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High Efficient Pd Based Core-Shell Nanowire Catalysts for O_2 Dissociation

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Abstract:

The adsorption and dissociation of O_2 on the core-shell M@Pd nanowires (M=3d, 4d, 5d transition metals) are studied using the first-principles density functional method. Suitable core atoms are determined based on the stability of the core-shell NWs and their efficiency for O_2 dissociation. With the consideration of the stability and cost, we found that Fe, Co, Ni, Cu, Ru, Ir atoms have lower price than Pd and favor at the core even with O adatom at the surface. The formed M@Pd core-shell nanowires are active for O_2 dissociation with activation barriers no larger than 0.25 eV. The results may serve as a guide for the design efficient Pd based nanocatalysts for O_2 dissociation.

Keywords: Core-shell structure; Nanowire; oxygen molecule dissociation; Pd based catalyst;

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1. **INTRODUCTION**

The dissociation of O_2 on metal surfaces or clusters is a crucial reaction step in many chemical processes, from low temperature water gas shift, oxidation of CO, to more complex oxygen reduction reactions (ORR)[1-5]. The dissociative adsorption of O_2 has been argued to be rate limiting in the oxidation of NO to NO_2[6-8]. The interaction between O_2 and Pd surfaces has been an attractive research topic for years,[9-16] and recent attention is mainly focused on Pd stepped surfaces that are typically more active than flat surfaces due to the change of electronic and geometric features.[17] Interestingly, Lahti *et al.* [13] show that the step microfacets of Pd (211) are very active and the dissociation of O_2 molecules occurs at room temperature. They attributed the activity enhancement to the formation of valley-like structure on the microfacets near the step edge. One important feature of this valley-like structure is the ensemble of four Pd atoms that may easily trap and cleave O_2 molecules. However, the density of these active ensembles is very low since high index step surfaces are less stable than the low index surfaces. Recently, we have investigated the adsorption and dissociation of O_2 molecules on the DI (double icosahedron) Pd19 nanocluster by using the density functional calculations and ab-initio molecular dynamics simulations.[18] Exceptionally high activity was found for oxygen bond cleavage over its waist region, with an energy barrier of only 0.06 eV and a reaction time of 0.5 ps. This stems from the availability of valley-like Pd_4 ensembles. Moreover, this cluster is quite stable in reaction conditions up to 500 K, so it can be a good candidate for the development of excellent nanocatalysts. It appears to be beneficial to expand DI-Pd19 with more valley-like structures on their surfaces, e.g., forming helix Pd nanowires. In fact, the valley-like structures also have other implications. Ho et al found that this special valley-like structures have high activity for CO_2[19], NO[20], N_2[21] dissociation on DI-Ru19 or DI-Ni19 clusters.

Recently, nanotubes (NTs), nanorods (NRs), and nanowires (NWs) structures[22, 23] have attracted much attention in catalytic applications due to their high surface-to-volume ratios and unique geometries. Several reports have shown that both elemental Pt and Pd nanowires and nanotubes consistently maintain improved activity and durability as compared with analogous Nano-Particles/C motifs.[24-31] Experimentally, Ding et al. [32] prepared the Ni@Au core-shell nanowires by using the rapid, redox-transmetalation reaction method and characterized the Ni@Au core-shell NWs in detail via instrumental techniques such as scanning electron microscope (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD). Gong et al.[33] recently prepared ultrathin Pd NWs surrounding individual multiwalled carbon nanotubes (Pd_{NW}/MWNTs) by using the electrostatically induced self-assembly method and placed a platinum monolayer (PtML) on the Pd_{NW}/MWNTs to form Pd–Pt core–shell NWs. They found that these Pd–Pt core–shell NWs exhibit activities both several times of those of the Pt/C and even remarkably higher than those of PtML/Pd/C. The improved activities, coupled with the long-term durability, illuminate a promising avenue to design this core-shell NWs ORR electrocatalysts. The fabrication of the proposed M@Pd core-shell NWs and the verification of their activity are highly expected. Bimetallic NWs, moreover, offer the additional prospect with tunable activity and lower cost compared with pure Pd NWs. Core–shell NWs are excellent candidates because they have well-defined geometries when synthesized in controlled environments and the core atoms may serve as anchors to withstand reaction-driven deformations. Furthermore, their electronic structure and catalytic activity can be tuned in a broad range by changing size, shape, and mixture of core and shell atoms. While it is still difficult to access useful information regarding size and shape of NWs and the mutual influence between NWs and reactants through experimental means, considerable insights can be established through computational simulations using the first-principles method based on density functional theory (DFT).

In this work, we study the adsorption and dissociation of O_2 on the Pd shell nanowires with 3d, 4d, 5d transition metal (TM) cores. Based on the cohesive energy and segregation energy with or without O atom adsorption, we determine the stable core-shell nanowires and study how the foreign core atoms affect the oxygen molecule adsorption and dissociations.

2. COMPUTATIONAL METHODS

Spin-polarized calculations are performed using the Vienna Ab-Initio Simulation Package (VASP)[34, 35]. The Sc_sv, Y_sv, Nb_pv pseudopotentials are used for Sc, Y and Nb, respectively. Normal pseudopotentials are used for other elements. Specifically, the 3p4s3d electrons of Sc, 3d4s electrons of Ti, V, Cr, Mn, Fe, Co, Ni, 3d4p electrons of Cu, Zn, 4s4p5s4d electrons of Y, 4p5s4d electrons of Nb, 4d5s of Zr, Mo, Tc, Ru, Rh, Pd, Ag, Cd, 5d6s electrons of the 5d TM atoms, and the 2s2p electrons of oxygen are treated as valence electrons. The ionic cores are represented by the projector augmented wave (PAW) potentials[36]. The exchange and correlation interactions among electrons are described at the level of the generalized gradient approximation (GGA), using the Perdew–Burke–Ernzerhof (PBE) functional [37]. The Gaussian smearing[38] method with a half-width of 0.05 eV is employed to accelerate convergence of electronic charge densities. The Kohn–Sham orbitals are expanded using plane waves with a well-converged energy cutoff of 400 eV. The M@Pd NWs are simulated with supercells with the dimensions of 18×18 Å in the x, y directions and periodically continued in the z direction as shown in Fig 1(a) with the length of the supercells optimized for different cores atoms. According to the stoichiometry, the core-shell NWs are denoted as M4@Pd20 NWs in the following. This ensures a sufficient separation between their periodic images for at least 9 Å. The Brillouin zone (BZ) integrations for the M4@Pd20 NWs are sampled with a 1×1×2 k-point mesh generated via the Monkhorst–Pack scheme.[39] All atoms are fully relaxed according to the calculated atomic forces, with criterions that require energies and forces to converge to better than 1.0×10^{-5} eV/atom and 0.01 eV/Å, respectively. The climbing image nudged elastic band method (CI-NEB)[40], with a spring constant between adjacent images of 5.0 eV/Å, is adopted to identify the reaction paths and transition states (TS). The activation energies (E_a) are calculated from the total energy difference between the transition (E_b^{TS}) and initial states (E_b^{IS}),

$$E_a = E_b^{TS} - E_b^{IS} \quad (1).$$

The adsorption energy of an O_2 molecule is defined by

$$E_{ads} = (E_{O_2} + E_{surface} - E_{O_2/surface}) \qquad (2),$$

where the surface represents NWs; E_{O_2} is the energy of an O_2 molecule in its gas-phase; $E_{O_2/surface}$ and $E_{surface}$ are the total energies of the surfaces with and without the O_2 adsorbate, respectively. The dissociation adsorption energy (E’$_{ads}$), i.e. the adsorption energy of dissociated oxygen molecule is defined by

$$E^{'}_{ads} = \frac{E_{O_2} + E_{surface} - E_{2O/surface}}{2} \qquad (3),$$

where $E_{2O/surface}$ is the total energy of the surface with two O atoms located at the hollow sites neighboring or further apart. The E’$_{ads}$ can be decomposed into two parts:

$$E^{'}_{ads} = \frac{E_{surface} + E_{O_2} + E_{2o/surface}}{2} = \frac{E^{frozen}_{2o/surface} - E_{2o/surface}}{2} + \frac{E_{surface} + E_{O_2} - E^{frozen}_{2o/surface}}{2}$$

$$= E_{gr} + E_{oa} \qquad (4),$$

where $E^{frozen}_{2O/\mathrm{surface}}$ is the energy of the oxygen atoms bound NWs in a frozen structure as that of the bare NWs. E_{gr} is defined as the energy due to the geometric relaxation, and E_{oa} is the oxygen affinity to the metal surface. The Bader charge[41] analysis scheme is applied to determine the atomic charges and charge transfer.

3. RESULTS AND DISCUSSION

3.1. Structure Stability

The structural stability of different NWs is characterized by three quantities: a) the cohesive energy (E_{coh}), which quantifies the relative stability of isomers and is defined as

$$E_{coh} = \frac{\sum_{i}^{n} E_i - E_{surface}}{n} \qquad (5),$$

where E_i represent energies of the constituent atoms of the supercell; b) the change of cohesive energy (ΔE_{coh}) due to introducing dopants, which reflects the benefit of substituting the central Pd atoms with other element,

$$\Delta E_{coh} = E_{coh}(M4@Pd20) - E_{coh}(Pd24) \qquad (6);$$

c) the segregation energies (E_{seg}). For the bimetallic surfaces, elements with lower surface energies generally tend to take the surface sites. However, as the size of NWs decreases to 1 nm in diameter, this tendency may change due to various factors such as the quantum confinement effect and the change of bonding features. We thus also examine the stability of the segregated structures in NWs M3Pd@Pd19M which are obtained by swapping a surface Pd atom with a M atom in the NW M4@Pd20. The segregation energies (E_{seg}) are calculated by

$$E_{seg} = E(M3Pd@Pd19M) - E(M4@Pd20) \qquad (7).$$

Based on our previous work[42] on screening the good Pt based core-shell nanoparticles. Suitable core atoms should provide $\Delta E_{coh}>0$, and $E_{seg}>0$ and the adsorption of O_2 or O atoms would not induce much structure deformations to change the symmetry of the formed NW M4@Pd20. Based on the calculations we find that the M4@Pd20 NWs with Sc, Y, Zr, Hf, Ag, Cd, Hg, Au, Hg as the core atoms have the negative E_{seg} values, indicating that these elements are not favorable at the core; while the Zn4@Pd20 NW has a negative ΔE_{coh} value and the Pt4@Pd20 NW can also be excluded due to high cost of Pt and lower stability during the O_2 adsorption. Therefore, the possible good cores for the M4@Pd20 NWs are determined to be the 3d atoms of Ti, V, Cr, Mn, Fe, Co, Ni, Cu; the 4d atoms of Nb, Mo, Tc, Ru, Rh; and the 5d atoms of Ta, W, Re, Os, Ir, which satisfy all the conditions with $\Delta E_{coh}>0$, and $E_{seg}>0$ as shown in Table 1, and the adsorption of oxygen would not induce much structure deformations to change the symmetry. Here we check Van-der-Waals correction for L_z of the Pd nanowires with 5d elements as cores. It is found that the Van-der-Waals correction[43] only introduces tiny changes in L_z (less than 0.1 Å).

3.2. The adsorption and dissociation of O_2 on the M4@Pd20 NWs

Similar to our previous researches[18, 44] and other studies[19, 20], based on the NWs M4@Pd20 with the selected core atoms, we first test the adsorption and dissociation of O_2 at the b-h-b site. We have also explored other adsorption sites of O_2 on the Pd24 nanowires, e. g, the bridge site, the top site, and the t-h-b site. We found that the t-h-b site converged to the b-h-b site. The bridge site and the top site are less stable than the b-h-b site by 0.16 and 0.8 eV, respectively, at which the adsorbed O_2 molecules are less activated with shorter O-O bond length (1.28, 1.34 Å) than that at the b-h-b site (1.41 Å). So we select the b-h-b site as the starting points and study the dissociation of adsorbed O_2. The detailed adsorption, dissociation properties of the bare Pd NWs and the Pd based core-shell NWs are shown in Table 2, which shows that the early transition metals core atoms (e.g., Ta, Nb, W) transfer more electrons (1.48~2.8 e) to the shell Pd atoms and have lower O adsorption energies (0.96~1.10 *vs* 1.20~1.42 eV) than the late transition core metals (e.g. Mn, Fe, Co, Ni, Cu, Pd). Especially, the Ta atom as the core has the lowest O adsorption energy (0.96 eV). Tang et al.[45] showed that the charge redistribution between core and shell becomes an important factor for lowering the d-band center of Pd-shelled particles. From the Fig. 2 (a, b), it is found that the more electrons transferred from the core atoms, the lower the d-band center becomes, and hence the lower the O atom adsorption energy, which is in agreement with Tang et al.'s conclusions.[45] From the Fig. 3, we can see that the 4d electronic density of states (DOS) near the Fermi level of a surface Pd atom on Ta@Pd is much smaller than those on the pure Pd NWs. The lower d-band center and the scarce states at the Fermi level make the much lower O atom adsorption energy of Ta@Pd NW.

Based on the formula 4, we know that the E'_{ads} can be decomposed into two parts: E_{gr} and E_{oa}. E_{gr} is defined as the energy due to the geometric relaxation, and E_{oa} is the oxygen affinity to the metal surface. The E'_{ads} value for Mo seems surprisingly larger compared with those for the nearby elements, which is attributed to the larger $\mathrm{E_{gr}}$ for Mo compared with those for the nearby elements (0.20 eV *vs* 0.15, 0.10 eV). The adsorption geometry is changed more significant for Mo compared with those for the nearby elements. However, the structure deformation does not change the symmetry of the formed NW M4@Pd20. From the Fig. 4 (a), it is found that the E_{a} for O_2 dissociation scales with the E'_{ads}, i.e. the stronger of dissociation adsorption energy of oxygen, the lower the dissociation barrier, which coincides with the Brønsted–Evans–Polanyi (BEP) relationship[46]. We found that the E_{a} scales much better with the E_{oa} than with E'_{ads} as demonstrated in the Fig. 4 (a, b). For all the selected core atoms listed in Table 1, the formed M@Pd core-shell nanowires are found to be active for O_2 dissociation with activation barriers no larger than 0.55 eV.

Finally, since the stability of the M@Pd core-shell nanowires may be affected by the adsorption of oxygen, we now discuss if the effective core atoms may be pulled out to the shell by the oxygen adatoms. As listed in Table 2, we found that for the following atoms of Ti, V, Cr, Mn (3d); Nb, Mo (4d); Ta, W, Re (5d) as the core, the segregation energy become negative under oxygen atom adsorption. These atoms should be ruled out due to the poor stability upon oxygen adsorption. While for the core atoms of Fe, Co, Ni, Cu, Tc, Rh, Ru, Os, Ir (shown in bold face in Table 1), the values of E'_{seg} with an O adatom are lowered, but still keep positive, showing their high stability. Considering the cost, it is found that the Os and Rh are much more expensive than Pd, and the Tc is the ray-emitting element which would be rule out. We propose that the Fe, Co, Ni, Cu, Ru, Ir as the core can not only reduce the cost the Pd NWs, but also have good stability. The M@Pd core-shell nanowires with these atoms as the core are quite active for O_2 dissociation with activation barriers no larger than 0.25 eV. The small activation energy barriers suggests that O−O bonds can be spontaneously cleaved once O_2 drops near the valley like structure of the M@Pd core-shell nanowires in ambient conditions. Furthermore, the weakened O−O bond can be easily broken by interactions with CO or other molecules (NO, NH_3, H_2O, ROH, etc.).

4. CONCLUSIONS

The adsorption and dissociation of O_2 on the M@Pd nanowires (M=3d, 4d, 5d transition metals) are studied using the first-principles density functional method. Suitable core atoms are determined based on the stability of the core-shell NWs and their efficiency for O_2 dissociation. With consideration of the stability and cost, we found that the Fe, Co, Ni, Cu, Ru, Ir atoms have lower price than the Pd and favor at the core even with O adatom at the surface. The formed M@Pd core-shell nanowires are active for O_2 dissociation with activation barriers no larger than 0.25 eV. The activation barrier (E_a) for O_2 dissociation scales with the O atom adsorption energy (E'_{ads}), as well as the O atom affinity energy (E_{oa}), which coincides with the BEP relationship. The results may serve as a guide for the designing efficient Pd based nanocatalysts for O_2 dissociation.

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Table 1 The pure Pd NWs and the Pd based M4@Pd20 NWs properties, including the d band center (ε_d) of the surface Pd atom; the number of electrons transferred from the core atom (C); the length of Z dimension (L_z), the values in parenthesis represent the L_z values with Van-der-Waals correction; the change of cohesive energy (ΔE_{coh}) and the segregation energies with (E'_{seg}).

systems	ε_d (eV)	C(e)	Lz(Å)	E_{seg}(eV)	ΔE_{coh}(eV)
Ti	-1.94	1.40	9.8	1.64	22.02
V	-2.3	1.81	9.57	2.10	17.30
Cr	-2.04	1.50	9.43	1.47	7.68
Mn	-1.77	1.11	9.43	0.56	7.21
Fe	-1.89	0.85	9.42	1.24	12.46
Co	-1.97	0.73	9.35	1.31	11.78
Ni	-1.85	0.50	9.27	0.94	8.07
Cu	-1.64	0.32	9.26	0.55	3.32
Nb	-2.1	1.46	10.32	2.10	24.51
Mo	-2.14	1.44	9.76	2.14	16.79
Tc	-2.04	1.28	9.61	1.86	17.40
Ru	-1.85	1.30	9.55	1.49	15.28
Rh	-1.78	0.77	9.7	0.78	8.59
Pd	-1.6	0.42	9.65	0	0
Ta	-2.22	2.80	10.32 (10.31)	2.25	30.94
W	-2.36	2.22	10.16 (10.14)	1.83	25.69
Re	-2.08	1.50	9.89 (9.87)	1.99	20.65
Os	-1.96	0.83	9.83 (9.74)	2.03	20.34
Ir	-1.8	0.37	9.85 (9.81)	1.79	14.68

Table 2 The O_2 adsorption and dissociation properties on the pure Pd NWs and the Pd based M4@Pd20 NWs, including the adsorption energy of dissociated oxygen molecule (E'_{ads}); the dissociation barrier of O_2 (E_a); the oxygen affinity of the E'_{ads} (E_{oa}); the geometric relaxation of the E'_{ads} (E_{gr}); the bond distance (dO-O) of adsorbed O_2, and the segregation energies (E'_{seg}) with O atom adsorption.

systems	E'_{ads}(eV)	E_a(eV)	E_{oa}(eV)	E_{gr}(eV)	dO-O(Å)	E'_{seg}(eV)
Ti	1.20	0.33	1.04	0.16	1.40	-0.63
V	1.22	0.51	1.07	0.15	1.42	-0.44
Cr	1.22	0.32	1.11	0.11	1.42	-0.24
Mn	1.22	0.23	1.14	0.08	1.41	-0.18
Fe	1.20	0.25	1.09	0.11	1.42	0.56
Co	1.21	0.22	1.14	0.07	1.42	0.78
Ni	1.23	0.1	1.16	0.07	1.43	0.47
Cu	1.31	0.12	1.23	0.08	1.43	0.52
Nb	1.09	0.54	0.95	0.15	1.41	-1.30
Mo	1.29	0.4	1.09	0.20	1.43	-0.80
Tc	1.20	0.34	1.10	0.10	1.42	0.74
Ru	1.30	0.2	1.22	0.08	1.42	0.94
Rh	1.20	0.17	1.12	0.08	1.42	0.35
Pd	1.42	0.11	1.29	0.12	1.41	0
Ta	0.96	0.55	0.83	0.13	1.39	-1.30
W	1.10	0.48	1.00	0.10	1.41	-0.69
Re	1.19	0.35	1.09	0.10	1.43	-0.57
Os	1.32	0.2	1.20	0.11	1.43	0.37
Ir	1.25	0.22	1.09	0.16	1.42	0.57

Figure Caption

Fig 1 (Color online) The models for the (a) M4@Pd20 NWs with (M=3d, 4d, 5d TM). The L_z in (a) is the length of the supercell for the NWs. (b) The geometrical structures of the initial state (IS), transition state (TS), final state (FS) for the dissociation of O_2 on the M4@Pd20 NWs.

Fig 2 (a) The dissociated adsorption energy of the O_2 molecule plotted as a function of the d-band center of the surface Pd atom of Pd-shelled NWs; (b) The electrons transferred from the core atoms plotted as a function of the d-band center of the surface Pd atom of the Pd-based M4@Pd20 NWs.

Fig 3 The DOS of the surface Pd 4d states on the Ta4@Pd20 NW and the pure Pd NW.

Fig 4 The barrier for oxygen dissociation on the Pd-based M4@Pd20 NWs plotted as a function of the dissociated adsorption energy of the O_2 molecule (a), and of the oxygen affinity energy (b).