Characterization and catalytic activity of palladium dispersed on Kratschmer–Huffman (K–H) soot

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Palladium dispersed on K–H soot, both before and after extraction with solvents, is shown to exist in a range of oxidation states and is an active catalyst for the disproportionation of cinnamyl alcohol to cinnamaldehyde and dihydrocinnamyl alcohol under conditions where a commercial Pd/C catalyst is inactive.

Despite the tremendous amount of research in recent years on C_{60} and fullerenes in general, there have been relatively few studies on the nature of the soot produced by the Kratschmer–Huffman (K–H) technique[1] both before and after extraction with different solvents. There have, however, been reports describing the residual soot after extraction with solvents such as toluene and trichlorobenzene (TCB) as consisting of bucky tubes[2] or giant fullerenes.[3]

We have recently shown[4] from oxidative stability studies that K–H soot after extraction with toluene and subsequently with TCB has, rather surprisingly, a lower oxidative stability compared to fullerenes. This clearly indicated that solvent-extracted K–H soot still contained fullerene-like materials and was therefore different from the other forms of carbon. Consequently, since Pd/C is a well known commercial catalyst, we have in the present work dispersed palladium on K–H soot both before and after extraction with toluene and TCB, characterized the palladium/soot samples and evaluated their catalytic activity. It is shown that dispersion of $Pd(NO_3)_2$ on the different soot samples, followed by reduction of the $Pd(NO_3)_2$ with excess formaldehyde, leads to the palladium on the soot samples being present in a range of oxidation states. The dispersed palladium selectively catalyses the oxidation of one of the components of the soot. Also, these Pd/soot samples show good catalytic activity in the disproportionation of cinnamyl alcohol to cinnamaldehyde and dihydrocinnamyl alcohol. Under identical conditions, a commercial Pd/C catalyst is virtually inactive.

The soot was produced by the contact-arc vaporization of graphite.[1] The condensed soot (S) was extracted repeatedly with toluene to ensure all soluble fullerenes had been extracted. This residual soot S_1 was then refluxed twice with 500 ml portions of TCB and the TCB-insoluble soot coded as S_2. The soot samples S_1 and S_2 were heated under a nitrogen atmosphere at 200 and 300 °C respectively for 4 hours to remove the last traces of any solvent. The dispersion of palladium on the soot samples was done *via* the published method.[5] This involved the dispersion of palladium nitrate on the soot samples in an aqueous medium followed by the reduction of the palladium nitrate with formaldehyde.

The TGA, in an oxygen atmosphere, of the Pd/soot samples show that oxidation takes place in two distinct stages with the major portion of all the samples undergoing very rapid oxidation below 400 °C and the remaining part getting oxidized much more slowly at temperatures of over 600 °C. We have shown from previous studies[5] that S, S_1 and S_2 without any palladium dispersed on them have peaks in the differential TGA patterns (at 408, 377 and 368 °C, respectively) corresponding to the oxidation of their major component. Interestingly, on the dispersion of palladium, not only does the oxidation of the major component of the soot samples take place much faster, with the differential TGA peak being very sharp, but there is also quite a substantial reduction in the oxidation temperature from 408 to 282 °C in the case of Pd/S. The reduction is less dramatic in the cases of Pd/S_1 and Pd/S_2 (from 377 to 341 °C and from 368 to 345 °C, respectively). The oxidation of the other component which takes place above 600 °C is essentially unaffected by the palladium dispersed on it, with the peaks in the differential TGA pattern remaining broad, indicating that the oxidation of this component of soot is not catalysed by the dispersed palladium.

The XPS of the palladium dispersed on the different soot samples show that the palladium is present in a range of oxidation states as evident from the very broad experimental peak observed in all three soot samples. The experimental peak in the case of Pd/S can be curve-fitted with three pairs of peaks with the binding energies (E_B) of the $3d_{5/2}$ state being 334.7, 336.2 and 338.4 eV and a spin–orbit splitting of the $3d_{5/2}$ and $3d_{3/2}$ states of 5.4 eV. The peaks at 334.7 and 338.4 eV can be assigned[6] to Pd^0 and Pd^{2+}, respectively. The peak at 336.2 eV would then correspond to a palladium species with an oxidation state intermediate between 0 and +2. The E_B values for the $3d_{5/2}$ state of palladium in the case of Pd/S_1 are 334.8, 336.0 and 338.1 eV and the corresponding values for Pd/S_2 are 334.6 eV, 336.2 eV and 338.3 eV. In the case of palladium dispersed on activated carbon under conditions identical to those employed for the soot samples, the XPS showed only one pair of peaks with the E_B of the $3d_{5/2}$ state being 334.8 eV and a spin–orbit splitting of 5.3 eV corresponding to Pd^0 species.

It is evident, therefore, that under conditions where $Pd(NO_3)_2$ is reduced to the metal on activated carbon, the $Pd(NO_3)_2$ in the case of the soot samples undergoes only partial reduction to give a range of oxidation states. Fullerenes are known to be very good electron acceptors[7] with C_{60} being capable of accepting up to six electrons. However, it would appear from the present work that soot samples, even after extraction of the soluble fullerenes with solvents, have electron acceptor properties.

Since the palladium dispersed on the soot samples was present in a range of oxidation states and was found to catalyse the oxidation of the soot samples, the catalytic activity of the three Pd/soot samples was evaluated as such without attempting any further reduction of the dispersed palladium. To investigate the potential of the Pd/soot samples as oxidation catalysts, the oxidation of cinnamyl alcohol was attempted. It was found that on refluxing the catalyst with cinnamyl alcohol in toluene under an atmosphere of oxygen, 74% conversion to an almost equimolecular mixture of cinnamaldehyde and dihydrocinnamyl alcohol was observed (Table 1). In the cases of the Pd/S_1 and Pd/S_2 samples a similar disproportionation took place although the yields were lower. Under identical conditions a commercial Pd/C catalyst gave a conversion of 4% and the sample of palladium dispersed on activated carbon showed no activity.

On repeating the reaction in an argon atmosphere, a similar disproportionation of cinnamyl alcohol was observed although the conversions were a little lower in the case of Pd/S. The high activity of the Pd/soot samples for the disproportionation of cinnamyl alcohol can perhaps be attributed to the dispersed palladium being present in different oxidation states with the oxidized palladium species acting as sites for dehydrogenation and the Pd^0 centres being responsible for hydrogenation.

It is evident, therefore, that the behaviour of palladium dispersed on K–H soot both before and after extraction with solvents is very different from that of palladium dispersed on conventional carbon supports. In the case of the soot samples the dispersed palladium nitrate precursor on reduction with excess formaldehyde undergoes only partial reduction to give a range of oxidation states between 0 and +2 whereas under identical conditions the palladium nitrate dispersed on activated carbon is reduced to Pd^0. The dispersed palladium in the case of the Pd/soot samples selectively catalyses the oxidation of one of the components of soot. Also the Pd/soot samples are very good catalysts for the disproportionation of cinnamyl alcohol to a mixture of cinnamaldehyde and dihydrocinnamyl alcohol whereas under identical conditions a commercial Pd/C catalyst is inactive. Our results therefore gain significance in view of the fact that carbon is a very important support for several industrially useful metal-supported catalysts. More recently[8] nanotubes have been used as supports for metals such as Ru, Fe and Fe–Cu but our studies indicate that metals dispersed on K–H soot itself could function as novel and active catalysts. Further studies in this direction are being done.

Table 1 Disproportionation of cinnamyl alcohol on Pd/soot samples

Catalyst	Atmosphere	Conv. (%)	Cinnamaldehyde (%)	Dihydrocinnamyl alcohol (%)
Pd/S	O_2	74	37	36
	Ar	67	34	32
Pd/S_1	O_2	44	22	20
	Ar	41	21	19
Pd/S_2	O_2	42	21	20
	Ar	40	20	18
Pd/C	O_2	4	1.2	1.8
	Ar	3	1.7	1.3

Catalyst corresponding to 0.01 mmol palladium was refluxed with 2 mmol cinnanyl alcohol and 10 ml of toluene under an oxygen or argon atmosphere for 5 h.

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Footnotes

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