

A Nano-Fibrillated Mesoporous Carbon as an Effective Support for Palladium Nanoparticles in the Aerobic Oxidation of Alcohols “on Pure Water”**

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Abstract: A novel nano-fibrillated mesoporous carbon (IFMC) was successfully prepared via carbonization of the ionic liquid 1-methyl-3-phenethyl-1*H*-imidazolium hydrogen sulfate (**1**) in the presence of SBA-15. The material was shown to be an efficient and unique support for the palladium nanoparticle (PdNP) catalyst Pd@IFMC (**2**) in aerobic oxidation of heterocyclic, benzylic, and heteroatom containing alcohols on pure water at temperatures as low as 40 °C for the first time and giving almost consistent activities and selectivities within more than six reaction runs. The catalyst has also been employed as an effective catalyst for

the selective oxidation of aliphatic and allylic alcohols at 70–80 °C. The materials were characterized by X-ray photoelectron spectroscopy (XPS), N₂ adsorption–desorption analysis, transmission electron microscopy (TEM), and electron tomography (ET). Our compelling XPS and ET studies showed that higher activity of **2** compared to Pd@CMK-3 and Pd/C in the aerobic oxidation of alcohols on water might be due to the presence of nitrogen

functionalities inside the carbon structure and also the fibrous nature of our materials. The presence of a nitrogen heteroatom in the carbonaceous framework might also be responsible for the relatively uniform and nearly atomic-scale distribution of PdNPs throughout the mesoporous structure and the inhibition of Pd agglomeration during the reaction, resulting in high durability, high stability, and recycling characteristics of **2**. This effect was clearly confirmed by comparing the TEM images of the recovered **2** and Pd@CMK-3.

Keywords: aerobic oxidation • mesoporous carbon • palladium • supported catalysts • water chemistry

Introduction

Owing their excellent chemical stability, large surface area, and versatile structural properties, porous carbon materials have received wide applications in the field of catalysis.^[1] Among all reported porous carbon materials, the most attractive members are the ordered mesoporous carbons (OMC),^[2] which are synthesized by nanocasting with ordered mesoporous silica^[3] as a hard substrate. The nanostructure, electronic properties, and surface functionalities of mesoporous carbons is highly dependent on the carbon

source and synthetic conditions.^[4] Carbon materials containing heteroatoms were found to have improved physical and chemical properties.^[4–9] Antonietti et al.^[10] and Dai et al.^[11] independently proposed a new strategy for the synthesis of nitrogen-doped carbon materials from nonvolatile, task-specific, ionic liquids with either nitrile-functionalized imidazolium cations or cyanide-containing anions. Amongst the outstanding characteristics of these hybrid carbon materials are their high stability against thermal decomposition and tunable electronic properties. There has been no report, however, on the application of ionic-liquid-derived mesoporous carbons used as a support in chemical transformations. Herein, we present the synthesis of a novel nano-fibrillated mesoporous carbon by means of carbonization of a novel task-specific, ionic liquid, 1-methyl-3-phenethyl-1*H*-imidazolium hydrogen sulfate (**1**), in the presence of ordered mesoporous silica SBA-15^[3b] as a structure-transducing agent.^[12] It was also found that our new fibrous mesoporous carbon is an excellent support for the immobilization and stabilization of Pd nanoparticles and resulted in a highly effective and recyclable catalyst with outstanding performances at low temperature on water. Using compelling X-ray photoelectron spectroscopy (XPS) and electron tomography (ET) studies, we also discuss the effect of ultra-structural feature of our novel fibrous mesoporous carbon on the high unprecedented reactivity, and high stability of our catalyst system in the aerobic oxidation of alcohols on water.

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[**] We prefer to use the term “on water” instead of “in water”, because most of the alcohols which are used in our study are certainly water insoluble.^[23]

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Results and Discussion

SBA-15 was prepared using pluronic P123 ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, $M_{\text{av}}=5800$, Aldrich) and $(\text{EtO})_4\text{Si}$ under acidic conditions.^[3] In order to produce the described mesoporous carbon materials, a dispersion of a mixture of SBA-15 and compound **1** was prepared and heated at 900°C for 3 h under the flow of Ar. The silica component was dissolved by stirring the resulting product in 8% (w/v) NaOH aqueous solution for 24 h at 50°C , followed by successive washings with copious amount of deionized water and ethanol, and freeze dried to yield the powdered mesoporous carbon material, which is referred to as ionic-liquid-derived fibrillated mesoporous carbon (IFMC). IFMC was characterized by X-ray photoelectron spectroscopy (XPS), N_2 adsorption–desorption analysis, transmission electron microscopy (TEM), and electron tomography (ET). The N_2 adsorption–desorption isotherm of IFMC exhibited reversible capillary condensation/evaporation type-IV with an H2 hysteresis loop, which is characteristic of mesoporous materials. The nitrogen-sorption analysis also demonstrated that the IFMC has a BET surface area of $778\text{ m}^2\text{ g}^{-1}$ and a primary pore volume of $0.98\text{ cm}^3\text{ g}^{-1}$. The indistinct capillary condensation steps, compared with the parent SBA-15 template (Figures S2 and S3 vs. S5 and S6 in the Supporting Information), suggest a relatively broad size distribution for IFMC. This is in sharp contrast with those often observed for ordered mesoporous carbons with narrow pore size distributions. In addition, adsorption isotherms do not level off at relative pressures $p/p_0 > 0.8$, but increase, suggesting the presence of interparticle textural porosity in IFMC samples with high external surface area. The Barrett–Joyner–Halenda (BJH) pore size distribution of IFMC calculated from the adsorption branch further confirms the broad pore size distribution, with maxima centered at 3.3 nm. X-ray photoelectron spectroscopy (XPS) was employed to gain additional insight into the nature of the IFMC at atomic scale (Figure S7, Supporting Information). The signals located at about 285, 403, and 535 eV were assigned to C, N, and O, respectively.^[13,14]

High-resolution TEM and electron tomography were used to investigate the ultrastructure of the IFMC. The results indicated that the particle size of the IFMC samples (500 to 1000 nm) were identical to that SBA-15. The internal structure of these two materials is distinct from each other. While SBA-15 displays an ordered layer structure (Figure S1 in the Supporting Information), IFMC consists of bundle of nanofibers composed of nano-sized platelike particles (Figure 1 a, and Figure S4 in the Supporting Information). These images exhibit the formation of a relatively well-ordered array of carbon nanofibers, a feature that has not been reported in the previous OMC templated from SBA-15.^[1f,2b–c,4] This is to some extent surprising, because in our described method, it seems that SBA-15 was serving as a structural guide for the formation of nano-fibrillated carbon rather than a mould, which is normally observed in nanocasting-based protocols. The exact reason for the formation of these fibrillated structures in our IFMC is unclear at the moment.

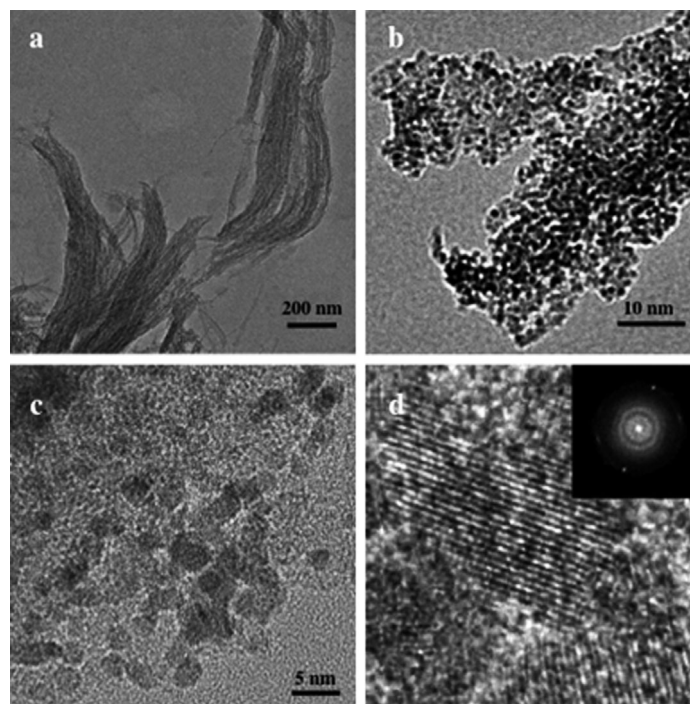


Figure 1. TEM images of Pd@IFMC. a) The fibrillar structure is clearly visible at low magnification. b) PdNPs and nanopores of the carbon matrix are easily detectable at higher magnification at underfocus values. c) Individual PdNPs with diameter between 2–4 nm are visible at high magnification. d) HRTEM image shows the crystalline structure of PdNPs having a d -spacing of 0.28 nm with the corresponding selected-area electron diffraction pattern (inset).

To provide more insight into how structural properties of IFMC could influence the catalyst performance and reusability of supported palladium species (Pd@IFMC, **2**), the ability of IFMC to immobilize and stabilize palladium nanoparticles in the aerobic oxidation of alcohols was investigated. Based on these results, it is evident that IFMC provides an efficient water-tolerant heterogeneous Pd-based catalytic system with unprecedented performance in the selective aerobic oxidation of alcohols into the carbonyl compounds in aqueous medium at low temperature. To prepare the Pd@IFMC, a uniform slurry of the IFMC in dry degassed tetrahydrofuran (THF) was allowed to react with an appropriate concentration of $\text{Pd}(\text{OAc})_2$ in THF, followed by reduction using hydrazine hydrate according to the reported procedures with slight modifications.^[12,15]

A monomodal distribution of crystalline metallic Pd particles ranging in size between 2–4 nm was observed in the TEM and HRTEM images of Pd@IFMC (Figure 1 b–d and Figure S8 in the Supporting Information). ET and 3D-reconstruction (see Methods section in the Supporting Information) were also applied to visualize the ultrastructure of the Pd@IFMC particles and distribution of the PdNPs on the mesoporous carbon matrix. (Figure 2, and Figure S19–S22 in the Supporting Information). The results clearly demonstrates that the PdNPs are not only associated with the external surface, but they are also well distributed inside the

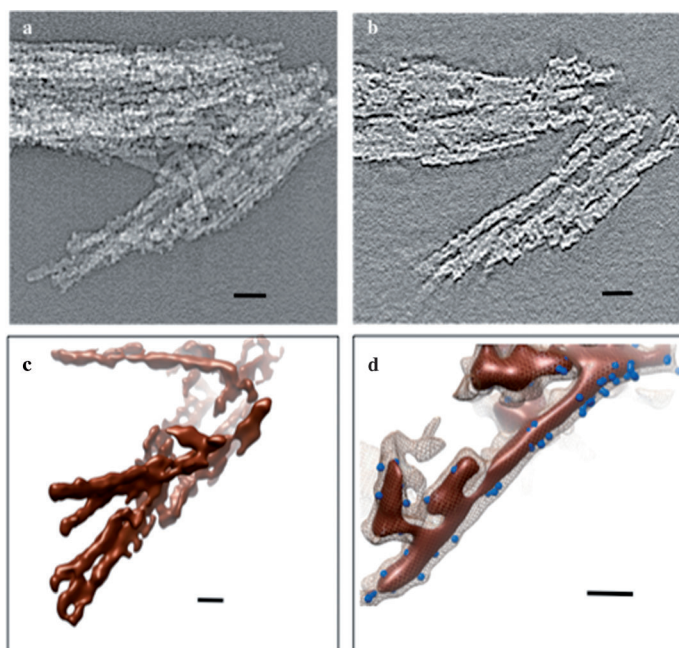


Figure 2. Electron tomographic images of Pd@IFMC. a) Projection of reconstructed volume. b) A 1 nm middle slice through the reconstruction. c) 3D surface representation of a portion of the tomogram presented in a) with individual fibers clearly visible. d) Localization of PdNPs (blue) at the exterior of individual fibers. Two contour levels are presented in the figure. Scale bar is 50 nm in a) and b), and 20 nm in c) and d).

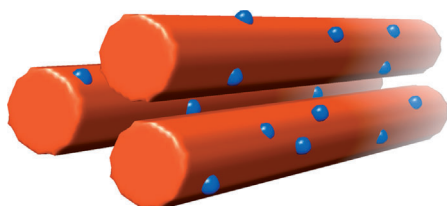


Figure 3. Diagram of the structure for Pd@IFMC: PdNPs (blue) are located on the exterior of the carbon fibers (brown) and within the interparticle mesopores.

mesopores of carbon particles (Figures 2d and 3 and Figure S20 in the Supporting Information). Although, a relatively high Pd concentration of 5% was used, no evident of PdNPs agglomeration was observed. The uniform distribution of the PdNPs is attributed to the high porosity and large surface area as well as the nanostructure of the IFMC. The porous structure of this material is evident in the tomogram shown in Figure 2. It is composed of bundles of approximately 10 nm thick fragmented carbon rods (Figure 2b and Figure S19 in the Supporting Information). The signals at 340.3 and 335.2 eV in the XPS spectrum were assigned to Pd 3d binding energies (Figure S11 in the Supporting Information). In particular, the binding energy of Pd 3d_{5/2} for the described Pd@IFMC sample was observed at 335.2 eV, which clearly confirms the presence of Pd in metallic (Pd⁰) states.^[14] The N₂-adsorption isotherm and pore size distribution of Pd@IFMC showed significant differences to those of

the original IFMC, indicating that the immobilization of PdNPs has been successfully achieved. The N₂ sorption results also confirm the stability of the porous structure after metal doping (Figures S9 and S10 in the Supporting Information).

The catalytic performance of Pd@IFMC was investigated in the aerobic oxidation of alcohols. The selective oxidation of the alcohols to their carbonyl compounds using molecular oxygen or air in the presence of heterogeneous and recyclable catalysts has attracted great attention in recent years.^[16] In particular, the development of new efficient catalyst systems for aerobic oxidation of alcohols in green solvents such as water appears very appealing.^[17] Amongst them, different supported and homogeneous catalyst including either palladium complexes or palladium nanoparticles have been developed for the aerobic oxidation of alcohols in water.^[17b–e] On the other hand, despite the significant progresses in improving catalytic activities, selectivities, substrate scopes, and recyclabilities, the majority of heterogeneous Pd based catalysts require high reaction temperatures (normally up to 80–110 °C), which are not suitable for thermally unstable substrates. Although several carbon-based metal catalysts such as Pd/C,^[18] Pt/C,^[17h,19] Au/C,^[20] and Ru/C,^[17a,21] have been developed for aerobic oxidation of alcohols, the use of high pressure of oxygen or air, high reaction temperature, and/or high catalyst loading (up to 5 mol%) are necessary to obtain satisfactory results. In addition, it is known that many of the reported carbon-supported catalysts are inactive for the aerobic oxidation of alcohols in water.^[17a] Notably, to the best of our knowledge, highly selective and efficient aerobic oxidation of alcohols in neat water at atmospheric pressure of air or oxygen and low temperature using heterogeneous Pd catalysts has not been reported to date.^[22]

The catalytic performance of **2** was first evaluated for the aerobic oxidation of 1-phenyl ethanol as a test reaction under different conditions. In this regard, we were interested in combining the advantages of using molecular oxygen or air as terminal oxidants with the possibility to use water as the reaction medium.

An initial experiment was carried out by using 0.5 mol% of **2** under atmospheric pressure of O₂ on water at room temperature. We prefer to use the term “reaction on water” instead of “reaction in water”, because most of the alcohols which are used in our study are certainly water insoluble.^[23] Interestingly, we found that the catalyst exhibited high catalytic activity and led to acetophenone in unexpected yields of 70% within 24 h (Table 1, entry 1). It was also noted that by a slight increase in the reaction temperature to 40 °C greatly enhanced the reaction efficiency, leading to a quantitative formation of acetophenone (Table 1, entries 2, 3). In separate experiments, the use of Pd@CMK-3 and commercially available Pd/C were shown to give inferior results, confirming the crucial role of our novel IFMC in obtaining excellent reactivity at temperatures as low as 40 °C (Table 1, entries 4, 5). Moreover, our previously developed catalyst system (Pd@SBA-15) was quite inactive in the same transformation under identical reaction conditions (Table 1,

Table 1. Optimization of the aerobic oxidation of 1-phenyl ethanol using various solvents, Pd supported catalysts, and different temperatures.

Catalyst ^[a] (x mol %)	T [°C]	Base	Solvent	t [h]	Yield ^[b] [%]	
1	2 (0.5)	RT	K ₂ CO ₃	H ₂ O	24	70
2	2 (0.5)	35	K ₂ CO ₃	H ₂ O	24	91
3	2 (0.5)	40	K₂CO₃	H₂O	15	> 99
4	Pd@CMK-3 (0.5)	40	K ₂ CO ₃	H ₂ O	15	50
5	Pd/C (0.5)	40	K ₂ CO ₃	H ₂ O	15	18 ^[c]
6	Pd@SBA-15 (0.5)	40	K ₂ CO ₃	H ₂ O	15	< 5 ^[23]
7	2 (0.5)	40	K ₂ CO ₃	toluene	15	68
8	2 (0.5)	40	K ₂ CO ₃	toluene	48	71 ^[d]
9	2 (0.5)	40	K ₂ CO ₃	CH ₃ CN	15	56
10	2 (0.4)	40	K ₂ CO ₃	H ₂ O	15	81
11	2 (0.4)	40	K ₂ CO ₃	H ₂ O	24	> 99
12	2 (0.3)	40	K ₂ CO ₃	H ₂ O	15	75
13	2 (0.3)	40	K ₂ CO ₃	H ₂ O	24	86
14	IFMC	40	K ₂ CO ₃	H ₂ O	15	NR
15	CMK-3	40	K ₂ CO ₃	H ₂ O	15	NR
16	–	40	K ₂ CO ₃	H ₂ O	15	NR
17	2 (0.5)	40	K ₂ CO ₃	–	15	< 5 ^[e]
18	2 (0.5)	40	K ₂ CO ₃	H ₂ O	15	95 ^[f]
19	2 (0.5)	40	K ₂ CO ₃	H ₂ O	15	79 ^[g]
20	2 (0.5)	80	–	H ₂ O	24	25
21	2 (0.5)	40	NaOH	H ₂ O	15	88
22	2 (0.5)	40	Na ₂ CO ₃	H ₂ O	15	82
23	2 (0.5)	40	Cs ₂ CO ₃	H ₂ O	15	> 99
24	2 (0.5)	40	K ₃ PO ₄	H ₂ O	15	76
25	Pd@CMK-3 (0.5)	40	K ₂ CO ₃	H ₂ O	15	15 ^[h]
26	Pd@CMK-3 (0.5)	40	K ₂ CO ₃	H ₂ O	15	15 ^[h]

[a] For the purpose of better comparison 5% Pd loadings were utilized for all studied supported palladium catalysts. [b] GC yields using biphenyl as internal standard after work-up. [c] The 5 wt % Pd/C catalyst was obtained from Merck Company. [d] About 10% benzoic acid was obtained as byproduct. [e] The reaction was carried out under solvent-free reaction conditions. [f] The reaction was carried out in the presence of 0.9 equivalents of K₂CO₃. [g] The reaction was carried out in the presence of 0.5 equivalents of K₂CO₃. [h] The reaction was carried out using the recovered Pd@CMK-3.

entry 6).^[24] A study of the same oxidation reaction in toluene and acetonitrile identified that this reaction was very sensitive to solvent, and interestingly pure water was the optimum choice of solvent (Table 1, entries 7–10). Next, catalyst loading was successfully reduced to 0.4 mol% without any loss of the reaction efficiency, while it was necessary to increase the reaction time to 24 h in order to ensure complete conversion (Table 1, entries 11, 12). It is worth noting that a further decrease in the catalyst loading from 0.4 mol% to lower ratios resulted in considerably lower yields (Table 1, entries 13, 14). Furthermore, no detectable oxidation occurred in the blank run and in those using the parent IFMC and CMK-3 or in the absence of solvent under the same reaction conditions (Table 1, entries 15–18). Notably, the present reaction is very sensitive to the amount of K₂CO₃ (entry 19, 20) and is very sluggish in the absence of K₂CO₃ even at 80 °C (Table 1, entry 21). To further determine the optimal experimental conditions, the impact of various bases such as K₂CO₃, Na₂CO₃, Cs₂CO₃, NaOH, and

K₃PO₄ were also studied. While all bases gave good-to-excellent product yields, only K₂CO₃ and Cs₂CO₃ resulted in quantitative formation of acetophenone under otherwise optimized reaction conditions (Table 1, entries 12, 22–25). We have chosen to employ K₂CO₃ as the base in the subsequent studies because it is much less expensive than Cs₂CO₃.

With the optimal reaction conditions established, we next examined the scope of this new catalytic aerobic oxidation

Table 2. Aerobic oxidation of benzylic alcohols using Pd@IFMC 2 on water.

	Ar	R	t [h]		Yield [%] ^[a]	
			O ₂	air	O ₂	air
1	Ph	H	5	10	> 99 ^[b]	> 99 ^[b]
2	4-(Cl)-C ₆ H ₄	H	12	24	> 99 ^[b]	> 99 ^[b]
3	3-(Cl)-C ₆ H ₄	H	10	24	> 99 ^[b]	> 99 ^[b]
4	4-(MeO)-C ₆ H ₄	H	2	8	> 99 ^[b]	> 99 ^[b]
5	4-(Me)-C ₆ H ₄	H	3	8	> 99 ^[b]	> 99 ^[b]
6	Ph	Me	12	24	> 99	91 ^[b]
7	Ph	Et	15	24	> 99	90 ^[b]
8	Ph	CH ₂ Ph	18	24	> 99	83 ^[b]
9	PhC(O)	Ph	10	24	> 99	> 99 ^[b]
10	Ph	Ph	24	24	> 99	78 ^[b]
11	cyclohexyl	Ph	24		72	
12	3-pyridyl	Me	24		60	
13	4-(MeS)-C ₆ H ₄	H	15		50	
14	Ph	H	24		> 99 ^[c]	
15	4-(Cl)-C ₆ H ₄	H	24		78 ^[c]	
16	3-(Cl)-C ₆ H ₄	H	24		82 ^[c]	
17	4-(MeO)-C ₆ H ₄	H	20		> 99 ^[c]	
18	4-(Me)-C ₆ H ₄	H	20		> 99 ^[c]	
19	2-(Cl)-C ₆ H ₄	H	24		92 ^[d]	
20	2,4-(Cl ₂)-C ₆ H ₃	H	24		87 ^[d]	

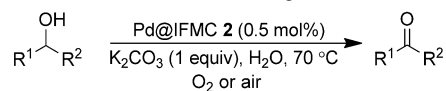
[a] GC yields. [b] 0.7 mol% of the catalyst. [c] Room temperature. [d] 70 °C.

reaction. As summarized in Table 2, various types of primary and secondary benzylic alcohols were selectively oxidized to their corresponding carbonyl compounds in excellent yields at 40 °C on water (Table 2, entries 1–11). It is also worth noting that the heterocyclic and heteroatom-containing alcohols are also compatible in this oxidation reaction (Table 2, entries 12, 13), which are generally problematic with many transition-metal-mediated aerobic oxidation protocols. It is interesting to note that highly efficient and selective aerobic oxidation of primary benzylic alcohols could be still achieved at room temperature (25–30 °C), but relatively longer reaction times were required for quantitative conversion (Table 2, entries 14–18). Such a high catalytic activity in the liquid-phase oxidation of alcohols on water at room temperature and at atmospheric pressure of O₂ using supported palladium catalysts has, to our knowledge, not yet been reported.^[22]

One of the interesting features of this protocol is its capability to oxidize sterically demanding substrates, although in these cases somewhat higher temperatures were needed to

obtain excellent results (Table 2, entries 19 and 20). Our preliminary studies showed that both aliphatic and allylic alcohols are less reactive than benzylic alcohols at room temperature and higher reaction temperatures of 70–80 °C were needed to ensure satisfactory product yields (Table 3).

Table 3. Aerobic oxidation of alcohols using Pd@IFMC **2** on water.



	R ¹	R ²	t [h]		Yield [%] ^[a]	
			O ₂	air	O ₂	air
1		1-octanol	24	24	98 ^[b]	67 ^[b]
2		2-octanol	24	24	90 ^[c]	58 ^[c]
3	PhCH ₂ CH ₂	Me	24		93 ^[c]	
4		cycloheptanol	24	24	98 ^[c]	54 ^[c]
5		cyclohexanol	24		95 ^[c]	
6	Ph(CH ₂) ₃	H	24		95 ^[b]	
7		2-cyclohexen-1-ol	15	24	>99	88 ^[c]
8		cinnamyl alcohol	24		84	
9		1-methyl-3-phenyl-2-propen-1-ol	24		80	
10		1,3-diphenyl-2-propen-1-ol	24		88	

[a] GC yields. [b] 1 mol % of the catalyst and 5 mol % of TEMPO at 80 °C. [c] 1 mol % of the catalyst at 80 °C.

Similarly, the present catalytic system was amenable to aerobic oxidation of both primary and secondary aliphatic alcohols, giving the respective carbonyl compounds in excellent yields with high selectivity (Table 3, entries 1–6) at 70–80 °C. In this regard, we discovered that several types of primary and secondary as well as cyclic allylic alcohols could also be effectively oxidized using the present catalyst system and gave good-to-excellent yields of the corresponding carbonyl products at 70–80 °C under otherwise similar reaction condition (Table 3, entries 7–10).

It is also worth mentioning that the present catalyst system could be utilized for oxidation of various types of alcohols, even while using the atmospheric pressure of air as oxidant (Tables 2 and 3). The major challenge when using small metal nanoclusters and metal-NP-supported catalyst systems is that their catalytic performance can rapidly diminish owing to the gradual agglomeration and formation of larger inactive aggregates.

To demonstrate the ability of IFMC to stabilize Pd nanoparticles and prevent the formation of Pd-black, the recyclability of **2** was examined by isolating the catalyst from the reaction mixture of aerobic oxidation of benzyl alcohol under optimal reaction conditions. In each run, after the completion of the reaction, the used catalyst was recovered by centrifugation and then washed with ethyl acetate and dichloromethane followed by large amounts of water to remove any remaining base. The recovered catalyst exhibited high but slowly decreasing activity over six consecutive runs (Figure 4 and Figure S18 in the Supporting Information). However, Pd leaching was determined by atomic absorption spectroscopy (AAS) to be less than 2 ppm. A HRTEM image of the recovered catalyst after the sixth re-

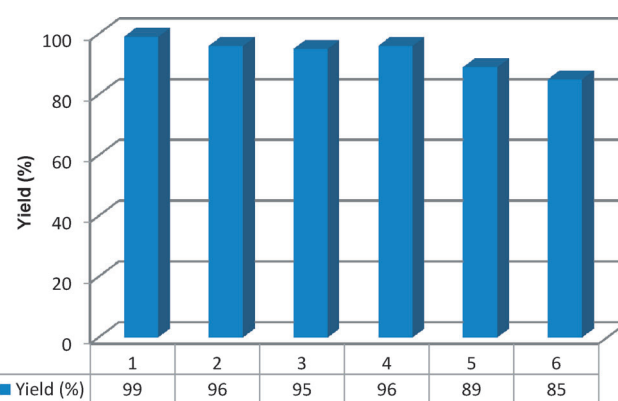


Figure 4. Recyclability chart of the aerobic oxidation of benzyl alcohol using Pd@IFMC **2**.

action run shows no appreciable difference in size and distribution of PdNPs compared to the fresh catalyst (Figure 5a).

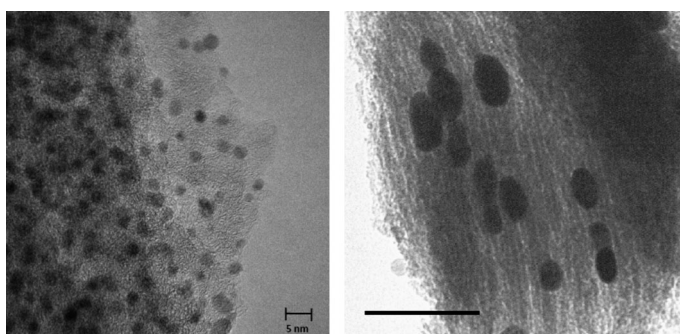


Figure 5. TEM images a) TEM image of the recovered catalyst after the 6th reaction runs (left) and b) Pd@CMK-3 from the aerobic oxidation of 1-phenylethanol on water (right). Scale bars are 5 nm in both images.

This result clearly indicates that no significant agglomeration of PdNPs occurred during the aerobic oxidation reaction. Therefore, the slowly decreasing in catalyst activity may be to some extent due to loss of Pd at the ppm level and also the partial loss of the catalyst during the recovery and washing stages. The N₂ physisorption measurement of the recovered catalyst also revealed an isotherm characteristic for mesoporous material with capillary condensation step at $p/p_0 \approx 0.4$ –0.8. The mean pore diameter and pore volume, as determined from the adsorption branch by the BJH method, are 2.42 nm and 0.52 cm³ g⁻¹, respectively. The surface area, evaluated by the classical BET method, was 529 m² g⁻¹. This nitrogen adsorption isotherm shows that, even after six runs, the material mostly retains its initial porosity and nanostructure.

Based on XPS data and ET studies, one reason for higher activity of **2** compared to Pd@CMK-3 and Pd/C in the aerobic oxidation of alcohols on water might be due to the presence of nitrogen functionalities inside the carbon structure and also the fibrous nature of our materials. The presence of

nitrogen heteroatoms in the carbaceous framework might also be responsible for the relatively uniform distribution of PdNPs throughout the mesoporous structure and the inhibition of Pd agglomeration during the reaction, resulting in high durability, high stability, and recycling characteristics of **2**. In order to further clarify this issue, we isolated Pd@CMK-3 from the aerobic oxidation of benzyl alcohol under optimal reaction conditions. The recovered Pd@CMK-3 was then studied by using transmission electron microscopy to hopefully find a reason for the lower activity of Pd@CMK-3. As can be clearly seen in this image (Figure 5b vs. 5a) Pd@CMK-3 showed an extensive agglomeration after the first reaction cycle under our described reaction conditions. This observation supports the notion that the extensive agglomeration of PdNPs in Pd@CMK-3 during the first reaction cycle is the major reason for its lower observed activity (Table 1, entry 25).

Conclusion

In conclusion, a novel mesoporous carbon (IFMC) with a unique nano-fibrous morphology was successfully prepared through the carbonization of ionic liquid 1-methyl-3-phenethyl-1*H*-imidazolium hydrogen sulfate (**1**) in the presence of SBA-15 as structural transducing agent. The material was then used as a powerful and effective support to stabilize PdNPs. The resulting composite material (Pd@IFMC; **2**) was shown for the first time to be an active catalyst for aerobic oxidation of alcohols with either molecular oxygen or air on water at room temperature and also at 40 °C, which is relatively low for such reactions. Remarkably, the current Pd@IFMC catalyst system shows much higher catalytic activity compared to Pd@CMK-3 and well-known Pd/C catalyst systems. It also shows superior reactivity than the previously reported metal NP/carbon catalyst systems on neat water at low temperatures. Besides the easy recovery and reusability of this catalyst, the employment of very mild reaction conditions and the possibility to perform the transformation in the absence of any organic solvent make this catalyst system a valuable candidate for green chemistry processes. We speculate that the unique properties discovered in the present nano-fibrillated mesoporous carbon would open new challenging areas in the design and synthesis of new types of supported catalyst systems employing various transition-metal nanoparticles for application in organic catalytic reactions under mild reaction conditions.

Experimental Section

General information: Pluronic P123 (EO₂₀PO₇₀EO₂₀ (EO = ethylene oxide, PO = propylene oxide), M_{av} = 5800) was purchased from Aldrich. Palladium(II) acetate was obtained commercially from Acros Organics. 1-Methylimidazole, 2-phenylethyl bromide, tetraethyl orthosilicate (TEOS), sulfuric acid (95–98%), hydrochloric acid (37%) and solvents were obtained from Merck Company and used without purification. (3-Mercaptopropyl)triethoxysilane and anhydrous potassium carbonate

were purchased from Fluka. 1,3-Dialkylimidazolium bromide was prepared according to standard methods and their purities were established before utilization by ¹³C NMR and ¹H NMR. Briefly, a solution of dry toluene (50 mL), freshly distilled 1-methylimidazole (73.1 mmol) and 2-bromo-1-phenylethane (80.3 mmol) was refluxed for 24 h under an argon atmosphere. The resulting two phase reaction mixture was then allowed to cool at room temperature. The separated ionic liquid (IL) layer was washed with dry toluene and dry Et₂O and dried under vacuum. The anion-exchange reaction was carried out in dry methylene chloride containing 1 mmol of 1,3-dialkylimidazolium bromide and 1 mmol of H₂SO₄. The solution was refluxed for 48 h until any hydrogen chloride by-product was removed. After evaporation of the solvent under vacuum, 1-methyl-3-phenethyl-1*H*-imidazolium hydrogen sulfate (MPIHS) **1** was isolated in good yield.

The carbonization process was performed in a Nabertherm furnace (L 3/11/P330) under an inert atmosphere of Ar. The pore structures of the prepared materials were observed by transmission electron microscopy (Philips CM-200 and Titan Krios TEM, see Supporting Information) and were verified further by the nitrogen sorption isotherm (Belsorp, BELMAX, Japan). The palladium content of the catalyst was determined using atomic absorption spectrometry (Varian) using the standard addition method. Gas chromatography analyses were performed on Varian CP-3800 using a flame ionization detector (FID) using suitable internal standards. NMR spectra were recorded using a Bruker (¹H frequency: 400 MHz, ¹³C frequency: 100 MHz).

Preparation of SBA-15: Briefly, 0.017 mol of pluronic P123 (EO₂₀PO₇₀EO₂₀ (EO = ethylene oxide, PO = propylene oxide), M_{av} = 5800, Aldrich) was dissolved in 193 mol of H₂O and 5.9 mol of concentrated HCl at 35 °C. Consequently, 1 mol of tetraethyl orthosilicate (TEOS) was added to the solution. The mixture was stirred vigorously at 35 °C for 20 h followed by an aging step at 80 °C for 24 h. The solid products were filtered off and washed with ethanol. After drying at room temperature, SBA-15 was obtained by subsequent removal of the surfactant by extraction with ethanol.

Preparation of IFMC (Ionic Liquid derived Nano Fibrillated Mesoporous Carbon): To synthesize IFMC, a dry acetonitrile solution of IL (1 mL of 1-methyl-3-phenethyl-1*H*-imidazolium hydrogen sulfate (MPIHS) **1** in 25 mL of acetonitrile) was added drop wise to a suspension of SBA-15 in acetonitrile. After 24 h of stirring at room temperature, the solvent was removed under reduced pressure. The resultant powder was impregnated with an aqueous solution of sulfuric acid (4 g H₂O, 0.14 g H₂SO₄) and placed at 100 °C in a vacuum drying oven. After 6 h, the oven temperature was increased to 160 °C and maintained for 6 h until a dark brown powder was obtained. MPIHS **1** (0.4 mL) was incorporated again into mesoporous silica hosts by the same procedure. The SBA-15/**1** composite was then kept in an argon flow at 900 °C for 3 h to carbonize the IL. In order to remove the silica template, the black powder was stirred in a solution of 2 M sodium hydroxide at 50 °C for 24 h. The filtered nanoporous carbon was washed several times with deionized water and ethanol and vacuum dried.

Preparation of Pd@IFMC 2 (IFMC-stabilized Pd nanoparticles): A suspension of IFMC (50 mg) in dry degassed THF (40 mL) was placed in a 100 mL round-bottom flask and sonicated for 30 min. Pd(OAc)₂ (0.036 mmol) was dissolved in THF (20 mL) and added to the IFMC suspension. To prepare the PdNPs onto IFMC, hydrazine hydrate (10 μL) was added to the suspension under vigorous stirring. After vigorous stirring at room temperature for 1 h, one drop of 30% H₂O₂ was added. The resulting Pd@IFMC **2** was filtered, washed several times with THF, and dried. The IFMC-stabilized PdNPs was stored in a sealed container.

Preparation of CMK-3 (carbon mesoporous from Korea):^[2a] Typically, the resultant template-free SBA-15 was impregnated with an aqueous solution of sucrose (1.25 g sucrose in 5 g H₂O) containing 0.14 g sulfuric acid and placed in a vacuum drying oven at 100 °C. After 6 h the oven temperature was increased to 160 °C and maintained for 6 h until a dark brown or black powder was achieved. The impregnation step was repeated once with sucrose (0.8 g). The resultant composite was kept in an argon flow at 900 °C for 2 h to carbonize the sucrose. In order to remove the silica template, the black powder was stirred in a solution of ethanol

and 1 M sodium hydroxide at 50 °C for 8 h. The CMK-3 carbon was filtered, washed several times with ethanol, and dried.

General procedure for the oxidation of alcohols: A mixture of alcohol (1 mmol), Pd@IFMC 2 (0.5 mol%), and K₂CO₃ (1.0 mmol) on pure deionized water (4 mL) was prepared in a two-necked flask. The flask was then evacuated and refilled with pure oxygen (balloon filled). The resulting mixture was stirred at 40 °C for the time indicated in Tables 2 and 3. The progress of the reactions were monitored by GC analysis using the internal standard method.

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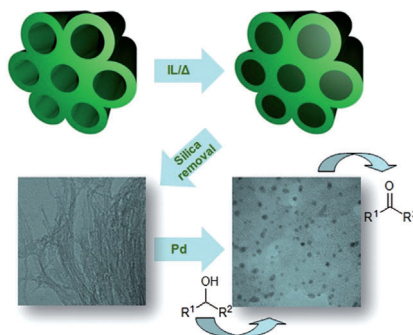
- [1] a) É. Sípós, G. Fogassy, A. Tungler, P. V. Samant, J. L. Figueiredo, *J. Mol. Catal. A Chem.* **2004**, *212*, 245–250; b) G. S. Chai, S. B. Yoon, J. H. Kim, J. S. Yu, *Chem. Commun.* **2004**, 2766–2767; c) F. B. Su, F. Y. Lee, L. Lv, J. J. Liu, X. N. Tian, X. S. Zhao, *Adv. Funct. Mater.* **2007**, *17*, 1926–1931; d) M. Sevilla, C. Sanchís, T. Valdés-Solís, E. Morallón, A. B. Fuertes, *J. Phys. Chem. C* **2007**, *111*, 9749–9756; e) X. Q. Wang, R. Liu, M. M. Waje, Z. W. Chen, Y. S. Yan, K. N. Bozhilov, P. Y. Feng, *Chem. Mater.* **2007**, *19*, 2395–2397; f) A.-H. Lu, W.-C. Li, Z. Hou, F. Schüth, *Chem. Commun.* **2007**, 1038–1040; g) K. I. Min, J. S. Choi, Y. M. Chung, W. S. Ahn, R. Ryoo, P. K. Lim, *Appl. Catal. A* **2008**, *337*, 97–104.
- [2] a) R. Ryoo, S. H. Joo, S. Jun, *J. Phys. Chem. B* **1999**, *103*, 7743–7746; b) S. H. Joo, S. J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki, R. Ryoo, *Nature* **2001**, *412*, 169–172; c) S. Jun, S. H. Joo, R. Ryoo, M. Kruk, M. Jaroniec, Z. Liu, T. Ohsuna, O. Terasaki, *J. Am. Chem. Soc.* **2000**, *122*, 10712–10713. For excellent reviews see: d) S. Polarz, M. Antonietti, *Chem. Commun.* **2002**, 2593–2604; e) F. Schüth, *Angew. Chem.* **2003**, *115*, 3730–3750; *Angew. Chem. Int. Ed.* **2003**, *42*, 3604–3622; f) A.-H. Lu, F. Schüth, *Adv. Mater.* **2006**, *18*, 1793–1805; g) J. Lee, J. Kim, T. Hyeon, *Adv. Mater.* **2006**, *18*, 2073–2094.
- [3] a) C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710–712; b) D. Zhao, J. Feng, Q. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka, G. D. Stucky, *Science* **1998**, *279*, 548–552; c) J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins, J. L. Schlenger, *J. Am. Chem. Soc.* **1992**, *114*, 10834–10843.
- [4] A.-H. Lu, A. Kiefer, W. Schmidt, F. Schüth, *Chem. Mater.* **2004**, *16*, 100–103.
- [5] A. Vinu, P. Shrinivasu, D. P. Sawant, T. Mori, K. Ariga, J. S. Chang, S. H. Jhung, V. V. Balasubramanian, Y. K. Hwang, *Chem. Mater.* **2007**, *19*, 4367.
- [6] W. Li, D. Chen, Z. Li, Y. Shi, Y. Wan, G. Wang, Z. Jiang, D. Zhao, *Carbon* **2007**, *45*, 1757–1763.
- [7] C. M. Yang, C. Weidenthaler, B. Spliethoff, M. Mayanna, F. Schüth, *Chem. Mater.* **2005**, *17*, 355–358.
- [8] M.-M. Titirici, A. Thomas, M. Antonietti, *J. Mater. Chem.* **2007**, *17*, 3412–3418.
- [9] Y. Shin, G. E. Fryxell, W. Um, K. Parker, S. V. Mattigod, R. Skaggs, *Adv. Funct. Mater.* **2007**, *17*, 2897–2901.
- [10] a) J. P. Paraknowitsch, J. Zhang, D. Su, A. Thomas, M. Antonietti, *Adv. Mater.* **2010**, *22*, 87–92; b) W. Yang, T.-P. Fellerger, M. Antonietti, *J. Am. Chem. Soc.* **2011**, *133*, 206–209.
- [11] a) J. S. Lee, X. Wang, H. Luo, G. A. Baker, S. Dai, *J. Am. Chem. Soc.* **2009**, *131*, 4596–4597; b) J. S. Lee, X. Wang, H. Luo, S. Dai, *Adv. Mater.* **2010**, *22*, 1004–1007.
- [12] See Supporting Information for experimental details.
- [13] A. B. Fuertes, *Microporous Mesoporous Mater.* **2004**, *67*, 273–281.
- [14] J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, *Handbook of X-ray Photoelectron Spectroscopy*, Physical Electronics, Eden Prairie, MN, **1995**.
- [15] Z. Jin, D. Nackashi, W. Lu, C. Kittrell, J. M. Tour, *Chem. Mater.* **2010**, *22*, 5695–5699.
- [16] a) J.-E. Bäckvall, *Modern Oxidation Methods*, Wiley-VCH, Weinheim, **2004**; b) T. Mallat, A. Baiker, *Chem. Rev.* **2004**, *104*, 3037–3058.
- [17] For more recent leading references on aerobic oxidation of alcohols in water see: a) N. Komiya, T. Nakae, H. Sato, T. Naota, *Chem. Commun.* **2006**, 4829–4831; b) Y. Uozumi, R. Nakao, *Angew. Chem.* **2003**, *115*, 204–207; *Angew. Chem. Int. Ed.* **2003**, *42*, 194–197; c) K. Mori, T. Hara, T. Mizugaki, K. Ebitani, K. Kaneda, *J. Am. Chem. Soc.* **2004**, *126*, 10657–10666; d) G.-J. ten Brink, I. W. C. E. Arends, R. A. Sheldon, *Science* **2000**, *287*, 1636–1639; e) B. Feng, Z. Hou, H. Yang, X. Wang, Y. Hu, H. Li, Y. Qiao, X. Zhao, Q. Huang, *Langmuir* **2010**, *26*, 2505–2513; f) Y. M. A. Yamada, T. Arakawa, H. Hocke, Y. Uozumi, *Angew. Chem.* **2007**, *119*, 718–720; *Angew. Chem. Int. Ed.* **2007**, *46*, 704–706; g) P. Maity, C. S. Gopinath, S. Bhaduri, G. K. Lahiri, *Green Chem.* **2009**, *11*, 554–561; h) Y. H. Ng, S. Ikeda, T. Harada, Y. Morita, M. Matsumura, *Chem. Commun.* **2008**, 3181–3183; i) H. Tsunoyama, H. Sakurai, Y. Negishi, T. Tsukuda, *J. Am. Chem. Soc.* **2005**, *127*, 9374–9375; j) J. Yang, Y. J. Guan, T. Verhoeven, R. Santen, C. Li, E. J. M. Hensen, *Green Chem.* **2009**, *11*, 322–325.
- [18] a) T. Mallat, A. Baiker, *Catal. Today* **1994**, *19*, 247–283; b) G. An, M. Lim, K.-S. Chun, H. Rhee, *Synlett* **2007**, 95–98.
- [19] a) P. Korovchenko, C. Donze, P. Gallezot, M. Besson, *Catal. Today* **2007**, *121*, 13–21; b) I. Reile, A. Paju, M. Eek, T. Pehk, M. Lopp, *Synlett* **2008**, 347–350; c) T. Mallat, C. Bronnimann, A. Baiker, *Appl. Catal. A* **1997**, *149*, 103–112.
- [20] a) G. J. Hutchings, S. Carrettin, P. Landon, J. K. Edwards, D. Enache, D. W. Knight, Y.-J. Xu, A. F. Carley, *Top. Catal.* **2006**, *38*, 223–230; b) Y. Önal, S. Schimpf, P. Claus, *J. Catal.* **2004**, *223*, 122–133.
- [21] S. Mori, M. Takubo, K. Makida, T. Yanase, S. Aoyagi, T. Maegawaz, Y. Monguchi, H. Sajiki, *Chem. Commun.* **2009**, 5159–5161.
- [22] To our knowledge there is only one example of aerobic oxidation of alcohols using homogeneous Pd(OAc)₂/Et₃N catalyst system at room temperature: M. J. Schultz, C. C. Park, M. S. Sigman, *Chem. Commun.* **2002**, 3034–3035.
- [23] N. Shapiro, A. Vigalok, *Angew. Chem.* **2008**, *120*, 2891–2894; *Angew. Chem. Int. Ed.* **2008**, *47*, 2849–2852, and the references therein.
- [24] a) B. Karimi, S. Abedi, J. H. Clark, V. Budarin, *Angew. Chem.* **2006**, *118*, 4894–4897; *Angew. Chem. Int. Ed.* **2006**, *45*, 4776–4779; b) B. Karimi, A. Zamani, S. Abedi, J. H. Clark, *Green Chem.* **2009**, *11*, 109–119.

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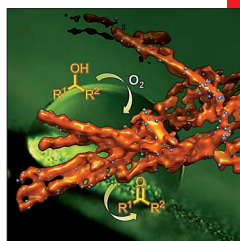
B. Karimi,* H. Behzadnia, M. Bostina,
H. Vali ■■■■-■■■■

A Nano-Fibrillated Mesoporous Carbon as an Effective Support for Palladium Nanoparticles in the Aerobic Oxidation of Alcohols “on Pure Water”



Chemical aerobics! A new nano-fibrillated mesoporous carbon were successfully prepared by the carbonization of the ionic liquid 1-methyl-3-phenethyl-1*H*-imidazolium hydrogen sulfate in the presence of SBA-15. The material was shown to be an efficient and highly exciting support for PdNPs catalyst in aerobic oxidation of alcohols with on pure water at temperature as low as 40 °C for the first time.

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The selective aerobic oxidation.....of alcohols to the corresponding carbonyl compounds occurs effectively “on water” in the presence of Pd nanoparticles (blue circles) supported on a novel nano-fibrillated mesoporous carbon (Pd@IFMC). The 3D-Electron tomogram of Pd@IFMC is depicted on a drop of water (as the background) to highlight the “green” feature of the process. For more information see the Full Paper by B. Karimi et al. on page ■ ■ ff.