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CO 和 H₂ 分子在 Cu(111)面的吸附和溶剂化效应

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摘要： 采用广义梯度近似(GGA)密度泛函理论(DFT)的 PW91 方法结合周期性模型, 在 DNP 基组下, 利用 Dmol³ 模块研究了 CO 和 H₂ 在真空和液体石蜡环境下在 Cu(111)表面上不同位置的吸附. 计算结果表明, 溶剂化效应对 H₂ 和 CO 的吸附结构参数和吸附能的影响非常显著. 在液体石蜡环境下, H₂ 平行吸附在 Cu(111)表面是解离吸附, 而CO 和 H₂ 在两种环境下的垂直吸附都是非解离吸附. 相比真空环境吸附, 在液体石蜡环境中, Cu(111)吸附 CO 时, 溶剂化效应能够提高 CO 吸附的稳定性, 同时有利于 CO 的活化. 在真空中, H₂ 只能以垂直方式或接近垂直方式吸附在 Cu(111)表面. 当 Cu(111)顶位垂直吸附 H₂, 相比真空环境吸附, 溶剂化效应能够提高 H₂ 吸附的稳定性, 但对 H₂ 的活化没有明显影响. Cu(111)表面的桥位或三重穴位(hcp 和 fcc)垂直吸附 H₂ 时, 溶剂化效应能明显提高 H₂ 的活化程度, 但降低 H₂ 的吸附稳定性; 在液体石蜡中, 当 H₂ 平行 Cu(111)表面吸附时, 溶剂化效应使 H—H 键断裂, 一个 H 原子吸附在 fcc 位, 另一个吸附在 hcp 位.

关键词： 密度泛函理论; CO 分子; H₂ 分子; Cu(111)表面; 溶剂化效应
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CO and H₂ Molecules Adsorption on Cu(111) Surface and Solvent Effects

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Abstract： The calculations were performed by using density functional theory (DFT), where the generalized gradient approximation (GGA) corrected exchange-correlation functional proposed by Perdew and Wang (PW91) was chosen together with the doubled numerical basis set plus polarization basis sets (DNP), using the Dmol³ implementation of the conductor like solvent model (COSMO), to investigate CO and H₂ adsorption on Cu(111) surface in vacuum and liquid paraffin. It is found that both structural parameters and relative energies are very sensitive to the COSMO solvent model. According to the monitor bonding function of the Dmol³, CO and H₂ adsorption on Cu(111) surface are both nondissociative adsorption when the Cu surface is adsorbed by CO and H₂ in vacuum or liquid paraffin except H₂ parallel adsorption in liquid paraffin which is dissociative adsorption. The results show that solvent effects can improve the stability of CO adsorption on Cu(111) surface and the extent of CO activation in liquid paraffin. H₂ can be not parallel adsorption on Cu(111) surface in vacuum, but it is nearly vertical or vertical adsorption. When H₂ is vertical adsorption on Cu(111) surface at top site, solvent effects can improve the stability of H₂ adsorption on Cu(111) surface, there is no influence on H₂ activation. When H₂ is vertical adsorption on Cu(111) surface at bridge, fcc and hcp sites in liquid paraffin, the stability of H₂ adsorption on the Cu(111) surface decreases compared with H₂ adsorption in vacuum, however, the extent of H₂ activation increases. As H₂ is parallel adsorption on Cu(111) surface in liquid paraffin, H—H

bond is broken by solvent effects. One H atom adsorbs on Cu(111) at fcc site, and another H atom is at hcp site.

The formation of dimethyl ether (DME) from syngas conversion has been recently attracting more and more attention, because of its potency for using as a transportation fuel or as a fuel additive. To date, the catalysts with the best catalytic performance are $Cu/ZnO/Al_2O_3$ which are used predominantly in the industrial DME synthesis process starting from synthesis gas, a mixture of H_2 and CO[1−3]. In "one-pot" synthesis of DME, there are two methods: one is gas phase method, the other is liquid phase method. Gas phase method uses the fixed bed in which syngas are reacted on the catalyst surface. Liquid phase method uses the slurry reactor where the catalyst is dispersed in a liquid medium such as liquid paraffin, the syngas first dissolves into liquid paraffin, and then reacts on the catalyst surface[1−5].

In "one-pot" synthesis of DME, the role of metallic copper in the reaction mechanism has been widely discussed in the literature over the past 20 years and remains a matter of debate[6−9]. Today, it is widely accepted that the final active catalyst is obtained by reduction of CuO to metallic Cu under a diluted H_2 flow before feeding the synthesis gas mixture[1,6,7]. Because of the importance of adsorption and interaction, the interaction of CO or H_2 molecules and Cu(*hkl*) surface has been studied in fixed bed as the first step in the synthetic procedure by many researchers[10−13]. To our best knowledge, despite of the intense experimental activity[1−9], a detailed researching of the general rules governing the interaction mechanism of CO and H_2 with Cu surface in liquid paraffin is still missing. X-ray diffraction (XRD) characterization has proved that Cu(111) is the main surface of the copper[14,15], as being widely used in the previous theoretical investigations on the molecule adsorptions on transition metal surfaces[10−13]. Thus, the adsorption behavior of CO and H_2 molecules adsorbed on Cu(111) surface is studied in this article.

This analysis gives us some new insights for the understanding of the experiment[14,15] in which the CO adsorption on Cu(111) surface is influenced by liquid paraffin. The results may be of interest for researchers to attempt to investigate the interaction of CO and H_2 with Cu in fixed-bed and slurry reactors.

1 Calculated models and details

The calculations are performed using density functional theory (DFT)[16−18], where the generalized gradient approximation (GGA) corrected exchange-correlation functional proposed by Perdew and Wang (PW91)[19] was chosen together with the doubled numerical basis set plus polarization basis sets (DNP, including polarization *d*-function)[20]. The electronic structures are obtained by solving the Kohn-Sham (KS) equation self-consistently in the condition of spin unrestrict while the all-electron relativistic density functional theory is used for core electrons[21,22]. Self-consistent field procedure is carried out with a convergence criterion of 10^{-5}

a.u. on energy and electron density, and geometry optimizations are performed under the symmetry constraint with a convergence criterion of 10^{-3} a.u. on gradient, 10^{-3} a.u. on displacement, and 10^{-5} a.u. on energy.

The equilibrium lattice constants of Cu are a_{Cu}=0.3685 nm compared to an experimental value of a_{Cu}=0.3615 nm[23]. It is found that a good agreement between our computed datum and the experimental datum reported by Kittel[23]. Discrepancy is less than 2%. The substrates are modelled by four atomic layers of metal separated by a vacuum region of 1 nm thickness. The three uppermost substrate layers and CO molecule are allowed to relax, keeping the volume constant. A *p*(2×2) cell is used for the Cu(111) surface, resulting in a coverage of 0.25 monolayer (ML).

The simulation of solvent effect is based on the $Dmol^3$ implementation of COSMO[24,25]. COSMO is a continuum solvent model where the solute molecule form a cavity with radius a_0 surrounded within the dielectric continuum of permitivity ε that represents the solvent[26−28]. A dielectric constant used for the calculations in a big value represents a strongly polar medium. Contrarily, a dielectric constant under 5.0 stands for a nonpolar medium. A dipole moment of solvent, induced by that of the solute, interacts back to the dipole moment of solute to gain the stabilization energy for the system. The gas-phase geometry is used as its initial guess to start the full optimizations at the same level of PW91-GGA with dielectric constants of 2.06 and a radius a_0 automatically resorted from quantum mechanical procedures.

2 Results and discussion

In order to investigate the reliability of the calculation, we calculate the bond length and vibrational stretching frequencies of free CO, which are 0.1141 nm and 2116.1 cm^{-1}, respectively. There is in good agreement between our calculation and the experimental values of 0.1128 nm and 2143 cm^{-1} [29], respectively.

According to the Cu(111)-(2×2) surface morphology, there are
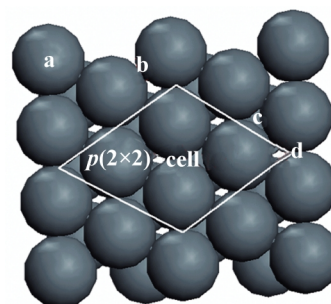
Fig.1   Top view of Cu(111) surface
(a) top site, (b) bridge (bri) site, (c) hexagonal-close-packed (hcp) site,
(d) face-centered cubic (fcc) site

four different adsorptive sites (Fig.1): top, bridge (bri), hcp, and fcc. Meanwhile, it is well known that the adsorption energy of C-down is more lower than that of O-down on the same adsorption site according to the experimental and calculated results [30], so we only calculate C adsorbing the Cu surface. The adsorption energy per CO molecule is defined as $E_{ads}=E(CO/slab)-[E(CO)+E(slab)]$ [31], where $E(CO/slab)$ is the total energy for the slab with the adsorbed CO on the surface, $E(CO)$ is the total energy of free CO, and $E(slab)$ is the total energy of the bare slab of the surface. Therefore, a negative E_{ads} value means exothermic adsorption, and a positive E_{ads} value means endothermic adsorption. The computed adsorption energies, structural parameters and charges of C and O atoms are listed in Table 1.

Fig.2 shows four different adsorptive models. In vacuum, CO interacts with one Cu atom and forms one Cu—C bond in top site, and the C—O bond (0.1154 nm) is elongated comparing to free CO (0.1141 nm). In bridge site (2-fold bridge site), CO interacts with two adjacent Cu atoms and forms two Cu—C bonds, and the C—O bond is elongated to 0.1172 nm. In fcc site (3-fold fcc site), CO interacts with three Cu atoms on the fcc site and the C—O bond is elongated to 0.1178 nm. In 3-fold hcp site, CO interacts with three Cu atoms on the surface by occupying hcp site, the carbon is adjacent to Cu atoms with the formation of three Cu—C bonds. The C—O bond in hcp is elongated to 0.1179 nm. The Cu—C distance varies from 0.1851 to 0.2059 nm and increases with coordination number. As the Cu surface adsorbs CO in liquid paraffin, all the C—O and Cu—C bonds of four adsorption models are longer than those corresponding bond of adsorption models in vacuum. According to the monitor bonding function of the Dmol^3, which can observe the process of molecular adsorption, Cu surface is adsorbed by CO in vacuum and liquid paraffin, which is nondissociative adsorption, which accords with the experiment results of HREELS, LEED, TPD and so on [32–34]. In both environments, the longer the C—O bonds, the longer the C—Cu bonds.

As shown in Table 1, the C—O bond increases with the number of Cu atoms with which the molecule binds in both environments. It is well known that there are two kinds of interaction of the metal and adsorbed molecules [35,36]. One is the interaction between the adsorbates, the other is the interaction between the

Table 1 Computed adsorption energies (E_{ads}) per molecule, C—O and C—Cu bond lengths (d) and Mulliken charges (q) of C and O as well as net charges (q) of CO at the different sites on Cu(111) surface for a coverage of 1/4 ML

		E_{ads}/eV	d_{Cu-C}/nm	d_{C-O}/nm	q_C/e	q_O/e	q_{CO}/e
vacuum	top	−0.90	0.1851	0.1154	0.383	−0.121	0.262
	bri	−0.91	0.1999	0.1172	0.345	−0.136	0.209
	fcc	−0.98	0.2057	0.1178	0.354	−0.144	0.210
	hcp	−0.97	0.2059	0.1179	0.344	−0.141	0.203
liquid paraffin	top	−1.05	0.1894	0.1176	0.372	−0.176	0.196
	bri	−1.09	0.2064	0.1181	0.315	−0.196	0.119
	fcc	−1.06	0.2094	0.1189	0.311	−0.207	0.104
	hcp	−1.06	0.2099	0.1188	0.303	−0.204	0.099
free CO				**0.1141**	**0.105**	**−0.105**	**0.000**
				(0.114)	(0.107)	(−0.107)	(0.000)

q_{CO}: net charge of CO, $q_{CO}=q_C+q_O$; The number in parentheses and bold values represent the calculated values for free CO molecule in liquid paraffin and vacuum, respectively.

metal and the adsorbates. There is no significant repulsion between adsorbed CO molecules at 1 ML [35], so the adsorptive structure is mainly influenced by the direct interaction of the CO and Cu. In other words, the bonds change trend of different models, which shows that the C—O bonds are mainly affected by Cu and CO interaction. The net charge of the adsorbed CO on the Cu(111) surface is also given in Table 1, compared with that of free CO. It shows clearly that the adsorbed CO molecules are partially positively charged, indicating electron transfer from CO into the copper surface. The elongation of the C—O bonds increases with the decreases of the net charges of adsorbed CO molecules. It indicates that the stronger electrons transfer from the surface into the antibonding orbital of CO with higher activation of the C—O bonds. When CO molecules are adsorbed on the Cu(111) surface, the C—O bonds in liquid paraffin are larger than in vacuum. It indicates that CO molecules are induced higher activation in liquid paraffin than in vacuum.

As given in Table 1, all four structures have exothermic adsorption energies, indicating that CO adsorption on Cu(111) surface is thermodynamically favored. The greater the exothermic adsorption energies, the more stable the adsorption models, so the thermodynamic preference of CO nondissociative adsorption shows the order of fcc ≈ hcp>bri ≈ top in vacuum. The adsorption energies and order agree well with the results using the PW91
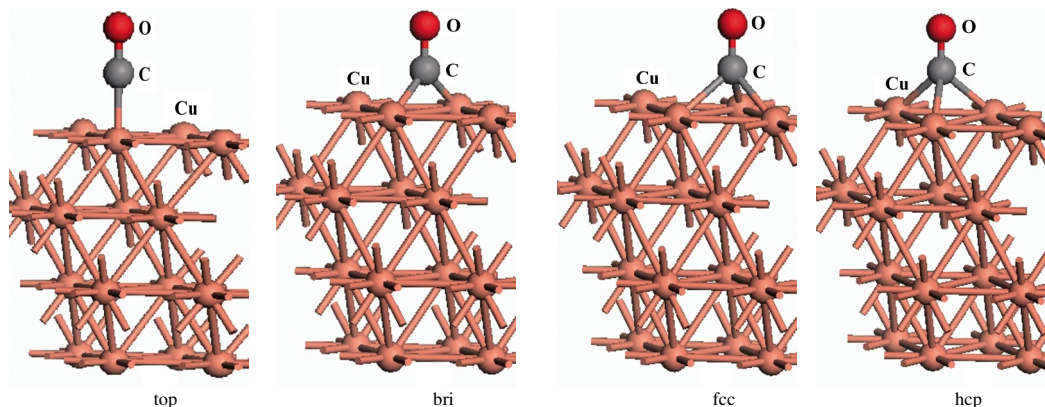
Fig.2 Structures of adsorbed CO on Cu(111) surface

code of VASP and the results using PBE[37,38]. The adsorption energies decrease about 0.15 eV for all the adsorption models influenced by solvent effects, it is interesting to find that the nondissociative adsorption energies are very similar for four different models. The result shows that liquid paraffin solvent can promote the stability of CO adsorption on the Cu(111) surface.

According to the same analysis method of CO adsorption on Cu(111) surface, we calculate H_2 vertical adsorption on Cu(111) surface. Fig.3 shows four different adsorptive models. For the adsorption of H_2 on the Cu(111) surfaces, the adsorption energies and structural parameters list in Table 2. From Table 2, it indicates that H_2 adsorption on Cu(111) surface is also thermodynamically favored according to the adsorption energies in vacuum, however, the adsorption energies are small, which equal to −0.11 eV in vacuum. The result is consistent with the theoretical calculation[39], and this is to be expected as H_2 is a nonpolar molecule. The optimized molecular axis of H_2 is nearly normal to the surface. It can be seen that the H—H bond length is almost equal, because H_2 adsorbs on different sites of Cu(111) surface in vacuum. The slightly elongated H—H bond length from free H_2 molecule (0.0749 nm) demonstrates that the H—H bond in adsorbed H_2 molecule gains somewhat activation[10,29]. This kind of weakly adsorbed behavior accords with the experimental observation[40].

Based on the adsorption energies of H_2 vertical adsorption on Cu(111) surface in liquid paraffin as given in Table 2, H_2 adsorption on Cu(111) at top site is exothermic, indicating that H_2 adsorption on Cu(111) at top site is thermodynamically favored. The adsorption energy at top site decreases about 0.21 eV compared with the adsorption energy in vacuum. However, as H_2 adsorption on Cu(111) surface at bridge, fcc and hcp sites, the three structures have endothermic adsorption energies, indicating that H_2 adsorption on Cu(111) is thermodynamically unfavored. The result shows that the adsorption energies are very sensitive to the COSMO solvent model.

According to the monitor bonding function of the Dmol³, H_2 vertically adsorbs on Cu surface in vacuum or liquid paraffin, which are both nondissociative adsorption. As given in Table 2, Mulliken charges of H_N which is nearer to Cu surface are negative in vacuum, however, they are positive in liquid paraffin at
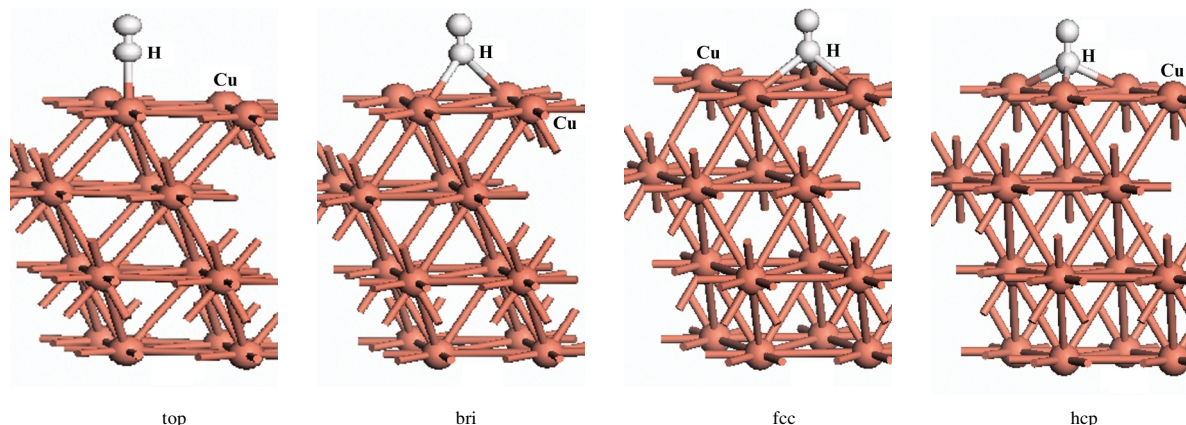
Table 2 Computed adsorption energies (E_{ads}) per molecule as H_2 vertical adsorption, H_2 and H—Cu bond length (d) and Mulliken charges (q) of H as well as net charges (q) of H_2 at the different sites on Cu(111) surface for a coverage of 1/4 ML

|		E_{ads}/eV	d_{Cu-H_N}/nm	d_{H-H}/nm	q_{H_N}/e	q_H/e	q_{H_2}/e
vacuum	top	−0.11	0.3124	0.0751	−0.019	0.005	−0.014
	bridge	−0.11	0.3440	0.0752	−0.017	0.003	−0.014
	hcp	−0.11	0.3354	0.0753	−0.019	0.004	−0.015
	fcc	−0.11	0.3380	0.0753	−0.019	0.004	−0.015
liquid	top	−0.32	0.2703	0.0751	−0.027	−0.003	−0.030
paraffin	bridge	0.06	0.1945	0.0806	0.034	0.015	0.049
	hcp	0.01	0.2121	0.0781	0.033	0.014	0.047
	fcc	0.09	0.2030	0.0799	0.042	0.021	0.063
free H_2				**0.0749**	**0.000**	**0.000**	**0.000**
				(0.0748)	(0.000)	(0.000)	(0.000)

d_{H-H}: H—H bond length, d_{Cu-H}: the distance from Cu atom to the nearest H atom, q_{H_N}, q_H: Mulliken charges of H atom nearer Cu surface and the other H atom, q_{H_2}: net charge of H_2; The number in parentheses and bold values represent the free H_2 molecule in liquid paraffin and vacuum, respectively.

bridge, fcc and hcp sites. Compared with the H—H bond length in vacuum and liquid paraffin, the H—H bond lengths are very close to each other in vacuum. However, the H—H bond length is elongated to 0.0781−0.0806 nm except H_2 adsorption on Cu (111) at top site in liquid paraffin. The reason may be that the H—H bond is vertical to Cu(111) surface at the beginning of the calculations for bridge, fcc, and hcp sites and tilting Cu(111) surface about 45° in the end of the calculations as H_2 adsorption on Cu(111) surface in liquid paraffin. However, there are not obvious changes as H_2 adsorption on top site of Cu(111) surface in vacuum and in liquid paraffin. As the H-H molecule tilting to Cu (111) surface in liquid paraffin, the Mulliken charges of H_N and H are positive. As a result, the H—H bond length is longer than that of in vacuum, indicating that solvent effects can improve the ability of H_2 activation, although the stability of H_2 adsorption on the Cu(111) surface decreases.

Xie *et al.*[41] found that the most molecular orientation for H_2 dissociation is to keep the H-H axis parallel to the Cu(100) surface. In our calculated results of H_2 molecular vertical to the Cu (111) surface, the solvent effects can improve the ability of H_2 activation. At the same time, H_2 molecular tilt about 45° after calculation. What will happen when the H_2 molecular is parallel

top   bri   fcc   hcp

Fig.3 Structures of H_2 vertical adsorption on Cu(111) surface
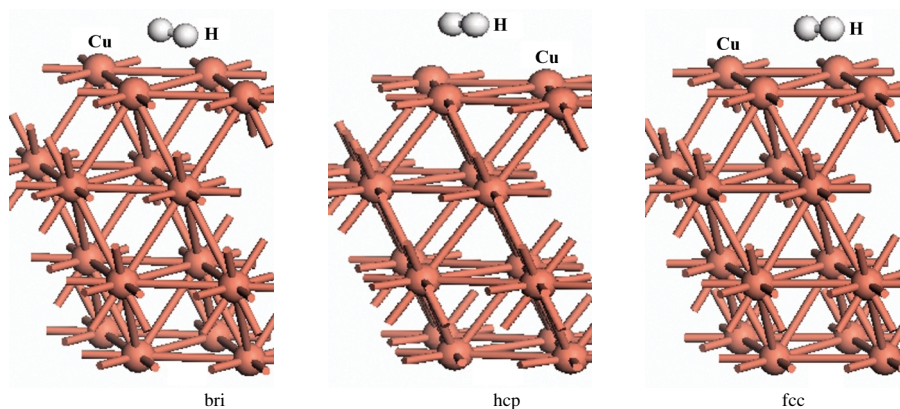
Fig.4   Initial structures of H₂ parallel adsorption on Cu(111) surface before geometry optimization
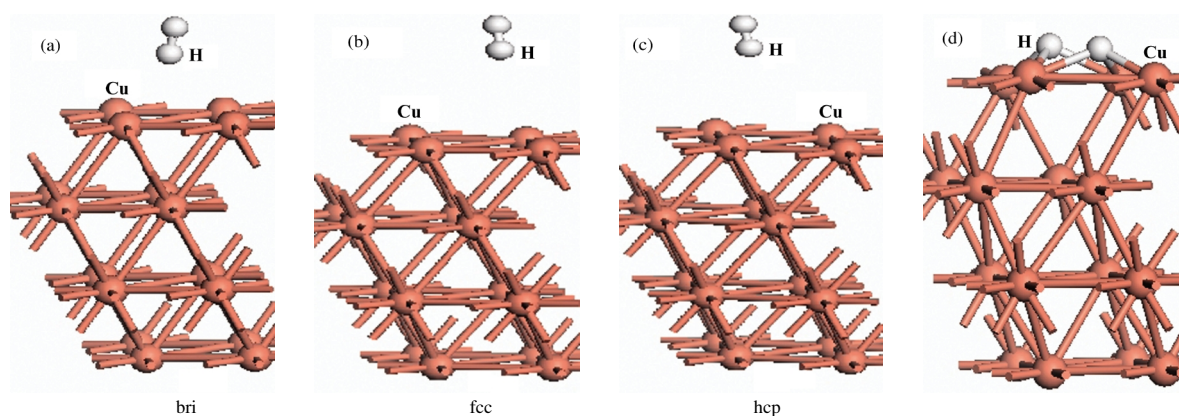
Fig.5   Structures of H₂ parallel adsorption on Cu(111) surface in vacuum and liquid paraffin after geometry optimization

(a, b, c) in vacuum, (d) in liquid paraffin

to the Cu(111) surface in vacuum and in liquid paraffin. In order to answer the question, we study the H-H axis parallel to the Cu(100) surface before optimizing configurations.

Fig.4 shows three different adsorptive models. For the parallel adsorption of H₂ on the Cu(111) surfaces in vacuum, the adsorption energies are equal to −0.10 eV, which is similar to the energies of H₂ vertical adsorption of on the Cu(111) surfaces in vacuum. At the same time, the structural parameters are similar in both adsorption models. The reason is that the H—H bond is parallel to Cu(111) surface at the beginning of the calculations for the bridge, fcc, and hcp sites and nearly vertical to Cu(111) in the end of the calculations (see Fig.5(a, b, c)). The result shows that H₂ is not parallel adsorbed on Cu(111) surface and only vertical adsorption. However, H₂ molecule is dissociated, as H₂ is parallel adsorption on Cu(111) surface for bridge, fcc and hcp sites in liquid paraffin. One H atom adsorbs on fcc site, and the other H atom adsorbs on hcp site (Fig.5(d)), and the adsorption energy is −4.65 eV. It indicates that the H—H bond is broken by solvent effects.

It should point out that the adsorption energies are positive in bri, fcc and hcp in liquid paraffin, however, the bond length of H—H is obviously larger than that in vacuum. The stronger the interaction between the metal and the adsorbates, the smaller the adsorption energies of H₂ on metal surface. In some related researches there are also some examples that the value of adsorp-

tion energy changes inconsistently with bond length. Moussounda *et al.*[42,43] studied CH₄ adsorption in Ni(111) and Pt(100) surfaces, and the results show that when CH₄ is adsorbed on the top site of Ni(111) surface, and when one H bond of CH₄ points to Ni(111) surface(t1), the C—Ni bond length is 0.3463 nm, the adsorption energy is −0.035 eV. When two H bonds point to Ni surface (t2), the C—Ni bond length is 0.3829 nm, the adsorption energy is −0.053 eV. When three H bonds point to Ni surface (t3), the C—Ni bond length is 0.3487 nm, the adsorption energy is −0.034 eV. A similar situation also occurs in Pt(100) surface. It indicates that when C—Ni bond becomes shorter, i.e., the interaction between adsorbate and metal is strong, the corresponding adsorption energy is relatively small (compared with t2). In other words, when the role of metaladsorbate is strong, there is also the smaller adsorption energy. Because there have been few reports on the adsorption behavior in liquid medium up to now, the further research is needed.

CO adsorption on Cu(111) surface is vertical after geometry optimization both in vacuum and liquid paraffin. The vertical adsorption H₂ becomes tilt about 45° in liquid paraffin after geometry optimization, while the parallel adsorption H₂ becomes two H atoms adsorbed on Cu surface in liquid paraffin after optimization. However, the vertical and parallel adsorption H₂ becomes vertical and nearly vertical after geometry optimization in vacuum. This shows the existence of the effect of circumstance

on adsorption.

3 Conclusions

Adsorption of CO and H₂ on the Cu(111) surface is investigated by using the generalized gradient approximation and the Perdew and Wang functional based on the density functional theory.

On the basis of the computed adsorption energies, CO adsorption is exothermic on Cu(111) surface for the top, bri, hcp, and fcc sites, and the ability of CO adsorption on the Cu surfaces is in the order of fcc ≈ hcp > bri ≈ top. Owing to solvent effect, the preference of CO adsorption on the Cu surface for the different sites increases, and the nondissociative adsorption energies are very similar for four different models. The adsorbed CO is partially positively charged with both nondissociative adsorption, and has elongated C—O bond lengths. The C—O bonds in liquid paraffin are longer than in vacuum, so solvent effects can improve the ability of CO activation.

As H₂ is vertical adsorption on Cu(111) surface, H₂ adsorption is exothermic on Cu(111) surface for all the adsorption sites in vacuum. The adsorption energy in liquid paraffin at top site decreases compared with the adsorption energy in vacuum, however, the other three structures have endothermic adsorption energies as H₂ adsorbs on Cu(111) surface at the bridge, fcc and hcp sites.

As H₂ is parallel adsorption on Cu(111) surface, the H—H bond is nearly vertical to Cu(111) after optimized in vacuum. However, the H—H bond is broken in liquid paraffin. One H atom adsorbs on fcc site, and the other H atom adsorbs on hcp site. The results show that both structural parameters and relative energies are very sensitive to the COSMO solvent model.

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