

Hydrogen dissociation on Au-substituted Pt clusters

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London-Eyring-Polanyi-Sato (LEPS) method has been used to study the dissociation of an H_2 molecule on Pt_{18} and $Pt_{17}Au$ clusters. It has been found that on Pt_{18} cluster, dissociation at bridge site is favoured; the dissociated H atoms ultimately being chemisorbed on top sites. On the $Pt_{17}Au$ cluster, on the other hand, dissociation at a top site is favoured when the dissociated species gets subsequently chemisorbed on bridge sites. Relevance of the work in understanding the catalytic reactions over alloy surfaces is discussed.

A complete understanding of the phenomenon of heterogeneous catalysis requires knowledge of the reaction pathways by which gas molecules dissociatively chemisorb on the metal/alloy surfaces. In order to understand the dynamics of gas molecules on surfaces a very simple but useful method, namely, the LEPS (London-Eyring-Polanyi-Sato) method has been used in the past with reasonable success¹⁻³. However, the systems studied so far in the LEPS scheme are the simple metal- H_2 systems. In practice, however, most of the industrial catalysts are the bimetallic systems. It will be of great interest, therefore, to extend the LEPS scheme to the H_2 /alloy system to study how the alloying affects the reaction pathways of a dissociative chemisorption reaction. Such a study would require knowledge of the chemisorption properties of the metals as well as of the alloys. Such studies were, however, lacking for a long time. Only recently, Casalone and Tantardini⁴ studied the chemisorption properties of hydrogen on Pt, Au and Pt-Au (111) surfaces, since Pt-Au alloys show improved catalytic activity and selectivity with respect to pure metals. They considered a large unit cell (LUC) with 18 metal atoms surrounded by a set of eight other large unit cells so that a total number of 162 metal atoms could be considered. The geometrical structure of the LUC is shown in Fig. 1. In the tight binding scheme they studied the chemisorption of a hydrogen atom on different surface sites of Pt, Au and Pt-Au (111) surfaces. The results indicated that on pure Pt and Au (111) surface the chemisorption bond on the top site is the strongest, while for Pt-rich Pt-Au (111) surface the centre hollow sites show maximum stability. It is the aim

of the present work to use these results as input parameters to study the H_2 dissociation on Pt_{18} (111) and $Pt_{17}Au$ (111) surfaces. In the latter system, the central Pt atom is substituted by an Au atom. We use the London-Eyring-Polanyi-Sato (LEPS) potential method to predict the reaction path for H_2 dissociation on the two systems.

Theoretical

In essence, for studying the dissociative chemisorption of a diatomic molecule AB on a metal/alloy surface the LEPS method relies on obtaining a molecule-solid surface potential in the form¹⁻³,

$$E_{LEPS} = Q_{AB} + Q_{AS} + Q_{BS} - [J_{AB}^2 + (J_{AS} + J_{BS})(J_{AS} + J_{BS} - J_{AB})]^{1/2} \dots (1)$$

where Q_{ij} is the Coulomb interaction and J_{ij} is an exchange interaction between centres i and j . The quantities Q_{ij} and J_{ij} may be obtained from the

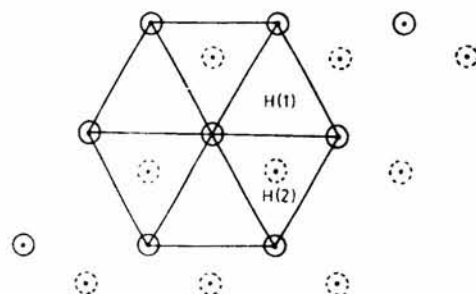


Fig. 1 – Geometrical structure of the large unit cell: The solid circles and the dotted circles indicate the metal atoms in the first and second layers respectively. H(1) site is the hollow site with no atom below in the second layer. H(2) site is the hollow site with an atom below in the second layer.

Morse bonding and antibonding functions expressed respectively as

$$(Q_{ij} + J_{ij}) / (1 + \Delta_{ij}) = D_{ij} \exp[-\alpha_{ij}(r - r_e)] \times \{\exp[-\alpha_{ij}(r - r_e)] - 2\} \dots (2)$$

and

$$(Q_{ij} - J_{ij}) / (1 - \Delta_{ij}) = (D_{ij}/2) \exp[-\alpha_{ij}(r - r_e)] \times \{\exp[-\alpha_{ij}(r - r_e)] + 2\} \dots (3)$$

In the expressions (2) and (3), D_{ij} is the dissociation energy; α_{ij} is the Morse parameter related to the frequency of vibration and r_e is the equilibrium separation. Δ_{ij} is the adjustable Sato parameter, to be chosen in such a way that a good agreement is obtained with the experimental values of the activation energy for dissociative chemisorption and the activation energy for desorption.

For the diatom-surface system then the E_{LEPS} describes a potential as a function of the diatom-surface distance (z , say) and the A-B separation (H-H distance) R . In principle, one has to calculate E_{LEPS} for all possible orientations of the H_2 molecule with respect to the surface and all possible approach paths of the molecule towards the surface. From a comparison of the E_{LEPS} values one has to find out the most probable dissociation path. For simplicity, however, we assume that the H_2 molecule remains parallel to the surface while approaching the surface from above. For symmetry reasons, we consider the dissociation configurations as shown in Fig. 2. Configuration (a) describes H_2 molecule dissociating above a bridge

position; the dissociated H atoms being ultimately chemisorbed on top positions. Configuration (b) corresponds to H_2 molecule dissociating on top position and the H atoms ultimately chemisorb on bridge positions. Configuration (c) considers dissociation of H_2 molecule above bridge position, the H atoms then chemisorbing on centre positions. And finally, the configuration (d) considers H_2 dissociation on top positions, the H atoms chemisorbing on the centre positions. The input parameters for the calculations are taken from the work of Casalone and Tantardini⁴ and are shown in Table 1. The parameter α is calculated from the second derivative of the potential curve about the equilibrium point. To study the dynamics of molecules we need to calculate E_{LEPS} for H atoms on various positions on the surface besides the top, bridge and centre sites. We obtain E_{LEPS} for these intermediate sites by linear interpolation method.

Results and Discussion

To proceed with the calculation of LEPS potential we first find the Sato parameter. $\Delta_{ij} = \Delta$ (assumed to be the same for all pairs). Δ is numerically chosen in such a way as to reproduce the experimentally obtained values of the activation energy for dissociation and the activation energy for desorption. The results are shown in Table 2.

Table 1 – The parameters used in the LEPS calculation⁴

Adsorption site	D(eV)		$r_e(\text{\AA})$		$\alpha(\text{\AA}^{-1})$	
	(a)	(b)	(a)	(b)	(a)	(b)
Top	2.89	2.65	1.45	1.40	0.96	0.98
Bridge	2.84	2.70	0.80	0.80	1.18	1.02
H(1)	2.72	2.71	0.66	0.66	1.35	1.19
H(2)	2.79	2.65	0.66	0.66	1.32	1.20

(a): H/Pt₁₈; (b): H/Pt₁₇Au; H(1): no atom in the 2nd layer; H(2): atom in the second layer (see Fig. 1).

Table 2 – Activation energy for dissociative chemisorption (E_1) and desorption (E_2) for different values of adjustable Sato parameter, Δ .

Sato parameter (Δ)	E_1 (kcal/mol)	E_2 (kcal/mol)
0.5	0	30.4
0.2	0	30.1
0.09	1.5	31.4
0.0	5.7	29.6
-0.2	17.5	28.8

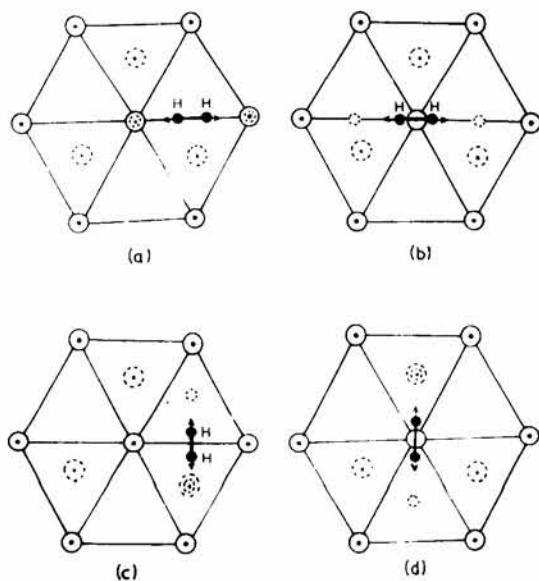


Fig. 2 – Approach geometries for H_2 chemisorption on Pt and Pt-Au(111) surfaces. For details see text.

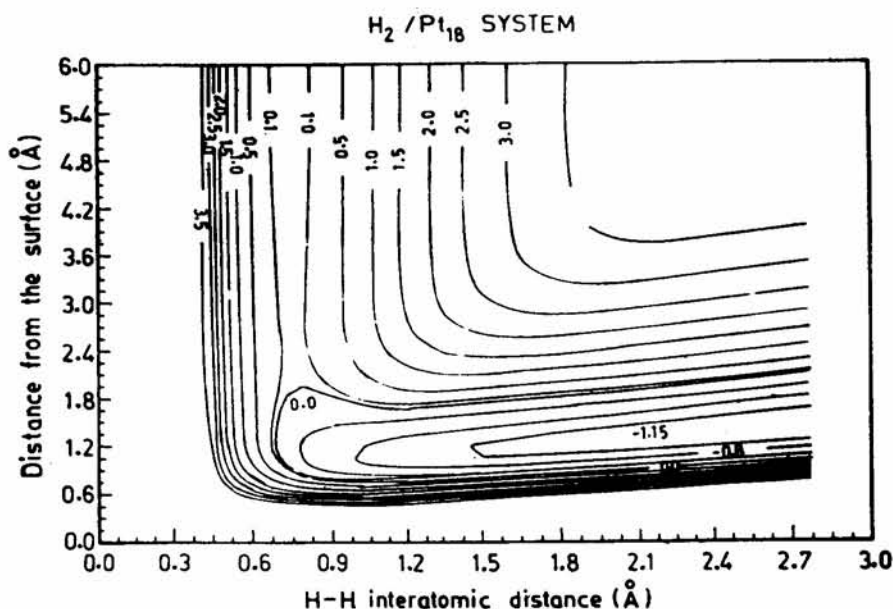


Fig. 3 – Equipotential contours for H₂ dissociation on Pt₁₈ surface in the configuration 2(a) [energy in eV].

It may be noted that for $\Delta = 0.2$ the dissociation is found to be a nonactivated process, while for negative values of Δ the activation for dissociation is very large and the activation for desorption is lower. It is known from experiments^{5,6} that the dissociative adsorption of hydrogen is an activated process on the Pt(111) surface with a barrier height, $E_1 \approx 0.5$ – 1.5 kcal/mol. It may be found from Table 2 that $\Delta = 0.09$ gives the barrier height of the order of 1.5 kcal/mol for the H₂/Pt₁₈ system. The desorption barrier E_2 for the above system is found to be of the order of 31 kcal/mol, which is again in good agreement with the thermal desorption results⁶⁻⁸. The equipotential contours for $\Delta = 0.09$ are shown in Fig. 3. The adsorption potential curve is shown in Fig. 4. The reference of the LEPS potential, as is used in the Figs 3 and 4, is the binding energy of the H₂ molecule, i.e., -4.476 eV.

The summary of results obtained by the LEPS scheme is presented in Table 3. The first column describes the configuration and the cluster. The columns denoted by E_1 and E_2 give, as before, the activation barrier for dissociative chemisorption and the activation barrier for desorption respectively. It may be noted that for the H/Pt system the barrier for dissociative chemisorption is almost the same in all the configurations (ranging from 1.52 to 1.59 kcal/mol); however, the barrier for desorption is largest for configuration 2(a). This suggests that for the H₂/Pt system the dissociation takes place at the bridge site and the dis-

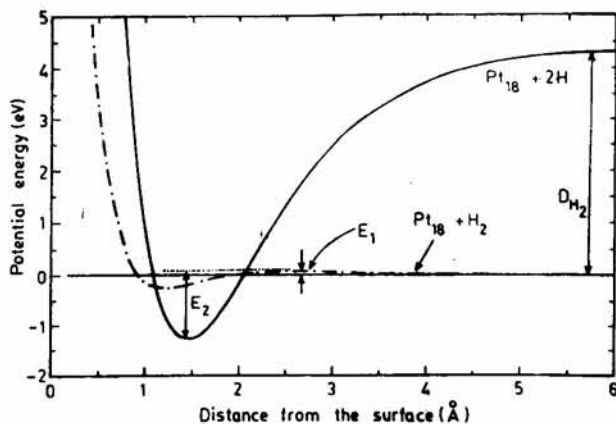


Fig. 4 – Surface-molecule potential for H₂ adsorption on Pt₁₈ surface (configuration 2(a)) [energy in eV].

Table 3 – Activation barriers for dissociative chemisorption and desorption for H₂/Pt₁₈ and H₂/Pt₁₇Au systems

Configuration/cluster	E_1 (kcal/mol)	E_2 (kcal/mol)
2(a): H ₂ /Pt ₁₈	1.54	31.4
2(a): H ₂ /Pt ₁₇ Au	1.73	20.1
2(b): H ₂ /Pt ₁₈	1.52	29.0
2(b): H ₂ /Pt ₁₇ Au	1.75	22.8
2(c): H ₂ /Pt ₁₈	1.59	21.5
2(c): H ₂ /Pt ₁₇ Au	1.71	21.2
2(d): H ₂ /Pt ₁₈	1.54	23.8
2(d): H ₂ /Pt ₁₇ Au	1.73	21.2

sociated H atoms get chemisorbed at top sites. For the $H_2/Pt_{17}Au$ system, on the other hand, the general value of barrier for dissociative chemisorption is of the order of 1.73 kcal/mol. However, the desorption barrier is highest (22.8 kcal/mol) for configuration 2(b) which corresponds to dissociation of H_2 molecule at top sites but chemisorption at bridge sites. Thus, alloying is found to change the reaction paths over metal surfaces. With chemisorption results for Pt clusters having more substituted Au atoms, it may be possible to obtain further changes in the reaction paths. In this way alloying may be selectively utilised in controlling the adsorption and desorption processes and finally controlling the heterogeneous catalytic reactions over metal/alloy surfaces. For example, it may be observed from Table 3 that E_1 for Pt-Au cluster is greater than E_1 for pure Pt clusters. This indicates that the adsorption barrier increases with alloying Pt by Au. This ultimately would decrease the activity of a reaction on the Pt-Au catalyst where H_2 dissociation is the rate-determining step.

It is known from the work of Sinfelt and his associates that the activity of group VIII metals for hydrogenolysis reactions of hydrocarbons decreases markedly in the presence of group IB metals⁹⁻¹². The inhibition of hydrogenolysis leads to improved selectivity for alkane isomerisation reactions and for reactions in which saturated hydrocarbons are converted to aromatic hydrocarbons. Studies on the effect of alloying is thus very important in understanding the selective catalytic behaviour of metals and alloys. Since adsorption and desorption of atoms and molecules are two important steps in the overall reaction mechanism, studies on the effect of alloying on the dissociation path is thus very important and we have attempted in this work to study just one such system, namely, the $H_2/Pt_{17}Au$ system. It is expected that studies on more such systems would enable us to understand better the dynamics of molecular dissociation.

There are, however, certain limitations of this calculation. To interpret the role of alloying on

the rate of catalytic reaction like ethane hydrogenolysis, etc., one has to study chemisorption on extended systems. In a typical catalytic system there are 200-2000 metal atoms per particle. The particles, usually do not have regular structures. Furthermore, even for a regular shape like cubooctahedron there are chemisorption sites like the corner sites, bridge sites and sites on fcc (100) and fcc (111)-like faces. An ideal study of molecular dynamics would involve studying chemisorption properties on such extended systems. Again in case of alloys there is surface segregation; the constituent metal atoms competing for favourable sites on these particles. Our present theoretical knowledge as well as experimental techniques are not accurate enough to provide the required chemisorption properties reliably. The present work is only the first step in our attempt to understand the problem systematically.

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