

General Structure–Reactivity Relationship for Oxygen on Transition-Metal Oxides

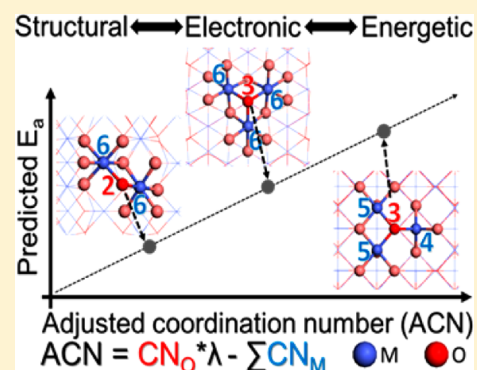
Victor Fung,[†] Franklin Feng Tao,[‡] and De-en Jiang^{*,†}

[†]Department of Chemistry, University of California, Riverside, California 92521, United States

[‡]Department of Chemical and Petroleum Engineering and Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, United States

S Supporting Information

ABSTRACT: Despite many recent developments in designing and screening catalysts for improved performance, transition-metal oxides continue to prove to be challenging due to the myriad inherent complexities of the systems and the possible morphologies that they can exhibit. Herein we propose a structural descriptor, the adjusted coordination number (ACN), which can generalize the reactivity of the oxygen sites over the many possible surface facets and defects of a transition-metal oxide. We demonstrate the strong correlation of this geometric descriptor with the electronic and energetic properties of the active sites on five facets of four transition-metal oxides. We then use the structural descriptor to predict C–H activation energies to show the great potential of using ACN for the prediction of catalytic performance. This study presents a first look into quantifying the relation between active site structure and reactivity of transition-metal-oxide catalysts.



The widespread adoption of density functional theory (DFT) has opened up new avenues in the use of computational methods to model and predict the structure–activity relationship of promising catalysts. Unfortunately, because of the inherent computational cost of fully ab initio techniques and the sheer number and complexity of possible catalytic materials and pathways to study, there has been much interest in developing approximate but fast methods of predicting catalytic activity based on DFT results. This “descriptor” approach based on adsorption energy, dissociation energy, d-band center, width, and so on has been employed successfully to transition-metal (TM) catalysts.^{1–3} Subsequent recent works have further demonstrated the concept of “structural” descriptors as a geometric-based method of catalyst screening and design for transition metals,^{4–7} which can be further extended to an “orbitalwise” description of coordination.⁸

Transition metal oxides (TMOs) are another class of materials of considerable interest and potential for heterogeneous catalysis. The complexity of TMO surfaces can be up to several orders of magnitude greater than TMs due to the multiple oxidation states, high density of surface defects, and complex electronic and spin structures. The inherent complexity of TMOs coupled to their industrial importance provides a strong impetus toward the development of broadly applicable and quantitative descriptors of their catalytic activity. In this work, we propose a structural descriptor to provide a first look into structure–reactivity relationships for the active oxygen sites of TMOs, corroborated by DFT calculations (see the Supporting Information (SI) for computational details).

Two commonly studied quantities to describe the oxygen reactivity on metal oxides are vacancy formation energy^{9–18} and H-adsorption energy.^{1,14,19–22} Vacancy formation energy measures the energy required to remove a lattice oxygen from the surface and has been suggested as a descriptor of catalytic performance.^{12,18,23} H adsorption has also been used in the correlations with the activation energies of C–H bond dissociation via the Bell–Evans–Polanyi (BEP) relationship.^{19–21,24} Besides the energetic descriptors, the electronic properties of solid catalysts in relation to their energetic properties or reactivity have been well demonstrated for TMs and other TM-based materials.^{18,25–30}

In search of a structural descriptor for TMOs, we were inspired by a recent success for such a descriptor for TMs. Calle-Vallejo et al. used coordination number and “generalized coordination number” as structural descriptors for TMs to describe the structural and electronic environment of the adsorption site and its nearest neighbors^{4–6} and correlated them to the d-band center. Inspired by their work, we think that the coordination number of the oxygen atom (CN_O) on TMO surfaces can be used as a structural descriptor. However, for metal oxides, the relevant CN_O rarely goes beyond one to four at the surface and cannot provide the same level of sensitivity and predictive ability as coordination in TMs. Therefore, we propose to include not only the coordination number of the surface oxygen site but also the coordination

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numbers of its neighboring *metal* atoms as a sum ($\sum CN_M$). Take the O–M–O*–M–O bonding motif as an example, with O* being the oxygen in question and M being a metal. The coordination number of O*, CN_O , is 2 in this case, while the sum of the coordination numbers of the coordinating M atoms, $\sum CN_M$, is $2 + 2 = 4$.

To correlate these coordination numbers to the electronic structure and reactivity of a metal oxide surface, a logical approach is to examine how they relate to the partial charge on the oxygen site, which is a good indication of reducibility. Indeed we found strong linear correlation of Bader charge³¹ with vacancy formation energy and H-adsorption energy associated with a surface oxygen site on various surfaces [(100), (110), (111), (211), and (311)] and types of TMOs (V_2O_3 , Cr_2O_3 , Co_3O_4 , and NiO), as shown in Figure S1 and Table S1 in the SI. So we only need to find a structural descriptor that is a function of CN_O and CN_M and at the same time correlates well with the O Bader charge. Intuitively, increasing CN_O will make the O Bader charge more negative by providing additional sources of electron density, that is, the metal cations. Meanwhile, increasing $\sum CN_M$ decreases Bader charge because the oxygen atoms in the second shell will withdraw electron density from the metal cations, leaving less to be transferred to the oxygen site.

We demonstrate the metal–oxygen electron-transfer model with successively larger clusters of Co_xO_y : The alternating electron-donating and -withdrawing effect of the successive neighboring oxygen and cobalt atoms can be seen in the Bader charge trend in Figure 1i. This leads to the oscillating Bader charges as each successive cobalt shell donates charge and oxygen shell withdraws charge until finally converging as it approaches the characteristics of a periodic surface. In theory, one can further refine this model by counting the coordination of further successively bonded atoms; the improvement to accuracy should rapidly converge as the difference in the subsequent coordination shells will vary less and less the further away from the oxygen atoms in question. So we will focus only on the first cobalt and oxygen shells here.

To identify a structural descriptor that is a function of both CN_O and CN_M , we need to examine the relationship between CN_O and $\sum CN_M$. As an example, here we use oxygen atoms on the Co_3O_4 surfaces, where CN_O can vary from 1 to 4. In plotting Bader charge versus $\sum CN_M$ in Figure 1ii, we can see that these two quantities exhibit a strong linear relationship; that is, by increasing $\sum CN_M$ one will make the O Bader charge more positive. More interestingly, we see the existence of multiple, parallel scaling lines in the Figure, distinguished by the CN_O of the surface oxygen sites. For an increasing value of CN_O , the line becomes more and more right-shifted, corresponding to a region of more negative Bader charge; the lines shift by an approximately constant value, labeled as λ . Therefore, we can formulate an “adjusted coordination number” (ACN), where we off-shift, or adjust, the offset of CN_O in relation to $\sum CN_M$; thus the ACN becomes a function of CN_O and $\sum CN_M$ and the data points in Figure 1ii can fall into one line. A straightforward construction of ACN can take the form of

$$ACN = CN_O * \lambda - \sum CN_M \quad (1)$$

where λ is a single parameter that fits the linear offset to Bader charge and is fixed for a specific oxide once its bulk structure is given. The quantities CN_O and $\sum CN_M$ are then subtracted

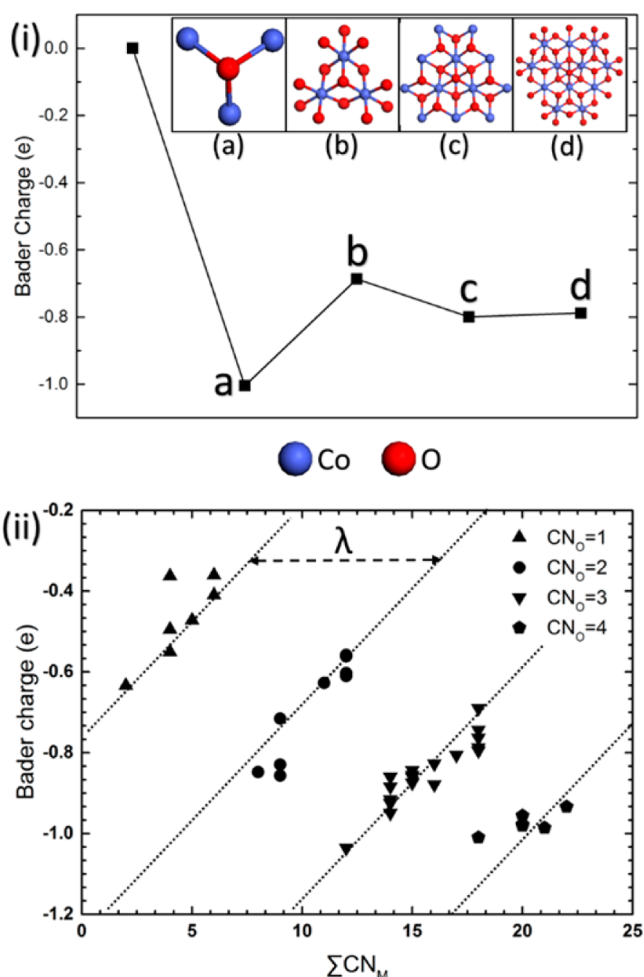


Figure 1. (i) Electron-donating and electron-withdrawing effect of the cobalt and oxygen shells in Co_3O_4 in a cluster model. The first point at the Bader charge of zero is represented by a single gas-phase O (red) atom. Points a–d represent adding successive “shells” of alternating cobalt (blue) and oxygen (red) to the central oxygen. The cluster model represents the coordination environment of a typical O site on Co_3O_4 (111). (ii) Coordination effect of the oxygen CN_O on shifting the CN_M relations versus Bader charge on Co_3O_4 . A near-constant separation between each CN_O is denoted by λ .

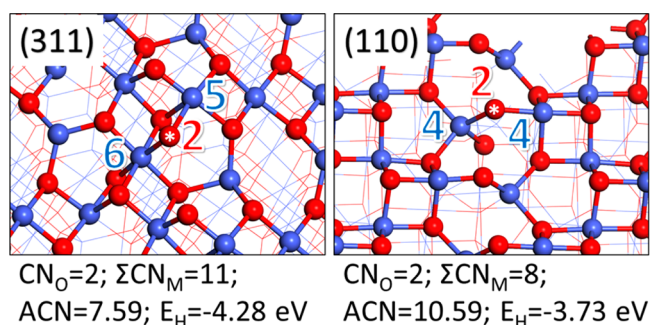


Figure 2. Coordination and reactivity of two different oxygen sites (labeled by an asterisk) on two Co_3O_4 surfaces: CN_O , $\sum CN_M$, ACN (adjusted coordination number), and E_H (H adsorption energy) are shown at the bottom. In the structures, the red numbers denote CN_O and the blue numbers denote CN_M . Co, blue; O, red.

from each other due to the opposing effects that they have on the Bader charge of the lattice oxygen in question. λ can be obtained by optimizing its value to maximize the linear

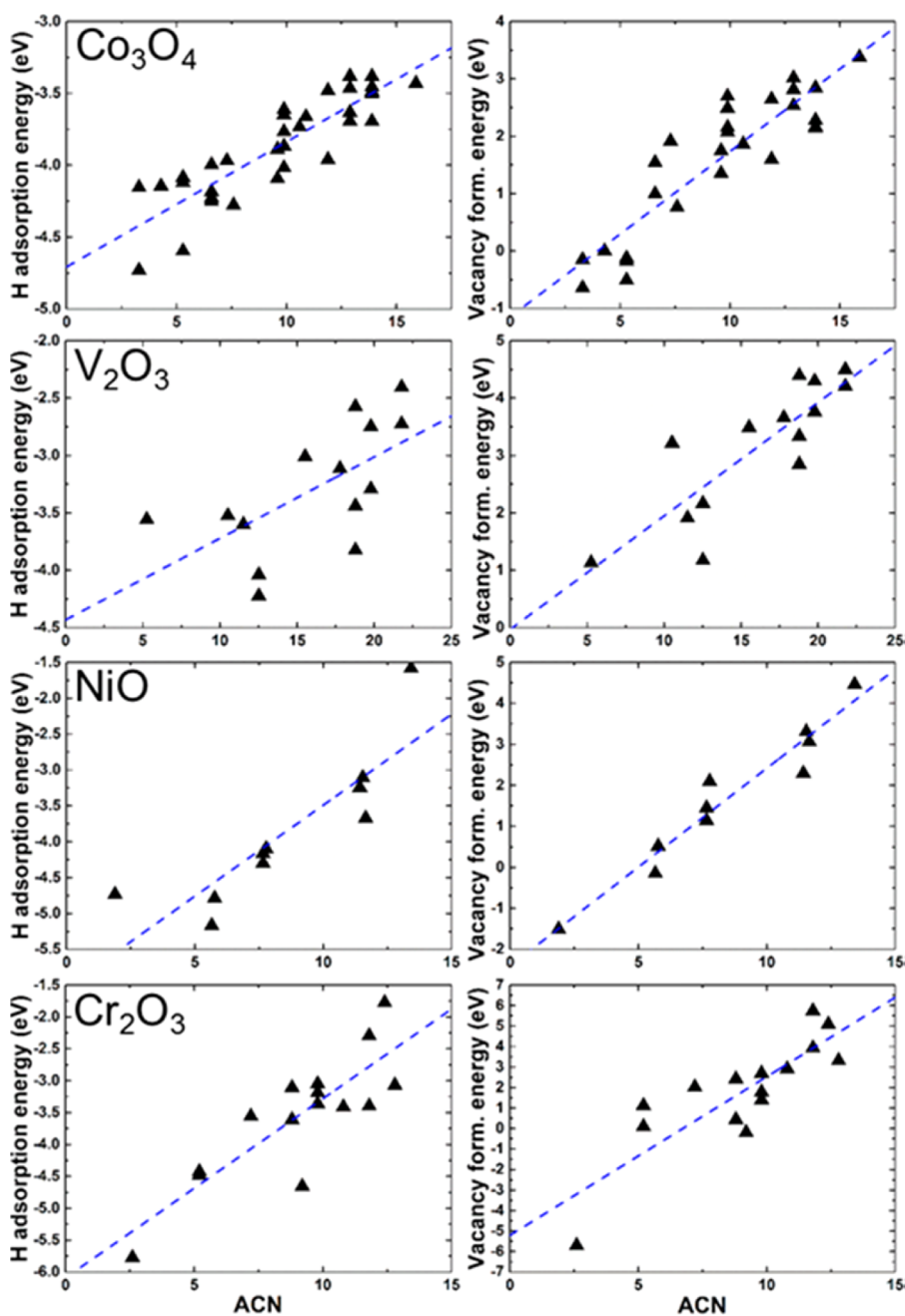


Figure 3. Linear correlation of adjusted coordination number (ACN) with H adsorption energy (left) and vacancy formation energy (right) for V_2O_3 , Cr_2O_3 , Co_3O_4 , and NiO . Each individual point denotes a unique individual oxygen site present on the surface of the metal oxide. λ values and linear-fit (dashed line) parameters are provided in Tables S2 and S3, respectively, in the SI.

correlation constant between ACN and Bader charge (see Table S2 for λ values and Figure S2 and Table S3 for the linear correlation between oxygen ACN and Bader charge).

The strength of ACN lies in giving an extremely fast, zeroth-order approximation of the local electronic structure of the lattice oxygen in question through its correlation with the Bader charge, which then correlates to reactivity. Through this, a general prediction of the oxygen site reducibility through its structural properties becomes clear. Figure 2 shows the calculation of ACN on two Co_3O_4 sites from different facets. Both have a low CN_O of 2, suggesting high reactivity but a different coordination of its neighboring metal atoms, leading to a different $\sum CN_M$. ACN for the (311) site calculated with eq 1 is 7.59, lower than that for the (110) site (10.59), correctly

predicting the stronger H-adsorption energy (E_H) on the (311) site.

Figure 3 demonstrates the strong correlation of ACN with H-adsorption energy and vacancy formation energy, two commonly used energetic descriptors. One can see that ACN applies to a wide range of TMOs with different stoichiometry, bulk structure, and metal oxidation states, exemplified by V_2O_3 , Cr_2O_3 , Co_3O_4 , and NiO . In addition to perfect surfaces (Figure S3) including (100), (110), (111), (211), and (311), defected facets and oxygen adatoms were also considered (Figure S4). The strength of the linear correlation for all studied metal oxides is surprisingly evident given the simplicity of the ACN model. Although noise in the correlation is to be expected, the deviations were found to be reasonably low (Table S3).

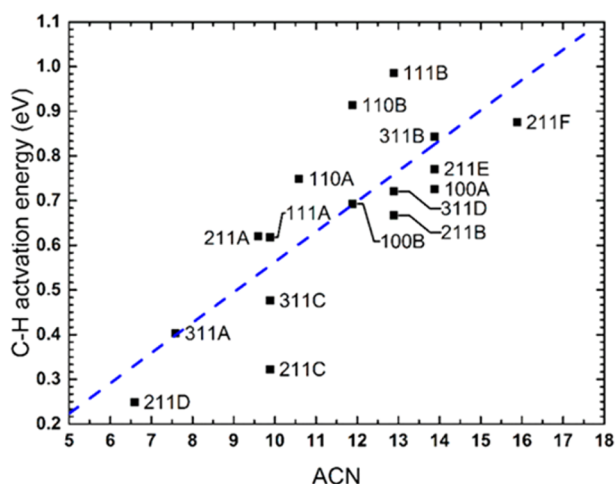


Figure 4. Correlation between the first C–H activation energy of ethane and adjusted coordination number (ACN). Linear best fit (blue line) and fitting parameters are given in Table S4 in the SI.

Therefore, we can conclude that, in general, oxygen with a lower ACN is more reducible and has higher reactivity for the relevant catalytic reactions.

Using Co_3O_4 as a system well studied both experimentally^{16,32–34} and theoretically^{15,16,20,35,36} for alkane activation and combustion, we apply ACN toward the prediction of C–H activation energies. Figure 4 shows the correlation of the first C–H activation energy of ethane on different Co_3O_4 surfaces with ACN, via a radical-forming reaction mechanism^{15,20,22} (transition states in Figure S5). A clear linear correlation can be seen whereby a lower ACN value correlates to a lower C–H activation energy with an RMSD of 0.13 eV or within the range of DFT error. This demonstrates the first usage of a structural descriptor toward directly predicting the otherwise computationally expensive DFT-obtained energy barriers.

The correlation between active site structure and energy barriers might be applicable toward the prediction of actual catalytic performance. For example, the morphology of Co_3O_4 has been shown to be controllable through the synthesis and treatment method, yielding exposed surfaces with different crystal facets and performance.^{33,37–40} For methane combustion, a reaction dependent on the same C–H activation energy trends, it has been shown experimentally that the reactivity trend follows the relation (211) > (110) > (100)³³ from Co_3O_4 nanoparticles synthesized with different shapes. In terms of ACN, the most active oxygen of the three surfaces has values of

7.6, 10.6, and 11.9, respectively, which is consistent with the experimental trend. Of course, methane combustion is a complex process, and more rigorous experimental and theoretical studies will be needed to firmly establish the correlation between the facet activity and the ACN descriptor.

In addition to the case of C–H activation on Co_3O_4 , we further extend the generality of ACN as a predictor of oxygen reactivity by studying its scaling relation with the adsorption of other important intermediates such as CH_3 , NH_2 , and OH. These adsorbates form on the surface in a variety of important reactions including hydrogen evolution, oxygen evolution and reduction, alkane activation and combustion, and nitrogen reduction, among others, and can be used as descriptors of catalytic activity.^{1,41} Similarly, strong linear correlations can be observed for these adsorbates in Figure 5. This result is promising in that it demonstrates the broad applicability of a single oxygen reactivity descriptor such as ACN as valid for the prediction of adsorption properties over a wide range of different atomic/molecular adsorbates, allowing for the screening of catalytic performance on a general level rather than on a case by case basis.

Herein we have proposed ACN as an approximate descriptor for the oxygen site, which we believe incorporates the major contributions of structure to oxygen reactivity. ACN is shown to be effective within the same oxide and bulk geometry but does not seem to be directly comparable across different oxides, as Figure 3 shows that different H-adsorption and vacancy formation energies will be obtained for the four TMOs at the same ACN. Nevertheless, on the basis of ACN, the path to subsequent refinements toward structure–reactivity relations becomes much clearer. In addition, ACN provides a structural basis for catalyst design by quantitatively identifying the effect of changing CN_O and CN_M to tune the oxygen selectivity to a desired state. In essence, ACN can greatly reduce the structural search space by boiling down the oxygen site geometry to just two parameters (CN_O and $\sum \text{CN}_\text{M}$).

Recent experimental and theoretical studies on gas-phase metal-oxide clusters and their reactivity^{42–44} identified different oxygen sites such as terminal $\text{M}=\text{O}$, bridging $\text{M}-\text{O}-\text{M}$, oxygen radical $\text{M}-\text{O}^*$, superoxide, and peroxide on the clusters. It will be interesting to see if the ACN descriptor can be applied to describe the reactivity of those oxygen sites as well. In addition, the effect of the spin states on reactivity is more pronounced in clusters,^{45,46} while its effect in our extended surfaces is indirectly taken into account in the ACN descriptor via the correlation with the Bader charge that is derived from spin-polarized calculations.

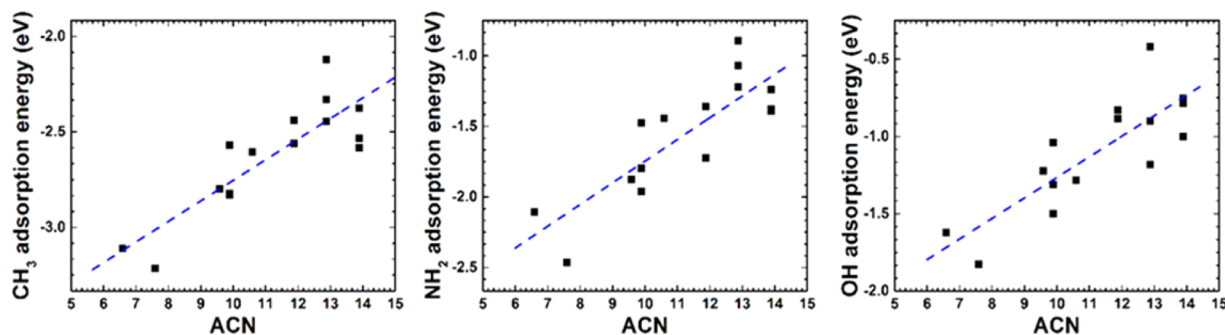


Figure 5. Correlation between CH_3 (left), NH_2 (middle), and OH (right) adsorption energies on the Co_3O_4 surfaces with adjusted coordination number (ACN). Linear best fits (blue lines) and fitting parameters are given in Table S5 in the SI.

In conclusion, we proposed a structural descriptor for TMOs called ACN, on the physical basis of oxygen partial charge, which captures the charge-transfer effect through the surface oxygen's metal coordination and the second-shell oxygen coordination. We demonstrated the strong correlation between ACN and the conventional descriptors of oxygen reactivity. Most importantly, we further applied the scaling relationships to reaction barriers for C–H activation, showing for the first time that a structural descriptor can have predictive power toward catalytic barriers. Finally, we have applied ACN to a number of other adsorbates, including CH₃, NH₂, and OH, and found that the same scaling relationships exist. These results demonstrate that ACN is a promising first step toward rigorously quantifying active site structural sensitivity to reactivity for TMOs. Subsequent studies corroborating theoretical predictions through ACN will help further validate structural descriptors as a practical tool for catalytic prediction.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.7b00861.

Computational details; correlation between descriptors of oxygen reducibility and linear fitting parameters; model surfaces and example calculations for ACN; example transition states for C–H activation of C₂H₆ on the oxide surfaces; DFT+U effect on scaling relations; example structure files (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: djiang@ucr.edu. Tel: +1-951-827-4430.

ORCID

Victor Fung: 0000-0002-3347-6983

Franklin Feng Tao: 0000-0002-4916-6509

De-en Jiang: 0000-0001-5167-0731

Notes

The authors declare no competing financial interest.

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