

Chemisorption of organics on transition metal surfaces

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Abstract:

By using non local density functional method (B3LYP), we studied the chemisorbed structures and binding energies of CH_x on transition metal (Ni, Cu, Ag and Au) cluster. Using the interstitial electron model, we considered a planer 8 atom cluster as a model for the (111) surface and calculated optimum structures of chemisorbed CH_x species on the surface.

On the Ni cluster, CH , CH_2 and CH_3 prefer a cap site. For CH_3 on a cap site, each hydrogen of CH_3 points toward Ni atom. These results show a good agreement with experimental and theoretical results. On the Cu and Ag cluster, CH , CH_2 and CH_3 also prefer a cap site. On the Au cluster, CH_3 prefers an on-top site, CH_2 prefers a bridge site and CH prefers a cap site.

Methods and Results:

1. Calculation

Method: Density functional theory (B3LYP)

Basis set: Gaussian basis set

Metals: Hay and Wadt effective core potential

Non Metals: 6-31G**

2. Model

The interstitial electron model suggests that the electronic configuration is s^1d^x for the (111) surface of these transition metals (Ni, Cu, Ag and Au). So we used a planer 8 atom cluster, which has a sd^x character, as the simplest cluster for studying closest packed surfaces.

We calculated the optimum geometries and binding energies of CH_3 , CH_2 , CH and C on the top, bridge and cap site (Fig.1). The bond length of the metal was fixed to the bulk distance.

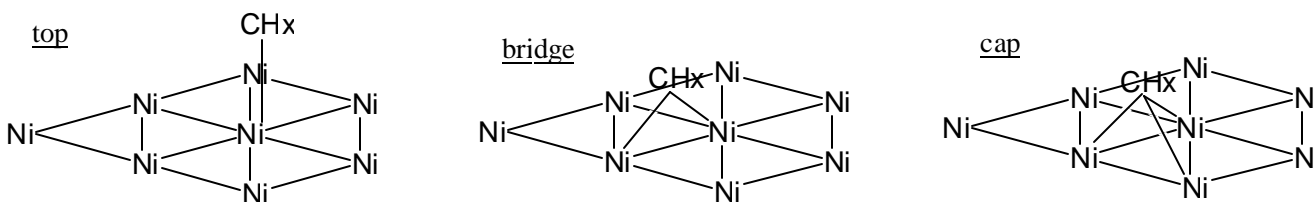


Fig.1 Calculated model of CH_x chemisorbed on Ni8 cluster.

3. Results

(1) Ni cluster

CH₃, CH₂, CH and C all prefer the cap site (Table1).

For CH₃ on cap site, there are two high symmetrical chemisorbed structures, eclipse and staggered. In the eclipse structure, each hydrogen of CH₃ points towards the Ni atom and in the staggered structure, each hydrogen of CH₃ points between the Ni atoms. On the Ni₈ cluster, CH₃ is more stable in eclipse than staggered about 5kcal/mol. This preference for eclipse structure shows a qualitative agreement with experimental results.

(a) Binding Energy (kcal/mol)					(b) Ni-C Bond Distance (Å)				
	CH ₃	CH ₂	CH	C		CH ₃	CH ₂	CH	C
top	19.29	53.27	44.42	65.81	top	1.96	1.82	1.66	1.63
bridge	21.35	66.40	98.01	92.79	bridge	2.19	1.92	1.74	1.73
cap	22.15	72.81	106.13	97.55	cap	2.25	2.00	1.82	1.78

Table1. Binding energy and bond distance of CH_x on Ni₈ cluster.

(2) Cu cluster

CH₃, CH₂, CH and C all prefer the cap site (Table2).

(a) Binding Energy (kcal/mol)					(b) Cu-C Bond Distance (Å)				
	CH ₃	CH ₂	CH	C		CH ₃	CH ₂	CH	C
top	5.60	30.71	28.68	20.18	top	2.18	1.94	1.87	1.81
bridge	10.67	49.51	55.35	56.12	bridge	2.28	1.95	1.84	1.96
cap	13.58	60.17	76.78	63.77	cap	2.32	2.01	1.88	1.91

Table2. Binding energy and bond distance of CH_x on Cu₈ cluster.

(3) Ag cluster

CH₃, CH₂, CH and C all prefer the cap site (Table3).

(a) Binding Energy (kcal/mol)					(b) Ag-C Bond Distance (Å)				
	CH ₃	CH ₂	CH	C		CH ₃	CH ₂	CH	C
top	1.87	18.41	16.04	14.59	top	2.70	2.16	2.18	2.21
bridge	1.43	24.72	27.37	27.41	bridge	2.57	2.17	2.05	2.24
cap	1.90	35.97	45.77	35.89	cap	2.66	2.25	2.08	2.29

Table3. Binding energy and bond distance of CH_x on Ag₈ cluster.

(4) Au cluster

CH₃ prefers an on-top site, CH₂ prefers a bridge site and CH prefers a cap site.

(a) Binding Energy (kcal/mol)					(b) Au-C Bond Distance (Å)				
	CH ₃	CH ₂	CH	C		CH ₃	CH ₂	CH	C
top	8.50	17.07	10.58	16.25	top	2.27	2.08	2.12	2.04
bridge	2.85	35.80	38.78	44.84	bridge	3.20	2.10	1.95	1.99
cap	2.59	33.73	68.19	54.07	cap	3.62	2.22	1.99	2.05

Table4. Binding energy and bond distance of CH_x on Au₈ cluster.