# Molecular level dispersed Pd clusters in the carbon walls of ordered mesoporous carbon as a highly selective alcohol oxidation catalyst†

**An-Hui Lu, Wen-Cui Li, Zhenshan Hou and Ferdi Schüth**

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**Ordered mesoporous carbon containing molecular-level dispersed Pd clusters in the carbon walls can be synthesized by the nanocasting pathway, which shows high selectivity for the oxidation of alcohols to aldehydes.**

The synthesis of novel catalysts with well-designed composition and structure tailored to the requirements of a particular application is one of the most active fields in catalysis research. Since some material parameters can nowadays be controlled on the atomic scale, a true design of catalytic materials seems to become possible. Mesoporous materials, which are among the most investigated catalytic solids in the past decade, have properties such as high surface area, narrow pore size distribution, associated with controllable composition and morphology, which are highly desired for catalysis applications and the tailoring of catalytic materials.[1] Moreover, the surface of the mesoporous materials can be further functionalized by physical or chemical methods to meet specific requirements in catalysis.

Generally, the functionalization strategies can be divided into four groups, if a mesoporous material is considered as a 3D grain, consisting of the external surface of the whole grain, channels within the grain, and the pore walls. (1) Functionalization of the external surface of the entire grain. One example for this strategy is the design of magnetically separable catalysts. Magnetic nanoparticles were selectively deposited on the external surface of mesoporous carbon or silica by reversibly blocking and opening the pore system.[2] (2) Functionalization of the inner mesopore surface. Most work has been focussed on porous silica materials,[3] such as modification of the surface by silylation.[4] (3) Doping of nanoparticles into the pore channels. This is quite general, and a conventional way for designing metallic nanoparticles supported on mesoporous materials by inclusion chemistry and impregnation, well known in catalyst preparation for other support materials for more than a century.[5] The last strategy (4), is the modification the pore walls by introducing foreign atoms, molecules or nanoclusters. This strategy has been widely used for the synthesis of organosilica materials, *e.g.* to incorporate organic species as bridges between silicon atoms in the wall.[6] The advantage of strategy (4) over strategy (3) is to keep the mesopores open and thus avoiding pore blocking effects, especially at high loadings. Therefore, porous materials prepared by this strategy can maintain the mesopore properties, *i.e.* facilitated mass transfer. Holmes *et al.* reported a method for fabrication of CMK-1 containing cobalt nanoparticles in the carbon wall.[7] The synthetic procedure consists of impregnation of cobalt nitrate solution into the MCM-48 template, followed by calcination and reduction, subsequent introduction of sucrose into the hard template, and finally, *via* carbonization and removal of silica, the cobalt containing CMK-1 was obtained. Woo and co-workers prepared ordered mesoporous carbon (CMK-3) with Pt nanoparticles (1–5 nm) embedded in the carbon walls using a similar method as Holmes.[8] The obtained Pt/CMK-3 can be used as a methanol-tolerant cathode material in direct-methanol fuel cells.

Despite the achievements reached by the aforementioned methods, the synthesis of atomically dispersed metallic nanoparticles on ordered mesoporous supports is still a challenge. Especially in the case of noble metals, it is important to prepare them with sizes as small as possible and highly dispersed throughout the support, in order to improve the catalytic efficiency and to minimize the cost. Molecular metal catalysts can be dispersed at the molecular level in a reactant, but recovering the expensive catalyst metals and ligands from the reaction mixture later on can be a problem. Solid catalysts are relatively easy to recycle, the preparation of stable metal species smaller than several nanometers in size, however, can be difficult.

In the present work, we report a successful synthesis of Pd supported on ordered mesoporous carbon (Pd-OMC), where highly temperature stable, molecular level dispersed Pd clusters ($<1$ nm) are uniformly embedded in the carbon walls. Pd supported on carbon (amongst other supports) has been used in the selective oxidation of alcohols to aldehydes, one of the most important fundamental transformations in synthetic chemistry.[9,10] However, Pd particle sizes in these catalysts typically are several nanometers, and some of these systems suffer from either from low activity or low selectivity. In contrast, our results show that the Pd-OMC exhibits strikingly high selectivity ($>99\%$) for alcohol (benzyl alcohol, 1-phenylethanol and cinnamyl alcohol) oxidation to the corresponding aldehydes while at the same time having relatively high activity. The synthetic pathway for preparing this material is shown in Fig. 1. After incorporation of polyacrylontrile (PAN) in the pore system of SBA-15 following published procedures,[11] the following steps are carried out. (1) Oxidation of PAN incorporated in the pore system of SBA-15 to improve the cross linking of PAN molecules. (2) Immersing the composite into $Pd(NO_3)_2$ aqueous solution to adsorb Pd cations by nitrogen groups. (3) Pyrolysis of the composite under argon to obtain the SBA-15/carbon composite. (4) Leaching out silica by NaOH or HF aqueous solution to generate Pd-OMC.

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*Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470, Mülheim an der Ruhr, Germany.*
*E-mail: schueth@mpi-muelheim.mpg.de; Fax: 0049 208 306 2395*

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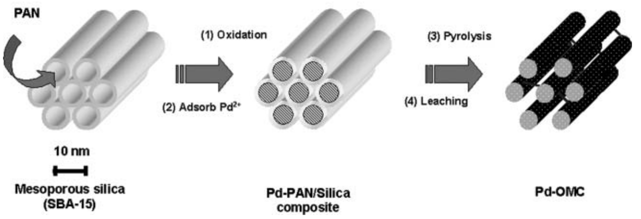

**Fig. 1** Schematic illustration of the synthetic procedure for Pd-OMC.

High-resolution TEM analysis was first applied to investigate the dispersion of the Pd clusters in the carbon support as well as the nanostructure of the carbon. As seen in Fig. 2, one can see the parallel lines that are characteristic for the ordered structure with hexagonal symmetry seen normal to the channel axis. Very few, on the order of five, Pd particles (of size 20 nm) are present on the external surface of a carbon grain, as seen in Fig. 2(a). In principle, incipient wetness brings the major amount of PAN precursor into the pores of SBA-15 due to the capillary force. However, it is inevitable that a small amount of the PAN species covers the external surface of the SBA-15 template. These PAN species can chemically adsorb Pd cations as well through their nitrogen groups. During the pyrolysis, the Pd cations on the external surface sinter to form larger clusters since no obstacle hinders the movement of the Pd clusters. However, inspecting the whole Pd-OMC sample by TEM, only a rather small number of such large Pd clusters can be found. At high magnification (Fig. 2(b)), it is difficult to find visible Pd clusters in the carbon framework. However, palladium is definitely present in the sample, as EDX analyses verifies the presence of Pd at a concentration of about 1.3 wt% with little deviation for different analysis spots. This indicates that Pd is homogeneously distributed throughout the entire sample, and that the Pd clusters – if there are any – are smaller than 1 nm in size.

Generally, noble metals easily form large particles on a flat surface at elevated temperatures, as often observed for catalysts prepared by impregnation and reduction. In our synthesis route, the nitrogen groups of the PAN molecules are anchors for chemically bonded $Pd^{2+}$-species, which are predominantly deposited in the pores of the SBA-15 template. During pyrolysis up to 750 °C, the Pd clusters have no possibility to grow, since they are confined/stabilized by the carbon framework and the silica walls. It was found that the formation of the large Pd particles on the external surface can be minimized by decreasing the concentration of the Pd solution and the pyrolysis temperature. TEM images (Fig. 2(c) and (d)) of sample Pd-OMC*, prepared using a lower concentration $Pd(NO_3)_2$ solution (40% of the more highly concentrated solution) and low pyrolysis temperature (650 °C), show almost no visible Pd particles, either on the external surface of the carbon supports or in the carbon walls. The EDX analysis shows a small peak at the position where Pd signals are expected, but it can not clearly be distinguished from the background noise. Therefore, the Pd content should be at or below the detection limit for Pd, which is around 1%. The presence and accessibility of Pd clusters are confirmed by the following catalytic test. These results confirm that the proposed synthetic procedure is advantageous compared to the impregnation method and direct pyrolysis of noble metal containing carbon precursors, where typically noble metal nanoparticles with bigger sizes and a broad size distribution are formed.[7,12]

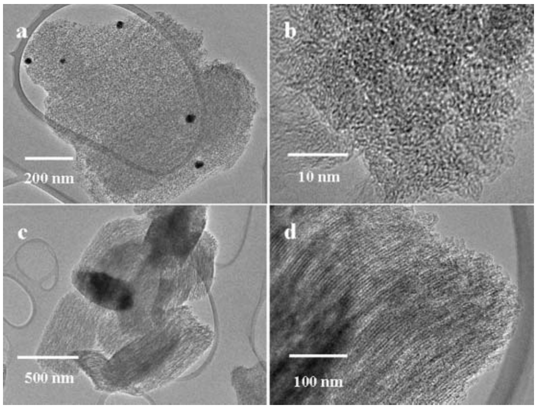

**Fig. 2** TEM images of Pd-OMC (high loading of Pd; a and b) and Pd-OMC* (low loading of Pd; c and d).

The structures of Pd-OMC and Pd-OMC* were further characterized by X-ray powder diffraction (XRD). The recorded XRD patterns are shown in Fig. 3, and a representative low-angle XRD pattern of Pd-OMC is shown as an inset to Fig. 3. The low-angle XRD pattern with well-resolved reflections proves the ordered structure of the Pd-loaded carbon, which is consistent with the TEM observation. The wide-angle XRD reflection of Pd-OMC shows reflections resulting from metallic Pd with only very low intensity and no reflection is observed which could be attributed to PdO. In contrast, the XRD pattern of Pd-OMC* synthesized with low Pd-concentration solution does not exhibit any detectable reflection from Pd, indicating that the Pd particles are too small to be detected by XRD and/or the Pd concentration is too low. This is also consistent with the TEM observations.

The pore structure of the OMC with Pd particles was determined by nitrogen sorption measurements, and isotherms are plotted in Fig. S1 (ESI†). All the isotherms are of type IV and exhibit hysteresis loops in the mesopore range. The specific surface area and pore volume are as high as 1000 $m^2\ g^{-1}$ and 1.0 $cm^3\ g^{-1}$, respectively. The pore size distributions were calculated by the BJH (Barrett–Joyner–Halenda) algorithm based on the adsorption branch (since the closure of the hysteresis occurs at about $p/p_0$ = 0.42, artefacts can not be excluded and therefore the adsorption branch was used) and are shown as an inset to Fig. S1 (ESI†). In the presence of Pd species, the obtained samples show an obvious

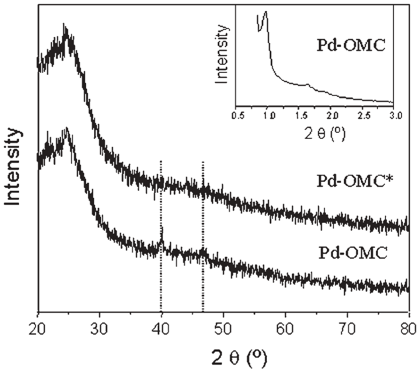

**Fig. 3** XRD patterns of Pd-OMC (high loading of Pd) and Pd-OMC* (low loading of Pd), Inset: Low-angle XRD pattern of Pd-OMC.

**Table 1** Oxidation of benzyl alcohol, 1-phenylethanol and cinnamyl alcohol by Pd-OMC and Pd-OMC*

| Substrate | $R_T$[a]/°C | $D$[b]/g ml$^{-1}$ | $X$[c] (%) | $S$[d] (%) |
|---|---|---|---|---|
| Benzyl alcohol | 80 | 0.52 | 42.3 | >99 |
| Benzyl alcohol | 100 | 0.52 | 78.4 | >99 |
| 1-Phenylethanol | 80 | 0.52 | 35.2 | >99 |
| Cinnamyl alcohol | 80 | 0.52 | 82.5 | >99 |
| Cinnamyl alcohol[e] | 80 | 0.52 | 44.7 | >99 |

[a] $R_T$: reaction temperature. [b] $D$: density of the reactant in the autoclave. [c] $X$: conversion. [d] $S$: selectivity to aldehyde. [e] Using Pd-OMC* with low Pd loading as catalyst.

bimodal pore system with increasing mesopore sizes. For Pd-OMC* pyrolyzed at 650 °C, the pore sizes are about 3.3 and 11 nm; whereas for Pd-OMC pyrolyzed at 750 °C, the pore sizes are about 3.0 and 11 nm. As we reported before, the presence of the bimodal pore size distribution implies well-developed pore interconnectivity and the accessibility of the pore system.[11] The improved pore interconnectivity can be better seen from the continuous uptake at higher relative pressure in the isotherms, which is different from the isotherm of normal CMK-3.[13] As earlier revealed by XPS analyses, PAN-based OMC contains different types of nitrogen groups depending on the pyrolysis temperature, mainly pyridinic and pyrrollic groups.[14] Additionally, here FTIR spectroscopy was used to analyze these samples. The FTIR spectra (not shown) of Pd-OMC, Pd-OMC* and OMC are quite similar to each other, and there are mainly three bands related to nitrogen containing groups. The band at 2222 cm$^{-1}$ is assigned to –C≡N stretching modes. The broad band with a peak appearing at 1602 cm$^{-1}$ is characteristic for carbon carbonized at low temperature and assigned to the stretching of C=C and C=N bonds, with a possible contribution from asymmetric stretching vibrations of –COO$^-$ groups. The broad band at 1300 cm$^{-1}$ is related to the symmetric stretching vibrations of COO$^-$ groups, and C–O, C–N and C–C stretching vibrations. FT-IR analysis thus supports the previous XPS result that N-containing groups are present in the materials.

The catalytic activity of Pd-OMC was tested in alcohol oxidation to give the aldehyde using supercritical $CO_2$ as reaction medium, and the results are compiled in Table 1. Alcohols including benzyl alcohol, 1-phenylethanol and cinnamyl alcohol were used as substrates. As seen from Table 1, under the conditions used, the selectivity to the corresponding aldehyde is in all cases higher than 99%. No detectable acid was found in the product, indicating that the alcohol was selectively converted to aldehyde. Even after a reaction time of 13 h no over-oxidation occurred. In the case of benzyl alcohol oxidation, the conversion was increased by nearly a factor of two when the temperature was raised from 80 to 100 °C. Repeated tests show similar activity and selectivity in subsequent runs, indicating the reusability and stability of the catalyst. The increased conversion observed for cinnamyl alcohol might be related to enhanced interaction between cinnamyl alcohol molecules and Pd-OMC due to the conjugated π-system. The conversion of cinnamyl alcohol over time at a reaction temperature of 80 °C is shown in Fig. S2 (ESI†). The plotted run is the second one for this catalyst. As can be seen, the reaction rate is high before 4.5 h, until the conversion of cinnamyl alcohol to its aldehyde exceeds 70%. However, then the reaction stops and the conversion reaches a plateau, possibly due to poisoning by the product. The recycled catalyst shows identical catalytic performance, indicating the good stability of the catalyst. For comparison, the same amount (based on mass) of Pd-OMC* with low Pd loading was used as catalyst for cinnamyl alcohol oxidation. For this catalyst, the selectivity is also higher than 99%. However, the conversion is lower than that of Pd-OMC, which is due to the lower Pd content. Our catalyst thus has superior performance compared to a previous Pd on activated carbon (5 wt% of Pd loading) catalyst which shows lower selectivity (78%) due to the over-oxidation of aldehyde to acid.[10]

In summary, we have established a synthetic pathway to create a Pd-OMC catalyst with almost atomic dispersion of the metal in a highly controlled manner, which has excellent catalytic properties in the oxidation of alcohols. It should be possible to generalize the synthetic strategy also to the synthesis of other highly dispersed noble metal species in the carbon walls, while keeping the mesopores open without any blocking effect.

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