]							
	GLYD	GA	TA	DHA	HPA	GLA	OA			
9.7	19.3	49.8	-	14.3	7.9	4.9	-	96.2		
33.4	-	68.5	9.3	-	-	6.2	5.4	89.4		
67.6	-	78.3	6.4	-	-	2.1	2.3	89.1		
48.9	-	73.2	5.8	-	-	3.7	4.6	87.3		
64.8	-	75.5	6.6	-	-	4.3	2.8	89.2		
43.6	-	70.6	6.8	-	-	6.3	4.8	88.5		
24.6	-	65.7	8.5	-	-	7.8	6.6	88.6		
46.8	-	74.8	5.7	-	-	4.9	3.8	89.2		
r	9.7 33.4 67.6 48.9 64.8 43.6 24.6 46.8	GLYD           9.7         19.3           33.4         -           67.6         -           48.9         -           64.8         -           43.6         -           24.6         -           46.8         -	Conversion [%]         GLYD         GA           9.7         19.3         49.8           33.4         -         68.5           67.6         -         78.3           48.9         -         73.2           64.8         -         75.5           43.6         -         70.6           24.6         -         65.7           46.8         -         74.8	mance of different carbon-supported Pt catalysts in GLY oxidation           GLYD         GA         TA           9.7         19.3         49.8         -           33.4         -         68.5         9.3           67.6         -         78.3         6.4           48.9         -         73.2         5.8           64.8         -         75.5         6.6           43.6         -         70.6         6.8           24.6         -         65.7         8.5           46.8         -         74.8         5.7	mance of different carbon-supported Pt catalysts in GLY oxidation under base           Selectivity [%]           GLYD         GA         TA         DHA           9.7         19.3         49.8         -         14.3           33.4         -         68.5         9.3         -           67.6         -         78.3         6.4         -           48.9         -         73.2         5.8         -           64.8         -         70.6         6.8         -           43.6         -         70.6         6.8         -           24.6         -         65.7         8.5         -           46.8         -         74.8         5.7         -	Selectivity [%]           Selectivity [%]           GLYD         GA         TA         DHA         HPA           9.7         19.3         49.8         -         14.3         7.9           33.4         -         68.5         9.3         -         -           67.6         -         78.3         6.4         -         -           48.9         -         73.2         5.8         -         -           64.8         -         75.5         6.6         -         -           43.6         -         70.6         6.8         -         -           46.8         -         65.7         8.5         -         -           46.8         -         74.8         5.7         -         -	mance of different carbon-supported Pt catalysts in GLY oxidation under base-free conditions. <sup>[a]</sup> Selectivity [%]           GLYD         GA         TA         DHA         HPA         GLA           9.7         19.3         49.8         -         14.3         7.9         4.9           33.4         -         68.5         9.3         -         -         6.2           67.6         -         78.3         6.4         -         -         2.1           48.9         -         73.2         5.8         -         -         3.7           64.8         -         75.5         6.6         -         4.3           43.6         -         70.6         6.8         -         6.3           24.6         -         65.7         8.5         -         -         7.8           46.8         -         74.8         5.7         -         -         4.9	mance of different carbon-supported Pt catalysts in GLY oxidation under base-free conditions. <sup>[a]</sup> Selectivity [%]           GLYD         GA         TA         DHA         HPA         GLA         OA           9.7         19.3         49.8         -         14.3         7.9         4.9         -           33.4         -         68.5         9.3         -         -         6.2         5.4           67.6         -         78.3         6.4         -         -         2.1         2.3           48.9         -         73.2         5.8         -         -         3.7         4.6           64.8         -         75.5         6.6         -         -         4.3         2.8           43.6         -         70.6         6.8         -         -         6.3         4.8           24.6         -         65.7         8.5         -         -         7.8         6.6           46.8         -         74.8         5.7         -         -         4.9         3.8		

[a] Reaction conditions: 25 mL GLY solution (0.1 mol L<sup>-1</sup>), 0.1 g catalyst, GLY/metal (mol/mol) = 250,  $T = 25 \circ C$ ,  $O_2$  flow rate = 20 mL min<sup>-1</sup>, reaction time = 8 h; GLYD: Glyceraldehyde; DHA: Dihydroxyacetone; HPA: Hydroxypyruvic acid; GLA: Glycolic acid; OA: Oxalic acid; CMB: Carbon mass balance.



slightly larger than that in Pt/pristine carbon and both catalysts have a low amount of SOFGs. Thus, the Lewis base, which is produced by the high-temperature treatment of the support, should be considered as a major contribution to the increase in GLY conversion on the Pt/K-AMC-900 catalyst. Furthermore, the GLY conversion on Pt/K-AMC-900 is lower than that on Pt/ K-AMC-600, which could be because of the larger Pt nanoparticles on the K-AMC-900 support. However, the effect of surface chemistry should also be considered.

To rule out the Pt size effect on the catalytic activity of carbon-based Pt catalysts, Pt catalysts of comparable sizes on different carbon supports with different surface chemistries should be tested. However, in the case of Pt/K-AMC, the sintering of the Pt nanoparticles cannot be avoided at 900 °C under N<sub>2</sub>. Kundu et al. reported that the direct heating of carbon supports under H<sub>2</sub> flow was more efficient to remove the SOFGs than that under N<sub>2</sub>, and the annealing of the catalyst support at high temperature showed less sintering of the metallic nanoparticles.<sup>[51]</sup> Thus, we used H<sub>2</sub> gas for the thermal treatment of the Pt/K-AMC catalyst at different temperatures.

After thermal treatment at 400 and 700 °C under H<sub>2</sub>, we analyzed the deconvolution data from the TPD-MS profiles (Figures S4 and S5) in Tables 2 and 3 and we concluded that the surface chemistry of K-AMC-400-H<sub>2</sub> and K-AMC-600 was very similar in terms of SOFGs. The K-AMC-700-H<sub>2</sub> and K-AMC-900 samples also showed similarities with regards to SOFGs. Importantly, Pt nanoparticles were still well dispersed and their sizes were relatively preserved on both Pt/K-AMC-400-H<sub>2</sub> and Pt/K-AMC-700-H<sub>2</sub> compared to the size of Pt particles on Pt/K-AMC according to the TEM and XRD results (Figures S6 and S7). Although we observed slightly larger Pt particles (3-4 nm) in the case of Pt/K-AMC-700-H<sub>2</sub>, they are still smaller than those observed on Pt/K-AMC-900 (5-6 nm). The catalytic performance results listed in Table 5 show that the GLY conversion (64.8%) on Pt/K-AMC-400-H<sub>2</sub> is comparable to that (67.6%) obtained on Pt/K-AMC-600, which is expected because of the similarity of these catalysts. Interestingly, the GLY conversion (43.6%) on Pt/K-AMC-700-H<sub>2</sub> is comparable to that (48.9%) obtained on Pt/K-AMC-900, although the Pt particle size is smaller. This indicates that the Pt nanoparticle size has a minor contribution on the catalytic performance of the catalyst (at least in this given size range of Pt nanoparticles). In addition, the GLY conversion on Pt/K-AMC-700-H $_2$  is considerably lower than that on Pt/K-AMC-600 and Pt/K-AMC-400-H<sub>2</sub>. As a result of the minor effect of the Pt particle size on GLY oxidation, these results reveal the key role that SOFGs play in this catalytic reaction.

According to mechanistic studies on GLY oxidation under basic conditions,<sup>[20, 52]</sup> NaOH does not only capture H<sup>+</sup> from one of the primary hydroxyl groups of GLY to initiate the reaction but it also promotes the adsorption of GLY on the Pt surface. Thus, under basic conditions, GLY molecules can adsorb easily onto metal surfaces with the aid of NaOH. However, under base-free conditions, the carbon surface should be hydrophilic enough to facilitate the adsorption of GLY molecules on the Pt surface. The carbon surface hydrophilicity originates from the presence of SOFGs. As carboxylic groups can impede the adsorption of GLY molecules on carbon surface, the presence of high-desorption-temperature SOFGs such as phenol, ether, and carbonyl/quinone groups is necessary for carbonsupported Pt catalysts to achieve a high catalytic activity for GLY oxidation under base-free conditions.

To further investigate the influence of the surface chemistry of activated carbon on glycerol oxidation, we performed a traditional activation experiment using nitric acid. Nitric acid is used frequently to activate carbon materials and introduce SOFGs on the surface of carbon supports to improve the catalytic activities of the carbon-based catalysts.<sup>[53]</sup> As noted from the TPD-MS profiles (Tables 2 and 3), the activation was successful because a large amount of SOFGs were introduced on the carbon surface. To exclude the Lewis base factor from the overall catalytic contributions, HNO3-AMC was not annealed at high temperature. After wetness impregnation, TEM and XRD results show that the size of the Pt particles on Pt/HNO<sub>3</sub>-AMC was around 2 nm. With similar amounts of SOFGs on the surfaces of both HNO<sub>3</sub>-AMC and K-AMC, a lower catalytic conversion was observed on the Pt/HNO3-AMC catalyst (24.6%) compared to Pt/K-AMC catalyst (33.4%). To find an explanation for this difference in the catalytic activities, we took a closer look at the TPD-MS data, more specifically, the CO/CO<sub>2</sub> ratio, which was used as an indication of the carbon surface acidity/basicity balance (in which a lower ratio represents a stronger surface acidity).<sup>[47]</sup> With a CO/CO<sub>2</sub> ratio of 1.4, the surface of K-AMC is more basic in terms of SOFGs than the HNO<sub>3</sub>-AMC, which has a ratio of almost 1. If we compare the two catalysts, the stronger basicity of K-AMC explains its higher catalytic activity well. In spite of a significant difference in the specific surface area, the external surface areas of HNO3-AMC and K-AMC are still comparable (Table 1 and Table S2).

After thermal treatment at 600 °C under N<sub>2</sub> flow, Pt/HNO<sub>3</sub>-AMC-600 showed a better catalytic activity (GLY conversion: 46.8%) than Pt/HNO<sub>3</sub>-AMC (24.6%) most likely because of the loss of acidic groups and the creation of Lewis base, however, its activity is still significantly lower than that of Pt/K-AMC-600 (67.6%). Given the similarities in the Pt particle sizes of both catalysts (Figure 4 and Figure S6), the lower catalytic activity observed on Pt/HNO<sub>3</sub>-AMC-600 could be explained by the lower amount of high-desorption-temperature SOFGs, specifically ether and carbonyl/quinone groups. These findings show the higher catalytic performance of Pt supported on KOH-activated carbon compared to the traditional HNO<sub>3</sub>-activated carbon for the GLY oxidation under base-free conditions.

Although we still have not confirmed whether the enhancement of the catalytic performance mainly comes from the presence of high-desorption-temperature SOFGs such as phenol, ether, and carbonyl/quinone groups or Lewis base, it is clear that the increase of the surface basicity of the carbon support induced by one of those two factors or both is beneficial for glycerol oxidation under base-free conditions. Although recent studies supported the contribution from either the high-desorption-temperature SOFGs or Lewis base on the carbon surface,<sup>[27, 28]</sup> this study shows that the combination of the high-desorption-temperature SOFGs and Lewis base leads to a better catalytic activity for AC-supported Pt catalysts under base-free conditions.

ChemCatChem **2016**, 8, 1699 – 1707



To evaluate the catalytic activity of Pt/K-AMC-600, the effect of reaction time and glycerol/Pt ratio on GLY oxidation over Pt/K-AMC-600 catalyst were studied, and the results are shown in Figure 6 and Table S3. The highest GA selectivity (89.6%) was achieved in the initial stage within 2 h of the reaction time (Figure 6). As the reaction time increased, the GLY conversion



**Figure 6.** Time course of GLY oxidation over Pt/K-AMC-600. Reaction conditions: 25 mL GLY solution (0.1 mol L<sup>-1</sup>), 0.1 g catalyst, GLY/metal (mol/mol) = 250, T = 25 °C, O<sub>2</sub> flow rate = 20 mL min<sup>-1</sup>.

increased and the GA selectivity decreased gradually. As the reaction time reached 8 h, the GLY conversion and GA yield reached 67.6% and 52.9%, respectively. After that, no further increase in GA yield was noted. The results summarized in Table S3 show that the GLY conversion increases if the GLY/Pt ratio decreases from 1000 to 250, whereas it remained almost unchanged if this ratio is further reduced to 150. Furthermore, the GA selectivity decreased with the decrease of the GLY/Pt ratio, and the overoxidation reactions were favored at a low GLY/Pt ratio.<sup>[54,55]</sup>

In this work, the high catalytic activities of Pt/K-AMC-600 and Pt/K-AMC-900 indicate that the basic carbon support plays an important role in GLY oxidation to GA under base-free conditions. In a previous study on GLY oxidation under base-free conditions, Tongsakul et al. suggested that the basic support (instead of the OH<sup>-</sup> under basic conditions) would initiate the alkoxide (RCH<sub>2</sub>O<sup>-</sup>) formation by the deprotonation of GLY molecules. The alkoxide would then be adsorbed on the Pt surface. The adsorbed intermediate (RCH2O\*, \* represents a site on the metal surface) would be dehydrogenated to RCHO\* with the aid of the adsorbed molecular oxygen (peroxo or superoxo form), and then the electron-deficient carbonyl carbon atom of RCHO\* would be attacked by the nucleophilic oxygen atom of water. The acidic derivative product is produced subsequently after a proton is abstracted by the adsorbed molecular oxygen.<sup>[13]</sup>

Similarly, in this study, we believe that basic SOFGs on the activated carbon support as well as Lewis bases would play a major role in the selective oxidation of GLY to GA.

Recycling experiments were conducted on Pt/K-AMC-600, Pt/K-AMC-900, Pt/K-AMC-400-H<sub>2</sub>, and Pt/HNO<sub>3</sub>-AMC-600 to ex-

amine their stabilities. The GLY conversions are very stable even after the reuse of Pt/K-AMC-600 and Pt/K-AMC-400-H<sub>2</sub> twice (Figure 7). Pt/HNO<sub>3</sub>-AMC-600 follows the same trend, whereas the catalytic activity of Pt/K-AMC-900 declines severely. According to previous studies, the phenol groups on the carbon surface play a vital role in the stabilization of Pd or Au nanoparticles by forming stable Pd–O–C or Au–O–C bonds.<sup>[26,56]</sup> Thus, the high catalytic stability is probably because of the presence of the phenol groups on K-AMC-600, K-AMC-400-H<sub>2</sub>, and HNO<sub>3</sub>-AMC-600 that interact strongly with Pt nanoparticles.



Figure 7. Results of the recycling of Pt/K-AMC-600, Pt/K-AMC-900, Pt/K-AMC-400-H<sub>2</sub>, and Pt/HNO<sub>3</sub>-AMC-600 in GLY oxidation.

### Conclusions

In this work, highly dispersed Pt nanoparticles supported on KOH-activated mesoporous carbon were prepared to catalyze the oxidation of glycerol (GLY) at room temperature under base-free conditions. The Pt/pristine carbon catalyst has a low activity in the absence of surface oxygen functional groups (SOFGs). The introduction of SOFGs to a carbon surface increases the hydrophilicity of the carbon surface, which improves the Pt dispersion. However, not all types of SOFGs are beneficial to the catalytic activity; the low-desorption-temperature carboxylic groups, which can impede the adsorption of GLY on the Pt surface, has a negative effect on catalytic activities, but high-desorption-temperature SOFGs, such as phenol, ether, carbonyl/quinone groups, enhance the catalytic performance by increasing the hydrophilicity and basicity of the carbon surface and by participating in the stabilization of the Pt nanoparticles. Pt nanoparticles supported on KOH-activated mesoporous carbon showed a higher catalytic activity than Pt nanoparticles supported on HNO3-activated mesoporous carbon mainly because of a more favorable acid/base balance on the carbon surface. The Lewis bases on the carbon surfaces created by high-temperature annealing should be also considered as a positive effect for a high catalytic activity. The control of the surface chemistry on the carbon surfaces plays a key role to optimize the catalytic performance of carbon-supported Pt catalysts for GLY oxidation under base-free conditions.



# **Experimental Section**

### Synthesis of catalyst supports and supported Pt catalysts

Mesoporous carbon was synthesized using a phenol-formaldehyde resin and commercial colloidal silica as a carbon precursor and a removable hard template, respectively. Phenol (9.15 g) and formaldehyde (15.8 g, 37 wt%) were dissolved in NaOH solution (50 mL, 0.2 м). The mixture was stirred at 70 °C for 60 min. Next, Ludox SM-30 sol (50 g, 30 wt%) was added to with stirring. The mixture was then transferred to a sealed bottle and heated at 80 °C for 3 days. The obtained gels were dried directly at 80°C in air followed by carbonization at 900  $^{\circ}$ C for 3 h with a heating rate of 5  $^{\circ}$ C min<sup>-1</sup> under N<sub>2</sub>. The mesoporous carbon was obtained by dissolution of the silica nanoparticles in 20 wt % NH<sub>4</sub>HF<sub>2</sub> solution. After stirring at RT for 48 h, the solution was filtered, and the residue was dried overnight in an oven. The obtained sample was designated as pristine carbon. The KOH-activated mesoporous carbon was prepared by mixing pure carbon (0.3 g) with a solution (30 mL) that contained KOH (1.2 g) at 90 °C for 6 h under stirring. Afterwards, it was dried at 90 °C for 12 h. Activation was performed by heating the sample at 750  $^{\circ}$ C for 1 h in a tubular furnace under N<sub>2</sub> at a rate of  $5\,^{\circ}\text{Cmin}^{-1}$ . To purify the activated carbon, it was washed several times with HCl (1 M) and then distilled water until the pH was neutral.<sup>[57]</sup> The obtained sample was designated as K-AMC. The K-AMC sample was treated thermally at 600 and 900  $^\circ\text{C}$  under  $N_2$  for 1 h at a heating rate of 10°Cmin<sup>-1</sup> to obtain K-AMC-600 and K-AMC-900, respectively. HNO<sub>3</sub>-activated mesoporous carbon (HNO<sub>3</sub>-AMC) was prepared as follows: mesoporous carbon (1 g) was first treated with concentrated HNO<sub>3</sub> (5 mL) at 90 °C for 6 h. The treated mesoporous carbon was collected by filtration, rinsed with water until pH 7, and then dried at 110°C overnight. Pt supported on pristine carbon or activated carbon catalysts were synthesized by the wetness impregnation reduction method. Typically, carbon or activated carbon (0.1 g) was dispersed in deionized water (10 mL) in a beaker by ultrasonication. H<sub>2</sub>PtCl<sub>6</sub> aqueous solution of the required concentration to obtain a content of  $\approx$  2 wt % Pt was added into the beaker, and the suspension was ultrasonicated for 10 min. The beaker was then placed on a stirrer for 2 h to equilibrate. Subsequently, NaBH<sub>4</sub> aqueous solution was injected quickly into the solution and kept under stirring for 1 h. The product was collected by filtration and washed with deionized water several times. The resulting black powder was dried in an oven overnight at 110°C and collected for catalytic tests. For comparison, Pt/K-AMC was also treated at 400 and 700 °C under H<sub>2</sub> flow with a heating rate of 10°C min<sup>-1</sup> to obtain Pt/K-AMC-400-H<sub>2</sub> and Pt/K-AMC-700-H<sub>2</sub>, respectively.

### **Catalyst characterization**

TEM images of the samples were recorded by using an FEI Titan 80 (300 kV). XRD patterns of the samples were recorded by using a Bruker D8 Advance diffractometer with CuK<sub>a</sub> radiation ( $\lambda = 1.5418$  Å) with a graphite monochromator (40 kV, 40 mA). XPS spectra were recorded by using an Axis Ultra DLD system (Kratos, UK) by using an AlK<sub>a</sub> radiation source (hv = 1486.8 eV). The binding energy was calibrated by taking the C1s peak (BE = 284.4 eV) as a reference. The XPS peaks were analyzed using a Shirley-type background and a nonlinear least-squares fitting of the experimental data based on a mixed Gauss/Lorentz peak shape. XPS quantification was performed by applying the appropriate relative sensitivity factors (RSFs) to the integrated peak areas. N<sub>2</sub> adsorption–desorption isotherms were obtained by using a Micromeritics ASAP 2420 instrument at -196 °C. Before the measurements, the sam-

ples were degassed under vacuum for approximately 12 h at 200 °C. The micropore volume and external surface area were calculated by the *t*-plot method. TPD-MS was performed by using a Micromeritics Autochem 2920 Chemisorption Analyzer connected to a MKS Mass spectrometer. Pure or activated carbon samples ( $\approx$ 50 mg) were placed in a U-type quartz cell, and the temperature was increased linearly from 50 to 1000 °C at a heating rate of 10 °C min under a flow of He (50 mL min<sup>-1</sup>).

#### Catalytic activity measurement

GLY oxidation was performed in a 50 mL three-necked flask equipped with a gas supply system, magnetic stirrer, condenser, and temperature controller. GLY aqueous solution (25 mL, 0.1 mol L<sup>-1</sup>) and the catalyst ( $\approx$  0.1 g) were added into the reactor. O<sub>2</sub> (99.9%) was introduced into the reactor at 20 mLmin<sup>-1</sup> via a mass-flow controller at atmospheric pressure. After 8 h reaction, the catalysts were removed by filtration, and the liquid products were analyzed by using HPLC equipped with an Aminex HPX-87H column (Bio-Rad Laboratories) and refractive index (RI) detector. The analysis conditions were set as follows: eluent, 5 mM H<sub>2</sub>SO<sub>4</sub>; flow rate, 0.6 mLmin<sup>-1</sup>; column temperature, 50 °C. The retention time and calibration curves for the observed products were determined by injecting the standard samples at different concentration levels.

# Acknowledgements

The authors gratefully acknowledge the support from Dr. Heiko Langer in ACL, KAUST. Contributions from Dr. Misjudeen Raji. Mr. Jeffrey Varrasso, and Mr. Mohammed Khalid to this work are also gratefully acknowledged.

**Keywords:** carbon · mesoporous materials · oxidation platinum · supported catalysts

- [1] R. Luque, L. Herrero-Davila, J. M. Campelo, J. H. Clark, J. M. Hidalgo, D.
- Luna, J. M. Marinas, A. A. Romero, *Energy Environ. Sci.* 2008, 1, 542–564.
   C. H. Zhou, J. N. Beltrami, Y. X. Fan, G. Q. Lu, *Chem. Soc. Rev.* 2008, 37, 527–549.
- [3] P. Gallezot, Chem. Soc. Rev. 2012, 41, 1538-1558.
- [4] J. S. Peng, X. L. Li, C. M. Tang, W. Bai, Green Chem. 2014, 16, 108-111.
- [5] C. M. Tang, J. S. Peng, G. C. Fan, X. L. Li, X. L. Pu, W. Bai, *Catal. Commun.* 2014, 43, 231–234.
- [6] J. F. Zhang, Y. L. Zhao, M. Pan, X. Z. Feng, W. J. Ji, C. T. Au, ACS Catal. 2011, 1, 32–41.
- [7] C. M. Tang, X. L. Li, Z. J. Zhai, N. Jiang, W. Bai, H. J. Gao, Y. W. Liao, RSC Adv. 2014, 4, 28875 – 28882.
- [8] G. Knothe, S. C. Cermak, R. L. Evangelista, Fuel 2012, 96, 535-540.
- [9] H. Tan, M. N. Hedhill, Y. Wang, K. Li, J. Zhang, S. Sioud, Z. A. Al-Talla, H. M. Amad, T. Zhan, O. E. Tall, Y. Han, *Catal. Sci. Technol.* **2013**, *3*, 3360– 3370.
- [10] G. W. Wu, C. X. Zhang, S. R. Li, Z. P. Han, T. Wang, X. B. Ma, J. L. Gong, ACS Sustainable Chem. Eng. 2013, 1, 1052–1062.
- [11] B. Katryniok, S. Paul, V. Bellière-Baca, P. Rey, F. Dumeignil, Green Chem. 2010, 12, 2079–2098.
- [12] M. Pilar Pico, A. Romero, S. Rodriguez, A. Santos, Ind. Eng. Chem. Res. 2012, 51, 9500-9505.
- [13] D. Tongsakul, S. Nishimura, K. Ebitani, ACS Catal. 2013, 3, 2199-2207.
- [14] S. Hirasawa, Y. Nakagawa, K. Tomishige, *Catal. Sci. Technol.* **2012**, *2*, 1150–1152.
- [15] D. Roy, B. Subramaniam, R. V. Chaudhari, ACS Catal. 2011, 1, 548-551.
- [16] B. N. Zope, S. E. Davis, R. J. Davis, Top. Catal. 2012, 55, 24-32.
- [17] A. Corma, S. Iborra, A. Velty, Chem. Rev. 2007, 107, 2411-2502.



- [18] B. Katryniok, H. Kimura, E. Skrzyńska, J. Girardon, P. Fongarland, M. Capron, R. Ducoulombier, N. Mimura, S. Paul, F. Dumeignil, *Green Chem.* 2011, 13, 1960–1979.
- [19] F. Porta, L. Prati, J. Catal. 2004, 224, 397-403.
- [20] D. Liang, J. Gao, H. Sun, P. Chen, Z. Y. Hou, X. M. Zheng, Appl. Catal. B 2011, 106, 423–432.
- [21] S. Carrettin, P. McMorn, P. Johnston, K. Griffin, C. J. Kiely, G. J. Hutchings, *Phys. Chem. Chem. Phys.* **2003**, *5*, 1329–1336.
- [22] V. Z. Radkevich, T. L. Senko, K. Wilson, L. M. Grishenko, A. N. Zaderko, V. Y. Diyuk, *Appl. Catal. A* **2008**, *335*, 241–251.
- [23] A. E. Aksoylu, M. Madalena, A. Freitas, M. F. R. Pereira, J. L. Figueiredo, *Carbon* 2001, 39, 175–185.
- [24] D. S. Su, J. J. Delgado, X. Liu, D. Wang, R. Schlögl, L. F. Wang, Z. Zhang, Z. C. Shan, F. S. Xiao, *Chem. Asian J.* **2009**, *4*, 1108–1113.
- [25] X. Xu, Y. Li, Y. T. Gong, P. F. Zhang, H. R. Li, Y. Wang, J. Am. Chem. Soc. 2012, 134, 16987–16990.
- [26] J. H. Xu, J. Zhao, J. Xu, T. T. Zhang, X. N. Li, X. X. Di, J. Ni, J. G. Wang, J. Cen, Ind. Eng. Chem. Res. 2014, 53, 14272 14281.
- [27] X. Y. Wan, C. M. Zhou, J. S. Chen, W. P. Deng, Q. H. Zhang, Y. H. Yang, Y. Wang, ACS Catal. 2014, 4, 2175 2185.
- [28] E. G. Rodrigues, M. F. R. Pereira, X. W. Chen, J. J. Delgado, J. J. M. Órfão, J. Catal. 2011, 281, 119–127.
- [29] D. Tongsakul, S. Nishimura, C. Thammacharoen, S. Ekgasit, K. Ebitani, Ind. Eng. Chem. Res. 2012, 51, 16182–16187.
- [30] A. Tsuji, K. T. V. Rao, S. Nishimura, A. Takagaki, K. Ebitani, *ChemSusChem* 2011, 4, 542-548.
- [31] A. Iriondo, J. F. Cambra, V. L. Barrio, M. B. Guemez, P. L. Arias, M. C. Sanchez-Sanchez, R. M. Navarro, J. L. G. Fierro, *Appl. Catal. B* 2011, *106*, 83– 93.
- [32] G. L. Brett, Q. He, C. Hammond, P. J. Miedziak, N. Dimitratos, M. Sankar, A. A. Herzing, M. Conte, J. A. Lopez-Sanchez, C. J. Kiely, D. W. Knight, S. H. Taylor, G. J. Hutchings, *Angew. Chem. Int. Ed.* **2011**, *50*, 10136– 10139; *Angew. Chem.* **2011**, *123*, 10318–10321.
- [33] C. Moreno-Castilla, M. V. López-Ramón, F. Carrasco-Marín, *Carbon* 2000, 38, 1995 – 2001.
- [34] Z. X. Wu, P. A. Webley, D. Y. Zhao, *Langmuir* **2010**, *26*, 10277–10286.
- [35] A. H. Lu, W. C. Li, N. Muratova, B. Spliethoff, F. Schüth, Chem. Commun. 2005, 5184–5186.
- [36] Y. Y. Lv, F. Zhang, Y. Q. Dou, Y. P. Zhai, J. X. Wang, H. J. Liu, Y. Y. Xia, B. Tu, D. Y. Zhao, J. Mater. Chem. 2012, 22, 93–99.

[37] C. Y. Yin, M. K. Aroua, W. M. A. W. Daud, Sep. Purif. Technol. 2007, 52, 403–415.

**CHEMCATCHEM** 

**Full Papers** 

- [38] J. L. Figueiredo, M. F. R. Pereira, M. M. A. Freitas, J. J. M. Órfão, Ind. Eng. Chem. Res. 2007, 46, 4110–4115.
- [39] J. L. Figueiredo, M. F. R. Pereira, M. M. A. Freitas, J. J. M. Órfão, Carbon 1999, 37, 1379 – 1389.
- [40] E. G. Rodrigues, J. J. Delgado, X. Chen, M. F. R. Pereira, J. M. Órfão, Ind. Eng. Chem. Res. 2012, 51, 15884–15894.
- [41] J. F. Vivo-Vilches, E. Bailón-García, A. F. Pérez-Cadenas, F. Carrasco-Marín, F. J. Maldonado-Hódar, *Carbon* 2014, 68, 520-530.
- [42] H. Valdés, C. A. Zaror, Langmuir 2002, 18, 2111-2116.
- [43] M. L. Toebes, M. K. van der Lee, L. M. Tang, M. H. Huis in't Veld, J. H. Bitter, A. J. van Dillen, K. P. de Jong, J. Phys. Chem. B 2004, 108, 11611– 11619.
- [44] M. A. Fraga, E. Jordão, M. J. Mendes, M. M. A. Freitas, J. L. Faria, J. L. Figueiredo, J. Catal. 2002, 209, 355–364.
- [45] M. Engelhard, D. Baer, Surf. Sci. Spectra 2000, 7, 1-68.
- [46] J. Q. Lei, X. Z. Duan, G. Qian, X. G. Zhou, D. Chen, Ind. Eng. Chem. Res. 2014, 53, 16309–16315.
- [47] S. S. Chen, P. Y. Qi, J. Chen, Y. Z. Yuan, RSC Adv. 2015, 5, 31566-31574.
- [48] J. A. Menéndez, J. Phillips, B. Xia, L. R. Radovic, Langmuir 1996, 12, 4404–4410.
- [49] C. León y León, J. M. Solar, V. Calemma, L. R. Radovic, Carbon 1992, 30, 797-811.
- [50] T. J. Fabish, D. E. Schleifer, Carbon 1984, 22, 19-38.
- [51] S. Kundu, Y. M. Wang, W. Xia, M. Muhler, J. Phys. Chem. C 2008, 112, 16869–16878.
- [52] N. Mimura, N. Hiyoshi, T. Fujitani, F. Dumeignil, RSC Adv. 2014, 4, 33416–33423.
- [53] L. Liu, Q. F. Deng, Y. P. Liu, T. Z. Ren, Z. Y. Yuan, Catal. Commun. 2011, 16, 81–85.
- [54] S. Gil, M. Marchena, L. Sánchez-Silva, A. Romero, P. Sánchez, J. L. Valverde, *Chem. Eng. J.* 2011, 178, 423–435.
- [55] N. Dimitratos, A. Villa, L. Prati, Catal. Lett. 2009, 133, 334-340.
- [56] T. Y. Xu, Q. F. Zhang, H. F. Yang, J. G. Wang, X. N. Li, Ind. Eng. Chem. Res.
- **2013**, *52*, 9783 9789. [57] J. Jin, S. Tanaka, Y. Egashira, N. Nishiyama, *Carbon* **2010**, *48*, 1985 – 1989.

Received: January 17, 2016 Published online on April 18, 2016