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INTERACTION OF DIPHENYLAMINE (DPA) WITH Cu_2O (110) AND (111) SURFACES

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Calculations of adsorption energies of diphenylamine (DPA) on Cu_2O (110):CuO and Cu_2O(111):CuO surfaces are carried out using density functional theory (DFT). This investigations are of importance in understanding from atomistic point of view the interactions of DPA with the heterogeneous catalyst, because is the product of the C-N coupling reactions between brombenzene and aniline. On both surfaces the dispersion forces are the dominant interactions, and for Cu_2O(110) surface contribute 100% to the binding to the surface. On (111) surface, to the binding it contributes as well the surface strain energies and the chemical interaction.

Keywords: dyphenylamine, Cu_2O(110):CuO and Cu_2O:CuO surfaces, DFT

1. Introduction

Lately the interaction of different molecules with the surfaces of cuprous oxide is intensively studied using density functional theory (DFT), such as to give an insight from atomistic point of view of its electronic structure and also to its interaction with various molecules [1,2,3,4]. We have studied previously the interaction of aniline and brombenzene with Cu_2O(110):CuO and (111):CuO surfaces [5]. In this article we continue to study the interaction of diphenylamine with the same surfaces because diphenylamine (DPA) represent the reaction product of the C-N cross coupling reactions between aniline and brombenzene in the presence of Cu_2O catalyst and potassium peroxide. Therefore the study of diphenylamine interaction with the Cu_2O surfaces is of interest to give an understanding from atomistic point of view in this direction. There is a real interest to transfer this reaction from homogeneous to heterogeneous catalysis and it was shown that Cu_2O might be an efficient catalyst for both C-N and C-S coupling reactions [6,7,8].

2. Surfaces and methods

The stoichiometric Cu_2O (111) surface is non-polar and has four chemically distinguishable types of surface atoms denoted as Cu_{cus}, Cu_{csa}, O_{suf} and O_{sub}, as shown in Fig. 1. The Cu_{cus} is a surface single-coordinated Cu^+ cation,

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which acts as a Lewis acid site; Cu_{csa} corresponds to a doubly-coordinate copper atom; O_{suf} is a three-fold coordinated oxygen anion on the outer-most surface, which acts as a Lewis base site while O_{sub} is a four-fold coordinated oxygen anion on the subsurface. The (111) surface consists of a basic three lateral unit with a copper layer sandwiched between two layers of oxygen. The atomic structure of the outermost layer the Cu_2O(110):CuO contains both Cu_{suf} atoms that are doubly coordinated and O_{suf} surface atoms that are three-fold coordinated oxygen anions. The slab consists of alternating CuO and Cu layers.

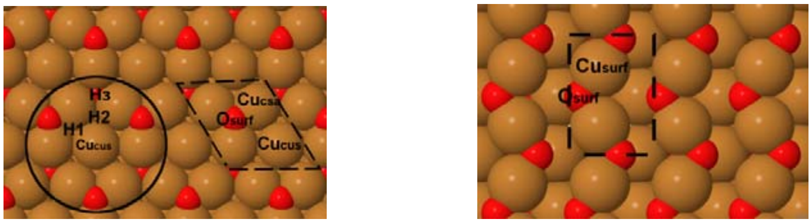


Fig. 1 Surface structures of Cu_2O (a) top view of Cu_2O (110):CuO (b) top view of Cu_2O (111):CuO. The unit cells of each type of surface are indicated by the dashed lines.

The interaction of the studied molecules with Cu_2O(111) and Cu_2O(110) surfaces have been studied by the mean of the periodic density functional theory (DFT) and has been carried out using GPAW [9] code. This is a real-space, grid-based, all-electron DFT code implemented in the projector-augmented wave (PAW) formalism [10]. The Atomic Simulation Environment (ASE) [11] provided an interface to GPAW. It was used the revPBE exchange correlation functional, implementation of the generalized gradient approximation (GGA). Because the studied systems imply the effect of van der waals interactions, beside the conventional DFT formalism, was included the dispersion interaction in the form of the vdW-DF approximation that uses the revPBE exchange functional. This fully non local vdW functional has been successfully applied to a broad range of systems with significant vdW interactions showing promising results [12, 13].

The primary parameter to converge with this method is the grid spacing. The calculations indicates that 0.2 Å is sufficiently fine to obtain reliably optimized geometries and energy differences.

First the bulk unit cell lattice parameter was obtained by relaxing the bulk with revPBE functional. It was found an equilibrium lattice constant of 4.35 Å, comparable with the experimental value of a = 4.27 Å. Next the slab geometries were relaxed using both functionals, with the centermost slab layer fixed to the bulk geometry. Despite the fact that relaxing with vdW-DF is relatively time consuming, it gives the best essential qualitative and quantitative description of the adsorption.The structures were allowed to relax, until all atomic forces were below 0.05 eV/Å. The models are 3 x 2 surface unit cell with periodic boundary conditions. This ensure that the neighboring molecules do not interact. The Brillouin zone integration was restricted to the Γ point of the reciprocal space, due to the large surface of supercell. Tests were performed using 2 x 2 *k*-points in periodic directions whitin the Monkhorst Pack scheme and it wasn't found a higher difference than 0.03 eV.

The slab thickness is five, respectively, four layers with the three respectively two bottom layers fixed during the optimizations ($Cu_2O(110)$:CuO, $Cu_2(111)$). The slabs were separated by a vacuum region of 20 Å in the z direction. Any dipole effects along this direction have been compensated by introducing a dipole vector with the same value in the opposite direction. To facilitate convergences, the Kohn-Sham states were populated using a Fermi-Dirac distribution with $k_bT = 0.1$ eV and total energies were then extrapolated to $k_bT = 0$ eV. In this scope it was used the Pulay [14] density mixing. Isolated molecules in the gas phase were treated taking into consideration the unit cells of the two surfaces.

2. Results and discussions

Compared to aniline and brombenzene molecules, in the case of DPA the interaction between the molecule and surfaces become more complex, because the size of the molecule increase and the number of accessible conformational states are larger (see Fig. 2). Therefore, attention has to be paid on the equilibrium orientation of phenyl groups. Their orientation is determined by the competition between two effects: the steric repulsion of the rings and the desired conjugation of the electronic π systems on the rings mediated through a lone electron pair orbital on the nitrogen atom. Various information is available for the structure of DPA at experimental and theoretical point of view [15]. At theoretical level the geometry optimization was performed by both semiempirical and ab initio methods. As expected the prediction of its structure and of its geometrical parameters at both theoretical and experimental levels depends strongly on the used methods and on the level of the theory [16,17,18,19]. But the study of the detailed molecular structure of DPA is not the purpose of our study.

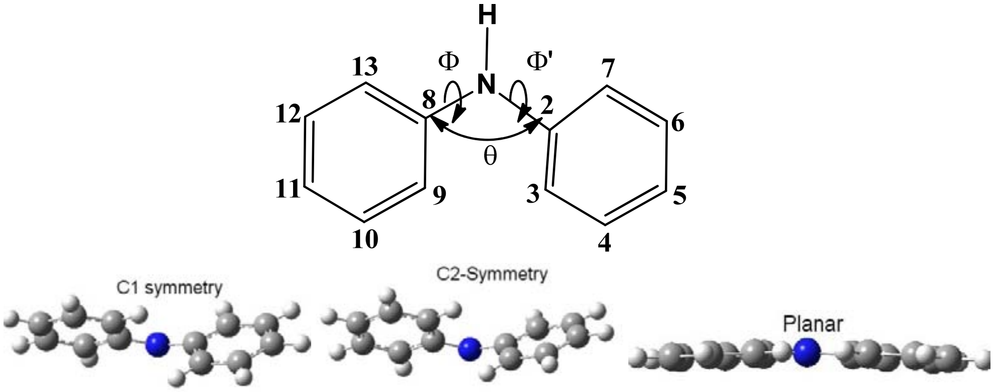


Fig.2. Diphenylamine (DPA) molecule, atom numbering, definition of the torsional angles $\Phi(C_2NC_8C_9)$ and $\Phi'(C_8NC_2C_3)$ of the phenyl groups around the C-N bonds and the C-N-C bond angle (θ) together with the explicit structures of C_1, C_2 and plane conformations.

Anyway, this molecule was identified mainly under two conformations: propeller like having a C_2 symmetry with equal torsion angles ($\Phi(C_8NC_2C_3)$= $\Phi'(C_2NC_8C_9)$) and a planar coordination of bonds around the N atom [16,17,20] and with a C_1 symmetry with the two torsion angles being different and the N atom having a pyramidal coordination [16,18,21]. Theoretically it was shown that the energy gap between the C_1 and C_2 conformations is small (≈ 0.04 kcal/mole).

Generally speaking about the interaction of flexible molecules with surfaces, the intrinsic conformational preferences of the free molecule might be altered in a different way when is in the presence of different surfaces. In most cases, to model the large flexible systems there is needed a multiscale approach [22,24].

Despite of extended conformational search limitations of DFT (high computational costs), in our study we have used only this approach because is still a powerful theoretical tool to gain insight in the trends in the adsorption energies for the system under consideration. In this study were considered both C_1 and C_2 conformations and supplementary the planar conformation, because this can be an intermediate on the surface under the reaction conditions. The optimization in the gas phase, for C_1 symmetry was performed starting from the geometrical parameters obtained by Xiao et. all [19], while for the C_2 symmetry it was started from the values obtained by the Budyka et. all. [20]. The energy gap between the C_1 and C_2 conformations, obtained either with revPBE or vdWDF is small (around 0.07 kcal/mol). The theoretical methods, afferent to these calculations were presented in detail in our previous work [5].

Table 1 contains some of the geometrical parameters of DPA molecule calculated in the gas phase and for the molecule adsorbed on the surface. In the table are found also the parameters determined experimentally and calculated by

Xiao et. all and by Budyka et. all. After optimization in the gas phase, the C_2 symmetry is broken. The differences between the two dihedral angles are relatively small (3.20^0). When compared with the experimental values or with the values obtained by Xiao et. al. or by Budyka et. al., most of the parameter differs with approx. $\pm 5^0$. There are cases when differences are higher, especially for the situations when dispersion forces are take into consideration.

The adsorption of the molecule on Cu_2O(110):CuO was done with the nitrogen atom above the active site oriented such as to minimize the possible inter – molecular interaction between neighboring cells. For this molecule is the only orientation we consider on the surface, because is not expected that other orientations to produce significant changes in the structure and also in the adsorption energies, especially that already it was shown that for the aniline and brombenzene molecules on the Cu_2O:CuO(110) surface, the adsorption energy do not differ at all with the orientation.

When the DPA molecule having the C_1 symmetry is adsorbed on the Cu_2O: CuO (110) surface, it converges towards a planar coordination of bonds around the N. The difference between the two dihedral angles reduces considerably and the structure tends towards the C_2 symmetry.

When is adsorbed in the C_2 symmetry, the geometrical values change only slightly when compared with the geometry of the molecule in the gas phase (Table 1). The dihedral angles of the planar structure are not zero but their values are below 100^0. After adsorption, its conformation doesn't change too much.

We have calculated the adsorption energy in two ways for each structure: once when we considered as reference energies, the optimized clean surface and optimized molecule in its C_1, C_2 and planar conformations in the gas phase and once when we considered the clean surface and the molecules frozen in their adsorbed geometries.

Table 1

Geometrical parameters for NH $(C_6H_5)_2$ calculated in the vacuum and after molecule was adsorbed on the surface under different configurations (C_1 symmetry, C_2 symmetry and planar) in the orthogonal and non-orthogonal cell.

$NH_2(C_6H_5)_2$		Φ $C_2NC_8C_9$	Φ ' $C_8NC_2C_3$	$<HNC_2^0$	$<C_2NC_8^0$	$<C_8NH^0$
C_1 Gas phase	Experiment[a][24]	173.3	-45.6	114.3 (av.)	123.5	114.3 (av.)
	MP2/6-31G* DPA1[a]	170.35	-48.85	-	124.8	-
	MP2/6-31G* [19] DPA2[b]	9.60	48.93		124.8	
	revPBE-	11.2	46.9	114.7	126.2	115.6

	orthogonal					
	revPBE-**non-orthogonal**	10.48	45.58	114.55	128.17	114.50
	vdW-DF-orthogonal	11.2	47	114.7	126.1	115.6
	vdW-DF-**non-orthogonal**	10.49	45.54	114.6	128.09	114.49
C_2 Gas Phase	Experiment	144.8	144.8	117.0 (av)	125.5	117.0 (av)
	B3LYP/6-31G* [20]	24.8	24.8			
	revPBE-**orthogonal**	28.8	25.6	115.3	128.8	115.8
	revPBE-**non-orthogonal**	46.95	46.95	114.66	126.12	115.64
	vdW-DF-**orthogonal**	30	26	115	129	115.5
	vdW-DF-**non-orthogonal**	11.45	11.45	114.5	126.57	115.63
Planar gas phase	revPBE-**orthogonal**	8.95	-9.5	111.72	135.87	111.86
	revPBE-**non-orthogonal**	4	-4.58	112.18	136.11	111.69
	vdW-DF-**orthogonal**	9.18	-9.68	111.69	135.84	111.89
	vdW-DF-**non-orthogonal**	4.51	-4.83	111.74	135.83	112.35
Cu_2O(110):CuO						
C_1	revPBE	12.7	26.7	114.4	130.9	114.6
	vdW-DF	17.9	33.3	114.5	130.2	114.8
C_2	revPBE	23.2	25.7	115.1	129.3	115.5
	vdW-DF	27.5	24	115.3	128.9	115.4
Planar	revPBE	5.63	-6.34	111.69	136.15	112.06

	vdW-DF	7.27	7.27	111.86	135.69	112.16
Cu$_2$O(111):CuO						
C$_1$	revPBE	14.37	28.56	114.82	130.69	114.12
	vdWDF	13.28	32.92	114.88	129.83	114.16
C$_2$	revPBE	8.77	35.10	114.11	130.19	114.38
	vdWDF	17.31	17.31	114.	130.43	114.55
Planar	revPBE	23.93	-13.38	111.21	135.36	111.93
	vdWDF	31.16	-12.18	111.05	135.06	111.62

[a] DPA1 and DPA2 are rotational optical isomers.

Therefore:

$$\Delta E_{ads}^{relax} = E_{surf+molec}^{relax} - E_{molec}^{relax} - E_{surf}^{relax} \tag{1}$$

where: $\Delta E_{surf+molec}^{relax}$ - is the energy of the optimized surface with a molecule on it;

E_{molec}^{relax} - is the energy of the optimized molecule in the gas phase in its corresponding symmetry (C$_1$, C$_2$, planar) ;

E_{surf}^{relax} - is the energy of the optimized clean surface;

and $\Delta E_{ads}^{\text{int}}$ that we denominate the adsorption interaction energy:

$$\Delta E_{ads}^{\text{int}} = E_{surf+molec}^{relax} - E_{molec}^{strain} - E_{surf}^{strain} \tag{2}$$

where: E_{molec}^{strain} - is the energy of the isolated molecule, frozen in its adsorbed geometry;

E_{surf}^{strain} - the energy of the clean surface, frozen in its adsorbed geometry;

$E_{surf+molec}^{relax}$ - the energy of the entire system after optimization either with revPBE or with vdW-DF;

We define the following relative energies :

- between the surface+C$_1$ molecule conformation, surface+C$_2$ molecule conformation and surface+planar conformation. As reference we take surface+C$_1$ molecule conformation system:

$$\Delta E_{rel,surf+molec}^{C_1-C_1,C_2-C_1,Pl-C_1} = E_{surf+molec}^{C_1,C_2,Pl} - E_{surf+molec}^{C_1} \tag{3}$$

- between the clean optimized clean surface and the surface frozen in its state after the adsorption:

$$\Delta E_{rel,surf}^{strain-relax} = E_{surf}^{strain} - E_{surf}^{relax} \qquad (4)$$

- between the optimized molecule (C_1,C_2 and Plane conformations) and the frozen molecule in its state, after adsorption :

$$\Delta E_{rel,molec}^{strain-relax} = E_{molec}^{strain} - E_{molec}^{relax} \qquad (5)$$

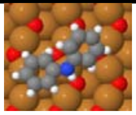
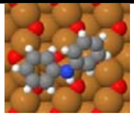
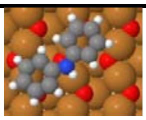
The magnitude of the van der Waals/dispertion forces is calculated as following:

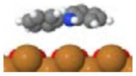
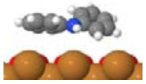
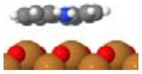
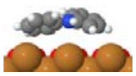
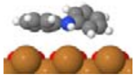
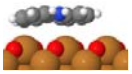
$$\Delta E_{\upsilon dW-mag} = \Delta E_{ads,\upsilon dW-DF}^{\mathrm{int}} - \Delta E_{ads,\mathrm{re}\upsilon PBE}^{\mathrm{int}} \qquad (6)$$

Analyzing the values of adsorption energies obtained at revPBE level (Table 2), $\Delta E_{ads,\mathrm{re}\upsilon PBE}^{relax}$ on $Cu_2O(110)$ reveals that there is a negligible interaction between the molecule and the surface, independently on the molecule conformation. This is confirmed by the interaction adsorption energy $\Delta E_{ads,\mathrm{re}\upsilon PBE}^{\mathrm{int}}$ values as well. The two energies are comparable, indicating that after adsorption the molecule and surface strain energies are not significant in the total value of adsorption energy. When the dispersions forces are taken into consideration, the adsorption energies increase considerably for all systems. For the planar molecule adsorbed on the surface the adsorption energy is slightly larger than for the other two. Comparing the stabilities of all three systems, the molecule adsorbed in C_1 symmetry one can say that is slightly more stable than the other two and is of order 0.02-0.07 eV. On the other hand these values are within DFT errors, therefore we cannot claim that C_1 is more stable than the other two. As a partial conclusion, one can say that the dispersion forces play an important role in the interaction of DPA with $Cu_2O(110)$:CuO surface contributing 100% to the total adsorption energy and this aspect will reflect in the catalytic activity of this surface, mostly on the capacity of the molecule to leave the surface. Comparing the magnitude of the van der Waals forces, obtained for aniline on the same surface, as expected their magnitude increases from 0.57 eV for aniline to 0.71-0.85 eV for DPA (depending on the DPA planarity).

Table 2

Relative energies of the systems (ΔE_{rel}) Adsorption energies (ΔE_{ads}^{relax}) and (ΔE_{ads}^{int}) for diphenylamine on $Cu_2O(110)$:CuO

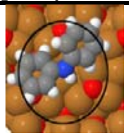
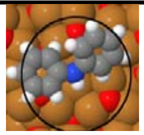
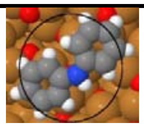
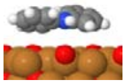
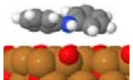
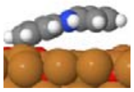
			
	C_1 symmetry	C_2 symmetry	Planar

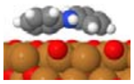
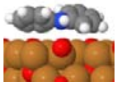
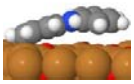
	(C_1)	(C_2)	(Pl)
Side **View** **RPBE**			
Side **View** **vdW-DF**			
$\Delta E^{C_1-C_1,C_2-C_1,Pl-C_1}_{rel,\mathrm{re}\upsilon PBE}\ /\ eV$	0	0.00	0.04
$\Delta E^{C_1-C_1,C_2-C_1,Pl-C_1}_{rel,\upsilon dW}\ /\ eV$	0	0.07	0.02
$\Delta E^{relax}_{\mathrm{ads,re}\upsilon PBE}\ /\ eV$	-0.05	-0.06	-0.09
$\Delta E^{strain}_{\mathrm{ads,re}\upsilon PBE}\ /\ eV$	-0.08	-0.07	-0.07
$\Delta E^{relax}_{\mathrm{ads,}\upsilon dWDF}\ /\ eV$	-0.77	-0.71	-0.89
$\Delta E^{strain}_{\mathrm{ads,}\upsilon dWDF}\ /\ eV$	-0.84	-0.78	-0.92

For the interaction with $Cu_2O(111)$:CuO surface we analyze first the adsorption interaction energy vales at revPBE level, $\Delta E^{strain}_{\mathrm{ads,re}\upsilon PBE}$ (Table 3).

Table 3

Relative energies of the systems (ΔErel), adsorption energies (ΔE_{ads}^{relax}) and (ΔE_{ads}^{int}) for diphenylamine on $Cu_2O(111)$:CuO

	 C_1 symmetry (C_1)	 C_2 symmetry (C_2)	 Planar (Pl.)
Side **View** **revPBE**			

Side **View** **vdW-DF**			
$\Delta E^{C_1-C_1,C_2-C_1,Pl-C_1}_{rel,\mathrm{re}\upsilon PBE} / eV$	0	-0.04	0.04
$\Delta E^{C_1-C_1,C_2-C_1,Pl-C_1}_{rel,\upsilon dW} / eV$	0	0.05	-0.25
$\Delta E^{relax}_{\mathrm{ads,re}\upsilon PBE} / eV$	-0.80	-0.85	-0.88
$\Delta E^{strain}_{\mathrm{ads,re}\upsilon PBE} / eV$	0.02	0.04	-0.73
$\Delta E^{strain-relax}_{rel,\mathrm{surf,re}\upsilon PBE} / eV$	-0.86	-0.84	-0.24
$\Delta E^{strain-relax}_{rel,\mathrm{molec,re}\upsilon PBE} / eV$	0	-0.05	0.09
$\Delta E^{relax}_{\mathrm{ads},\upsilon dWDF} / eV$	-1.21	-1.29	-1.55
$\Delta E^{strain}_{\mathrm{ads},\upsilon dWDF} / eV$	-0.78	-0.82	-1.59
$\Delta E^{strain-relax}_{rel,\mathrm{clean,re}\upsilon PBE} / eV$ **	-0.40	-0.4	-0.03
$\Delta E^{strain-relax}_{rel,\mathrm{molec,re}\upsilon PBE} / eV$ **	-0.02	-0.07	0.084

For DPA in C_1 and C_2 symmetries adsorbed on surface, no chemical interaction is registered. The value for the planar molecule adsorbed on the surface indicates a chemical interaction. This is possible because after optimization, one carbon of the phenyl ring end in being adsorbed ontop the most reactive site of the surface. By comparing for the C_1 and C_2 systems, $\Delta E^{strain}_{\mathrm{ads,re}\upsilon PBE}$ with the values of adsorption energies, $\Delta E^{relax}_{\mathrm{ads,re}\upsilon PBE}$, indicates that the strain energies of the surface and of the molecule after adsorption, contribute significantly to the total energy of adsorption (see Table 3), namely the surface strain energy is the one contributing significantly. For planar system the surface strain energy is much lower compared with the previous two systems, but overall the adsorption energy at revPBE level ($\Delta E^{relax}_{\mathrm{ads,re}\upsilon PBE}$) is approximately the same for all systems, the difference being the different magnitude of the each component energy that contribute to it ($\Delta E^{strain}_{\mathrm{ads,re}\upsilon PBE}$, $\Delta E^{strain-relax}_{rel,\mathrm{surf,re}\upsilon PBE}$, $\Delta E^{strain-relax}_{rel,\mathrm{molec,re}\upsilon PBE}$ - see Table 3). Therefore in the case of C_1 and C_2 systems the surface suffer a deformation such as that the final state of the surface is much more stable than the clean surface, while in the case of planar system the surface after adsorption goes in a state that is more stable than the clean surface but not as much as in the case of the other two systems. Similar behavior of the surface was reported before for the interaction with brombenzene and aniline molecules. By including the dispersion forces in the calculations, as expected they contribute significantly to the adsorption energy (see the values of the adsorption interaction energies in Table 3, $\Delta E^{strain}_{\mathrm{ads},\upsilon dWDF}$). The values of the adsorption energy, $\Delta E^{relax}_{\mathrm{ads},\upsilon dWDF}$, include as well the surface and molecule deformation energies and the chemical interaction. The lowest energy is registered for the planar system and this is due to the chemical interaction energy that contributes to the total adsorption energy. Concerning the magnitude of the van der Waals forces, they are in the same range as reported before, 0.71-0.86 eV. In this case the lower value corresponds to the planar system, due to a stronger chemical interaction.

3. Conclusions

The overall picture of our study concerning the interaction of diphenylamine with two surfaces of the Cu_2O oxide, is that vdW forces dominate the interaction between the DPA molecule in all three investigated configurations and the $Cu_2O(110)$ surface, contributing 100% to the total adsorption energy. For the adsorption on (111) surface, depending on the system, the chemical interaction, surface strain energies and van der Waals forces contribute each in a certain extent to the total adsorption energy.

The present results show a constant magnitude of the van der Waals forces that will influence the coverage of these species on the surface, hence influencing the catalytic activity, because their magnitude increased with replacing in aniline one hydrogen with one phenyl moiety.

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