SUPPORT INFORMATION

Computational Study

Platinum Electrodeposition on Unsupported Carbon Nano-Onions

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Energy calculations for the first ten orbitals of coronene and corannulene were carried out. A summary, including the first three orbitals following the frontier orbitals HOMO and LUMO, is shown in Tables 1 and 2. For both structures, we considered only those

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atoms containing central hexagon or pentagon. Figure 9 of the manuscript shows the structures of interest for both coronene and corannulene, with the final Pt atom location.

Table 1. Orbitals and population distribution for the system using coronene as calculation basis with ONIOM (QM/MM).

	CNOs	1Pt/CNOs	2Pt/CNOs	3Pt/CNOs
HOMO-3	C(1)-p=0.15	Pt(1)-d=0.36	Pt(2)-d=0.30	Pt(1)-d=0.28
	C(6)-p=0.15		Pt(1)-d=0.16	Pt(3)-d=0.27
	C(4)-p=0.14			
	C(3)-p=0.13			
HOMO-2	C(2)-p=0.19	Pt(1)-d=0.46	Pt(2)-d=0.30	Pt(2)-d=0.27
	C(5)-p=0.19		Pt(1)-d=0.29	Pt(3)-d=0.22
				Pt(1)-d=0.22
HOMO-1		Pt(1)-d=0.83	Pt(2)-d=0.47	Pt(2)-d=0.42
			Pt(1)-d=0.44	Pt(3)-d=0.25
				Pt(1)-d=0.25
HOMO		Pt(1)-d=0.67	Pt(1)-d=0.38	Pt(3)-d=0.23
			Pt(2)-d=0.36	Pt(1)-d=0.23
				Pt(2)-d=0.15
LUMO		Pt(1)-s=0.64	Pt(2)-s=0.23	Pt(2)-s=0.17
			Pt(1)-s=0.20	Pt(2)-d=0.15
			Pt(1)-d=0.11	Pt(3)-s=0.10
			Pt(2)-d=0.10	Pt(1)-s=0.10
LUMO+1			Pt(1)-s=0.24	Pt(3)-s=0.22
			Pt(2)-s=0.16	Pt(1)-s=0.22
				Pt(2)-p=0.12
LUMO+2	C(4)-p=0.18			
	C(1)-p=0.18			
LUMO+3	C(3)-p=0.17	C(3)-p=0.14		
	C(6)-p=0.16	C(2)-p=0.14		
	C(2)-p=0.11	C(6)-p=0.10		
	C(5)-p=0.10	Pt(1)-d=0.10		
		C(5)-p=0.10		

QM was calculated with LSDA/D95 for C atoms and LSDA/SDD for Pt atoms. Orbital data correspond to HOMO-LUMO energy and first three HOMO and LUMO levels with respect to the central hexagon where Pt atoms were located.

Table 2. Orbitals and population distribution for the system with the corannulene as calculation basis using ONIOM (QM/MM).

	CNOs	1Pt/CNOs	2Pt/CNOs	3Pt/CNOs
HOMO-3		Pt(1)-d=0.81	Pt(2)-d=0.50	Pt(3)-d=0.59
			Pt(1)-d=0.35	Pt(1)-d=0.17
				Pt(2)-d=0.16
HOMO-2		Pt(1)-d=0.28	Pt(1)-d=0.40	Pt(3)-d=0.25
		C(5)-p=0.11	Pt(2)-d=0.25	Pt(1)-d=0.23
		C(2)-p=0.11	Pt(1)-s=0.10	Pt(2)-d=0.23
HOMO-1	C(4)-p=0.21	Pt(1)-d=0.94	Pt(1)-d=0.47	Pt(1)-d=0.32
	C(1)-p=0.14		Pt(2)-d=0.47	Pt(2)-d=0.32
	C(2)-p=0.14			
HOMO	C(5)-p=0.19	Pt(1)-d=0.79	Pt(1)-d=0.39	Pt(3)-d=0.39
	C(3)-p=0.18	Pt(1)-s=0.10	Pt(1)-d=0.39	Pt(1)-d=0.27
				Pt(2)-d=0.27
LUMO		Pt(1)-s=0.48	Pt(2)-s=0.18	Pt(1)-s=0.15
			Pt(1)-s=0.18	Pt(2)-s=0.15
				Pt(3)-d=0.11
LUMO+1			Pt(1)-s=0.26	Pt(2)-s=0.14
			Pt(2)-s=0.26	Pt(1)-s=0.14
			Pt(2)-p=0.13	
			Pt(1)-p=0.13	
LUMO+2		Pt(1)-s=0.12		Pt(3)-s=0.18
LUMO+3		Pt(1)-p=0.14		Pt(3)-p=0.12
		C(4)-p=0.12		Pt(3)-s=0.10
		Pt(1)-d=0.10		
		C(3)-p=0.10		

QM was calculated with LSDA/D95 for C atoms and LSDA/SDD for Pt atoms. Orbital data correspond to HOMO-LUMO energy and first three HOMO and LUMO levels with respect to the central hexagon where Pt atoms were located.

Isolated CNOs, supported by the coronene, have an electronic population distribution in deeper orbitals. The opposite occurs for the system containing the corannulene. Electronic population is included for all C pentagon atoms with a single intervention of HOMO and HOMO-1 orbitals. Opposite to CNOs considering coronene, in the

corannulene case, electronic distribution was not present in the first LUMO orbitals. When a Pt atom is included, electronic concentration in d orbitals at the HOMO and HOMO-1 levels is observed for both systems. However, this value is larger in regards to the population contribution for the system containing the corannulene. Pt atom s orbitals contribute in the LUMO, even for the system containing the corannulene with contributions in p orbitals at the LUMO+3. For HOMO-1 HOMO-2 and HOMO-3 in the system with the corannulene, the electronic calculation at d orbitals continues to be larger for CNOs with 2Pt with respect to system containing the coronene. Considering 2Pt/CNOs, at HOMO-2, HOMO-1 and HOMO, a similar distribution on d orbitals appears in both structures with coronene and corannulene. Only the coronene showed d orbitals at LUMO. This electronic acceptor capability enhances its catalytic properties. Finally, for calculations with three Pt atoms, HOMO and LUMO orbitals presented similar behavior. However, the system containing the corannulene presented a superior d-orbitals contribution for HOMO. The presence of a larger d orbital contribution, at HOMO level, may be associated to a larger capability to form other compounds. As it occurred in the 2Pt/CNOs case, 3Pt/CNOs catalytic capacity is enhanced at the coronene structure due to a small increment in d orbitals, at LUMO electronic contribution.