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Article

General trends in Horiuti-Polanyi mechanism vs non-Horiuti-Polanyi mechanism for water formation on transition metal surfaces

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ABSTRACT

It is generally acknowledged in heterogeneous catalysis that hydrogenation follows the so-called Horiuti-Polanyi (HP) mechanism. In this work, a thorough investigation of the mechanism of hydrogenation of hydroxyl groups and O catalyzed by a series of transition metals was carried out through density functional theory calculations, as surface hydroxyls and O are very common species in many catalytic systems. It is found that different metal catalysts exhibit different mechanisms. On some metal catalysts, the non-HP mechanism is preferred, whereas the classic HP mechanism is favored on other catalysts. Detailed analyses of the metal-dependent mechanism shows that the activity toward the dissociation of H₂ decides which mechanism is preferred. On active catalysts, such as Ni and Pt, H₂ prefers to dissociate with strong H adsorption energies, which lead to the classic HP mechanism being favored. On inactive surfaces, on the other hand, the adsorption of H is weak, which results in the non-HP mechanism being preferred. The parameter η , which is a structural descriptor, was defined to understand the different mechanisms.

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1. Introduction

The hydroxyl group (OH) is perhaps one of the most common species in heterogeneous catalysis as it can play an important role as both a reductant and an oxidant. There are many types of industrial reactions involving the OH group, such as Fischer-Tropsch synthesis [1–3], methane reformation [4,5], ammonia oxidation [6], as well as the ethanol synthesis reaction [7]. In the process of carbon dioxide hydrogenation, a moderate amount of OH groups and some adsorbed O* are generated when water is used [8–11] that may cover the Cu surface, which block the active sites and affect the reaction rate

to some extent. Traditionally, the hydroxyl groups and adsorbed O are removed from catalyst surfaces by reduction with H adsorbed on the surfaces both experimentally and theoretically, which results in the formation of water via the so-called classic Horiuti-Polanyi (HP) mechanism [12–14]. This involves a three-step process, namely, H₂ adsorption, followed by dissociation, and hydrogenation by H. In the reduction reaction, H₂ is generally over a large quantity to increase the turn over frequency, and theoretical simulations are desirable for understanding the nature of the catalytic process.

Hydrogenation by adsorbed H, which is the HP mechanism, was generally acknowledged, and other possibilities were vir-

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tually neglected, until two interesting results were reported. The first result was that the non-Horiuti-Polanyi (non-HP) mechanism is favorable for the hydrogenation of acrolein when the catalyst used is Ag or Au, as revealed through our previous theoretical work [15], and the other one was that the reductant reacts with H through a H₂ molecule over supported Ag nanoparticles [16]. As for the catalyst, transition metals are widely used for hydrogenation reactions [17–20], especially, late transition metals are utilized for the oxycarbide redox reaction.

In addition to the two metals mentioned above, Cu is the active component in methanol synthesis [21,22], and Ni-based catalysts are used in the steam reforming of natural gas [23–25] ($C_xH_y + xH_2O \rightarrow xCO_2 + (x + y/2)H_2$) and in methanation [26,27] ($CO + 3H_2 \rightarrow CH_4 + H_2O$); Pt metal is often utilized as a catalyst in water-gas shift reactions [28], in which the coupling of OH* with H* is generally accepted [29]. It is well known that transition metals with different activities are widely used to catalyze hydrogenation reactions [17–19,30], but the hydrogenation mechanism may be sensitive to the surface type [15]. The following important questions remain to be answered. Are all the adsorbed OH* or O* hydrogenated via the HP mechanism? Are there any possibilities that OH* or O* are attacked by molecular H₂? If the answer is yes, when is the non-HP mechanism favored? To obtain a good understanding, systematic exploration of the reaction mechanism was carried out for representative transition metals, such as Ni, Pt, Cu, Ag, and Au, based on density functional theory (DFT) calculations in this work. Two surfaces with different Miller indices were investigated, including the stepped (211) surfaces and the flat (111) surfaces.

In this work, the adsorption and dissociation of H₂ were first studied. All the hydrogenation pathways were investigated and detailed comparisons are made. A structural descriptor has been introduced to analyze the structures based on the reaction mechanisms.

2. Model and method

First-principles energy calculations were performed within the density functional theoretical [31,32] framework by using Vienna *ab initio* simulation package [33–35]; Perdew-Burke-Ernzerhof functional with generalized gradient approximation [36] was employed to describe the exchange correlation between electrons [37]. PAW method [38,39] was used to describe the core-electron interactions, and the cut-off energy of the plane-wave basis set was set as 400 eV. For Ni, the calculations were carried out with spin-polarized. The geometry was relaxed using Broyden method, which stopped only when the force of the ions became less than 0.05 eV/Å. The lattice constants of the unit cells were optimized first and then periodic four-layer slabs were modeled as metal surfaces. The vacuum region between the slabs was in excess of 15 Å. $4 \times 4 \times 1$ k-point sampling of Monkhorst Pack scheme was used for the $p(1 \times 4)$ supercell of fcc(211) and the $p(3 \times 3)$ supercell of fcc(111) surfaces. The bottom two layers of the slab were fixed at the bulk truncated position, with the top two layers fully relaxed during the structural optimization. All the adsorption

geometries were optimized using a force-based conjugate gradient algorithm, while the transition states (TSs) of reactions were searched using a constrained minimization scheme [40–42]. The adsorption energy of surface-absorbed species *X* was defined as follows:

$$E_{\text{ads}}(X) = E_{X+\text{surface}} - (E_{\text{surface}} + E_X) \quad (1)$$

where $E_{X+\text{surface}}$, E_{surface} , and E_X are the optimized energies of the total adsorption system, the adsorbate in the gas phase, and the clean surface, respectively. A more negative value of E_{ads} suggests stronger binding on the surface.

3. Results and discussion

A series of metal surfaces was investigated for OH/O hydrogenation, including Ni, Pt, Cu, Au, and Ag. The mechanistic study of water formation from OH hydrogenation, as well as that of O* hydrogenation, was extended from the flat (111) surfaces to the stepped (211) surfaces.

3.1. H₂ dissociation

First, we examined the adsorption and dissociation of H₂ on the abovementioned metal surfaces. Fig. 1(c) shows that in the TS, two adsorbed H atoms occupy the fcc and top sites on the (111) surface, whereas they are located at the bridge and top sites along the stepped edge of the (211) surface, respectively. The corresponding energy values are listed in Table 1. Accordingly, the relationships between the dissociative energy barrier and the adsorption energy as well as the reaction energy could be mapped out, as illustrated in Fig. 1(a, b). The adsorption of H₂ on Cu, Ag, and Au surfaces is very weak, whereas a strong bonding is observed between H₂ and the catalytically active Ni surface. Particularly, at the stepped edge sites of Ni(211), the adsorption energy of H₂ ($E_{\text{ads}}(\text{H}_2^*)$) could reach −0.48 eV.

Pt catalysts find wide applications in redox reactions leading to water formation [43–46], as the dissociative adsorption of H₂ on Pt is very facile. It is found that the adsorption of H₂ on both Pt(211) and Pt(111) is very weak, but that the dissociative adsorption is reasonably strong [47,48]. The barriers for H₂ dissociation $E_a(\text{H}_{2,\text{dis}}^*)$ on Ni and Pt surfaces are very low (less than 0.2 eV), and the H–H bond can be easily broken. The strong driving force for H₂ dissociation renders the reaction strongly exothermic. Their energies are reduced by 0.65 and 0.87 eV over Ni(211) and Ni(111) surfaces and by 1.22 and 1.00 eV over Pt(211) and Pt(111) surfaces, respectively. The calculated results are in good agreement with those of Zhu et al. [46] on the reforming of methane on Ni(111).

Au and Ag surfaces display low activities toward H₂ adsorption and the barriers for H₂ dissociation are very high. The $E_a(\text{H}_{2,\text{dis}}^*)$ values exceed 1 eV on Ag(111), Au(111), and Ag(211). On the other hand, $E_a(\text{H}_{2,\text{dis}}^*)$ is 0.57 eV on Au(211) surface, which indicates that the activities of Au are distinct over different crystal surfaces. The H₂ dissociation reaction is endothermic on Au and Ag surfaces, which suggests that the forward reaction is unfavorable. On the two Cu surfaces, although the dissociative chemisorption energy $\Delta E(\text{H}_{2,\text{dis}}^*)$ is ~ -0.5 eV, the dissociation barrier $E_a(\text{H}_{2,\text{dis}}^*)$ requires an energy of ~ 0.5 eV.

Fig. 1. (a) Correlations between H₂ activation energy and adsorption energy on metal (211) and (111) surfaces; (b) correlations between H₂ activation energy and the energy of H₂ dissociation on metal (211) and (111) surfaces; (c) TS structures associated with H₂ dissociation. The red circles and square points represent the data of the (211) surfaces, whereas the green ones pertain to the (111) surfaces.

Subsequently, we studied the relations of E_a with E_{ads} and ΔE . Some correlations were identified, as shown in Fig. 1(a, b). It is found that there is no linear relationship between E_a and E_{ads} , but the data points are located at two different regions: the data points of inactive metals, which exhibit higher dissociation barriers and lower adsorption energies, can be found in the upper right corner, whereas those of active metals are observed in the bottom left area (Fig. 1(a)).

On the other hand, a linear correlation between E_a and ΔE can be observed, as revealed in Fig. 1(b). These results demonstrate that H₂ dissociation on these metals is strongly related to the adsorption of H*. It is clear that the data in the bottom left region represent the catalytically active metals for H₂ dissociation, whereas those at the upper right corner correspond to the catalytically inert metals for H₂ dissociation, though they may be possible catalysts for H₂ to hydrogenate OH*/O*. The bondings of H* with Pt and Ni surface atoms lower the energies E_v by 0.3–0.6 eV. Moreover, the H₂ dissociation barriers are no

more than 0.3 eV. These results are consistent with those of Phatak et al. [49]. On Ag(111), Au(111), and Ag(211), E_a are rather high, and the formed H* is also not stable on these surfaces. The H₂ dissociation may not proceed. Hence, the reaction equilibrium shifts to H₂ in the gas phase, which results in the attack of OH*/O* by H₂ becoming more probable. The H₂ dissociation performance on Cu surfaces is in the middle of the corresponding performances on the metal surfaces. Therefore, it is not easy to energetically assess whether H₂ can be activated. This will be further discussed in section 3.2.

3.2. Comparison of hydrogenation mechanisms

Both the classic HP hydrogenation and the non-HP hydrogenation mechanisms of OH*/O* reduction on metal surfaces were investigated. The energy profiles over three typical surfaces, which include inactive Ag(211), active Pt(211), and the moderately active Cu(211), are shown in Fig. 2.

3.2.1. Mechanisms of OH* removal

As illustrated by the solid line in Fig. 2, the two mechanisms of OH* hydrogenation were compared. H₂ dissociation was also considered, which is essential to understand the hydrogenation by H₂. It can be seen from Fig. 2(a) that, on Pt(211), the H₂ dissociation is easier to occur than coupling with OH* species, although the latter displays a lower energy barrier than the direct hydrogenation of OH* by atomic H* (0.25 eV vs. 0.90 eV); the data are listed in Table 2. This result suggests that the classic HP mechanism is more favorable than non-HP mechanism on active surfaces. Similar reaction characteristics are found on the Pt(111), Ni(211), as well as Ni(111), surfaces. Fig. 2(b) elucidates the difference between the two hydrogenation mecha-

Table 1

Adsorption energies (E_{ads}) of H₂, energy barriers (E_a), and enthalpy changes (ΔE) for H₂ dissociation and the distance between two H atoms in the TSs (D_{dis}).

	Metal	E_{ads}/eV	E_a/eV	$\Delta E/\text{eV}$	$D_{dis}/\text{\AA}$
(211) facet	Cu	-0.05	0.48	-0.50	1.39
	Au	0.00	0.57	0.06	1.35
	Ag	0.02	1.14	0.34	1.55
	Ni	-0.48	0.12	-0.65	1.28
	Pt	-0.04	0.10	-1.22	1.30
(111) facet	Cu	0.13	0.56	-0.49	1.38
	Au	0.01	1.00	0.45	1.33
	Ag	0.01	1.21	0.45	1.27
	Ni	-0.26	0.06	-0.87	1.13
	Pt	0.05	0.19	-1.00	1.15

Fig. 2. Energy profiles of the mechanism of OH*/O* hydrogenation by molecular hydrogen (dotted line), compared with those of the classic HP hydrogenation mechanism (solid line) and H₂ dissociation on representative surfaces: (a) Pt(211); (b) Ag(211); (c) Cu(211).

nisms on Ag(211), which is a representative inactive metal. H₂ dissociation exhibits the highest barrier (1.14 eV; Table 1), and the barrier for direct OH* hydrogenation by H* is 0.6 eV; the hydrogenation of OH* by H₂ reveals a barrier that is as low as 0.3 eV. Hence, the reduction of OH* by H₂ catalyzed by inactive metals offers an advantage over the mechanism of direct addition of atomic H*. The other inactive surfaces, such as Ag(111), Au(211), Au(111), and Cu(111), also exhibit this tendency, as observed in Table 2.

The difference in mechanism between OH* hydrogenation on active metals (Pt, Ni) and that on inactive metals (Ag, Au) is obvious. However, Cu(211) is a special case: it displays a moderate activity, which results in a dependence of the mechanism on the specific reaction condition. The H₂ dissociation and the hydrogenations by atomic and molecular hydrogens on Cu(211) are compared in Fig. 2(c). The hydrogenation of OH* by H₂* reveals a barrier that is comparable to that of H₂ dissociation (0.47 eV vs. 0.48 eV). Although the hydrogenation of OH* by H* exhibits a higher barrier than that by H₂, the adsorption of H* on Cu(211) is stronger than that of H₂*. As a result, the balance between the adsorption energy of H* and the H₂ dissociation barrier would determine which pathway is favored, and can be affected by the experimental reaction temperature and the partial pressure. Our results show that the non-HP mechanism dominates at low temperatures, whereas the classic HP mechanism is more favored when the temperature is significantly increased.

3.2.2. Mechanisms of O* hydrogenation

Considering the importance of adsorbed O* in heterogene-

ous catalysis, the hydrogenation of O* via the two different pathways was researched and the results on three representative surfaces are shown in the form of dotted lines in Fig. 2. On Pt(211) surface, H₂ dissociation is easier to occur than coupling with O* species, although the latter displays a much lower energy barrier than that for direct hydrogenation of O* by atomic H* (0.30 eV vs. 0.80 eV). Therefore, the classic HP mechanism is preferred. Similar results are obtained on the other three active surfaces, namely, Pt(111), Ni(211), and Ni(111).

On Ag(211), the hydrogenation of O* by H₂* reveals the lowest barrier (0.42 eV), in comparison with 0.58 and 1.14 eV for hydrogenation by atomic H* and H₂ dissociation, respectively. On Ag(111), Au(211), Au(111), Cu(211), and Cu(111), the barriers for hydrogenation by H₂ are found to be 0.38, 0.17, 0.51, 0.22, and 0.41 eV, respectively, whereas the H₂ dissociation barriers are 1.21, 0.57, 1.00, 0.48, and 0.56 eV, respectively. The energy barrier for the non-HP hydrogenation mechanism is lower than that for the classic HP mechanism on every surface except Au(111). On Au(111), the two barriers are nearly equal and the H₂ dissociative adsorption energy ($E_{\text{ads}}(\text{H}^*)$) is positive (0.23 eV); $E_{\text{ads}}(\text{H}_2^*)$ almost equals zero. Therefore, the effective barrier for O* hydrogenation by H* is 0.73 eV, which is higher than that for O* hydrogenation by H₂ (0.51 eV). In other words, the O* hydrogenation is similar to the OH* hydrogenation.

3.2.3. Trend of mechanism preference

A descriptor, $E_{\text{ads}}(\text{O}^*)$ was utilized to fit the energy barriers of both OH* and O* hydrogenations as well as those of H₂ dissociation on these surfaces, considering that the adsorption energy of O* may be of importance. The value of $E_{\text{ads}}(\text{O}^*)$ may be a

Table 2

Calculated energy barriers and the energy changes in OH* and O* hydrogenation reactions. The energy unit is eV.

Step	OH* + H*		OH* + H ₂ *		O* + H*		O* + H ₂ *	
	E_{a}	ΔE	E_{a}	ΔE	E_{a}	ΔE	E_{a}	ΔE
Cu(211)	1.00	0.31	0.47	-0.19	0.79	-0.76	0.22	-1.26
Au(211)	0.65	-0.89	0.45	-0.83	0.34	-1.77	0.17	-1.71
Ag(211)	0.59	-0.67	0.29	-0.37	0.58	-1.70	0.42	-1.40
Ni(211)	1.17	0.67	0.93	0.02	1.08	0.05	0.98	-0.71
Pt(211)	0.90	0.24	0.25	-0.98	0.80	-0.41	0.30	-1.63
Cu(111)	1.08	-0.16	0.28	-0.65	0.99	-0.66	0.41	-1.15
Au(111)	0.50	-1.51	0.22	-1.05	0.50	-1.52	0.51	-1.07
Ag(111)	0.72	-0.97	0.33	-0.52	0.97	-1.75	0.38	-1.30
Ni(111)	1.40	0.41	0.59	-0.46	1.25	0.27	0.82	-0.60
Pt(111)	0.59	-0.67	0.05	-1.24	1.02	0.01	0.41	-0.99

Fig. 3. Relations between the energy barrier and the O* chemisorption energy ($E_{\text{ads}}(\text{O}^*)$) for (a) OH* hydrogenation and (b) O* hydrogenation on a series of surfaces, in conjunction with the results for H₂ dissociation (the blue circles correspond to the classic HP hydrogenation mechanism, the red squares to hydrogenation by molecular hydrogen, and the green triangles to H₂ dissociation). Each column corresponds to one catalytic surface, and the solid dots represent the data obtained from the stepped (211) surfaces, whereas the hollow dots correspond to the flat (111) surfaces.

key measure of catalytic activity. The results are displayed in Fig. 3.

We can observe the following features in the figure. First, E_a ($\text{H}_{2,\text{dis}}^*$) changes linearly as a function of $E_{\text{ads}}(\text{O}^*)$. The more negative the $E_{\text{ads}}(\text{O}^*)$ value, the lower is the dissociation barrier, which indicates that there are some correlations between O* adsorption and H₂ reactivity, as reported by Wang et al. [50–52]. Secondly, E_a linearly increases with $E_{\text{ads}}(\text{O}^*)$ for both the hydrogenation pathways. The strong bonding between OH* and the surface atoms inhibits the reactivity and enhances the hydrogenation barrier. Thirdly, the fact that nearly all the red square points (corresponding to the hydrogenation by H₂) lie below the blue circles (which represent the HP mechanism) shows that the energy barriers of the non-HP mechanism are lower than those of the HP mechanism. However, the mechanism changes when the green line crosses the red line; the lines beyond the point of intersection are displayed in yellow in Fig. 3. Starting from the left hand side, the HP mechanism is preferred and, after the intersection point, the non-HP mechanism is favored. Of course, this is only a qualitative description of the trend.

It is obvious that the geometric effect should be of importance in determining which of the two mechanisms is preferred [53]. Fig. 4 shows the TS structures of OH*/O* hydrogenation on both (211) and (111) surfaces. For the pathway of hydrogenation by H₂, the TS structure of HO–HH/O–HH is parallel to the surface, with a relatively flat configuration, which results in a better orbital overlap. On the contrary, for the pathway of hydrogenation by H, the TS structure of HO–H/O–H is inclined to the surface, especially at the step edge site on (211). This agrees well with reports that metal (211) surfaces exhibit higher activities for bond breaking than metallic (111) surfaces [43,54,55].

3.3. Structure of hydrogenation by H₂

It is worth pointing out that whether the mechanism of hydrogenation by H₂ or the classic HP mechanism is favored depends on the nature of the TS structure, in particular, the distance between two H atoms is of importance. Our DFT calculations revealed the bond lengths between two H atoms in the TSs of hydrogenation by H₂ on all the metal surfaces (Table 3).

To characterize the TS structures of non-HP hydrogenation, the distance between H atoms is inadequate. Therefore, a parameter η was introduced, which is defined as follows:

$$\eta = \frac{(D_i - D_{\text{H}_2})}{(D_{\text{dis}} - D_{\text{H}_2})}$$

where D_i is the distance between two H in the TS of molecular hydrogenation of OH* or O*. D_{H_2} is the bond length of optimized H₂, which is calculated to be 0.75 Å in our work. D_{dis} is the distance between two H in the TS of H₂ dissociation.

The parameter η is a measure of the H–H separation in the TS of hydrogenation, and its value is $0 < \eta < 1$, by definition. The lower and upper boundaries represent the structure of the H₂ molecule in the gas phase and the H₂ dissociation structure in the TS, respectively. The higher the η value, the more similar is the structure of H–H in the TS of OH* or O* hydrogenation to that of H₂ dissociation. Fig. 5 shows the η values of all the steps of hydrogenation by H₂ on both (211) and (111) surfaces as functions of the metal d-band centers [56,57]. The η values for the Pt and Ni surfaces are not less than 0.4, being 0.65 (Pt(211)), 0.57 (Ni(211)) for OH* hydrogenation and 0.53 (Pt(211)), 0.55 (Ni(211)) for O* hydrogenation on the stepped surfaces vs. 0.64 (Pt(111)), 0.68 (Ni(111)) and 0.49 (Pt(111)), 0.63 (Ni(111)) on the flat surfaces. On the other hand, the η values of Au and Ag are less than 0.4, being 0.27 (Au(211)), 0.25 (Ag(211)), 0.18 (Au(111)), 0.31 (Ag(111)) and 0.16 (Au(211)), 0.12 (Ag(211)), 0.14 (Au(111)), 0.18 (Ag(111)), which correspond to the hydrogenation of OH* and O* by H₂. Likewise, on Cu surfaces, the η values are found to be 0.19 (Cu(211)), 0.34 (Cu(111)) and 0.23 (Cu(211)), 0.25 (Cu(111)) for OH* and O* for the non-HP mechanism.

Fig. 4. TS structures of OH* and O* hydrogenation on (211) and (111) surfaces. Red: O; white: H; light blue: Ni; dark blue: Pt; orange: Cu; gold: Au; sky blue: Ag.

It is clear that Ni and Pt are active catalysts, whereas Au and Ag are inactive. Therefore, the upper boundary is approximately determined by the η value of 0.49 for Ni and Pt, and the lower one by the η value of 0.31 for Au and Ag, which are displayed as brown and yellow triangles, respectively, in Fig. 5. The center for this region is determined to be $\eta = 0.41$ by calculating the geometric average of the η values. The boundary zone divides the data into two regions. On the left hand side of Fig. 5, i.e., η values below 0.41, the H–H distances in the TSs of

Table 3

Bond distances between two H atoms in the TSs of elementary steps, defined as $D_{\text{H-H}}$

$D_{\text{H-H}}/\text{\AA}$	H_2, dis^*	$\text{OH}^* + \text{H}_2^*$	$\text{O}^* + \text{H}_2^*$
Cu(211)	1.39	0.87	0.90
Au(211)	1.35	0.91	0.85
Ag(211)	1.55	0.95	0.84
Ni(211)	1.28	1.05	1.04
Pt(211)	1.30	1.11	1.04
Cu(111)	1.38	0.97	0.91
Au(111)	1.33	0.85	0.83
Ag(111)	1.27	0.91	0.84
Ni(111)	1.13	1.01	0.99
Pt(111)	1.15	1.01	0.95

Fig. 5. d-band centers of transitional metals as a function of the parameter η for the TSs of the hydrogenation reactions: the green squares and yellow up-triangles represent the reaction of OH*+H₂* on (211) and (111) surfaces, respectively, whereas the red circles and brown down-triangles represent the reaction of O*+H₂* on (211) and (111) surfaces, respectively.

non-HP mechanism are similar to the H–H distance in the gas phase, which is observed on inactive metal surfaces with highly negative values of d-band centers. On the right hand side of Fig. 5, the data points of η for the active metals are characterized by the d-band center located in the region beyond $\eta = 0.41$, which suggests that the H–H bond length is close to that of H–H dissociation distance and, thus, the HP mechanism can be distinguished from the non-HP mechanism.

Having presented the results above, it is worth discussing the results of Fig. 1 further. The boundary marked by $E_a = 0.4$ eV is found to realize the goal of dividing all the data points into two parts, as illustrated in Fig. 1(a, b). The region below 0.4 eV is the area in which H₂ can readily dissociate, namely, the catalytically active region for H₂ dissociation. The region above 0.4 eV is the area in which H₂ dissociation is not active. Interestingly, the energy of 0.4 eV is the entropy of H₂ in the gas phase at room temperature. In summary, H₂ dissociation occurs most likely in the region below 0.4 eV, whereas, in the region above 0.4 eV, the mechanism of hydrogenation by H₂ is preferred.

4. Conclusions

The non-HP mechanism of OH* and O* hydrogenation reac-

tions over a series of metals has been systematically investigated by DFT calculations and comprehensively compared with the classic HP hydrogenation mechanism. Some insights have been obtained. The H_2 dissociation activity over a catalyst decides whether the HP mechanism or the non-HP mechanism is preferred. It is found that the energy barriers of OH^*/O^* hydrogenation by H_2 are generally lower than those of direct hydrogenation of OH^*/O^* by H^* . On active catalysts such as Ni and Pt, H_2 molecules prefer to dissociate, with strong adsorption energies of H^* , which leads to the classic HP mechanism being favored. On inactive surfaces, e.g., Au and Ag catalysts, the H^* adsorption is weak and, therefore, the existence of H_2 molecules is thermodynamically preferred, which results in the non-HP mechanism being favored. Based on these interesting results, future research can be extended to surface alloys [58] to verify the universality of the conclusions. The parameter η was introduced to evaluate the hydrogenation mechanisms. When the η value is higher than 0.41, it signifies that the H–H structure in the TS of the hydrogenation reaction is similar to the H_2^* dissociation structure; the HP mechanism will then be favored. In contrast, the non-HP mechanism is favored if $\eta < 0.41$ and E_a of H_2^* dissociation is relatively high.

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Graphical Abstract

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General trends in Horiuti-Polanyi mechanism vs non-Horiuti-Polanyi mechanism for water formation on transition metal surfaces

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A thorough investigation of the Horiuti-Polanyi (HP) mechanism and the non-HP mechanism for hydroxyl/oxygen hydrogenation catalyzed by transition metals has been carried out through first-principles calculations, and the descriptor η was defined to understand the different mechanisms.

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过渡金属表面上水生成经典Horiuti-Polanyi机理与非Horiuti-Polanyi机理选择的总体趋势

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摘要: 在非均相催化加氢反应中, 氢气(H₂)一直被公认为是通过两步基元步骤参加还原反应的, 包括第一步的分子解离和之后的反应物与原子氢键合, 即所谓的Horiuti-Polanyi (HP)机理。直到我们研究组在Ag或Au催化丙烯醛加氢还原反应理论研究中发现非HP机理加氢路径存在时, 新的机理才被提出, 并引起广大研究者的浓厚兴趣。考虑到表面羟基(OH)和氧(O)在非均相催化体系中广泛存在, 如常见的过渡金属催化的费托合成、甲烷重整、水汽转化及氨氧化等反应, 基于第一性原理的密度泛函理论计算方法, 我们对OH/O在一系列过渡金属催化作用下还原生成水的微观机理进行了系统全面的探究。

研究发现, 不同金属对应于不同的催化氢化反应活性, 以及不同的催化反应机理。在某些金属上H₂以分子形式进攻反应物种的非HP机理有利, 而在其它金属上经典的H₂解离后参与氢化还原反应的HP机理更容易发生。详细分析显示, H₂的解离活性决定了反应机理的种类: 在对H₂解离具有催化活性的金属(如Pt、Ni)表面, 不论是(211)台阶面还是(111)平面, H₂解离几乎都是无能垒过程, 且伴随氢原子的强吸附, 反应放热明显, 导致活泼金属上HP机理更容易发生; 与之相反, 在不活泼的催化剂表面, H₂解离很难发生, 原子吸附也相当微弱, 相比于断键裂解, H₂更倾向于发生分子氢化的非HP机理。

另外, 本文还定义了一个新的结构描述符(η)来帮助理解两种机理发生的结构因素差异。 η 是衡量分子氢化过渡态结构(TS)中H–H键解离程度的参数, 根据其定义上下限数值分别设定为H₂在各催化剂表面解离过渡态的键长(D_{dis})和游离分子态的键长(D_{H_2})。结果显示, 易发生非HP机理的催化剂表面的TS结构对应的 η 参数普遍低于0.4, 即H–H原子对的确是以近分子形式参与氢化反应; 相反发生经典HP机理的催化剂表面, η 参数普遍在0.5–0.8, 即H–H即使以分子形式参与反应也是处于近解离状态, 这预示了以解离吸附氢参与反应的优选性。

关键词: 氢化反应; Horiuti-Polanyi机理; 水的形成; 过渡金属; 密度泛函理论

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