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Screening the activity of single-atom catalysts for the catalytic oxidation of sulfur dioxide with a kinetic activity model†

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An accurate prediction model of catalytic activity is crucial for both structure design and activity regulation of catalysts. Here, a kinetic activity model is developed to study the activity of single-atom catalysts (SACs) in catalytic oxidation of sulfur dioxide. Using the adsorption energy of the oxygen atom as a descriptor, the catalytic activities of 132 SACs were explored. Our results indicate the highest activity when the adsorption energy of oxygen equals -0.83 eV. In detail, single-atom Pd catalyst exhibits the best catalytic activity with an energy barrier of 0.60 eV. Most importantly, this work provides a new insight for developing a highly accurate and robust prediction model for catalytic activity.

Single-atom catalysts (SACs) have attracted increasing attention in the fields of catalysis, energy and environment, due to their high catalytic activity, excellent selectivity and the maximum atom utilization.^{1–4} With the active sites dispersed at the atomic level, SACs have been regarded as a model catalyst to reveal the mechanism of some complicated chemical reactions.^{5–7} In virtue of synchrotron radiation characterization and density functional theory (DFT) calculations, the design and regulation of the catalytic activity of SACs were performed experimentally and theoretically.^{8–10} Therefore, through the regulation of catalytic activity, potential candidate catalysts and reaction mechanism can be studied.

Based on the adsorption energy of H^* , the activity of single-atom Co catalyst supported on carbon nanotubes for the hydrogen evolution reduction (HER) was explored via doping atoms and tuning the surface curvature.¹¹ Through manufacturing defect sites, the free energy variation of the rate-determining step (RDS) was regulated to boost the activity of a single-atom Fe catalyst for the oxygen reduction reaction (ORR).¹² Through regulating the coordination environment of the Ni atom in the experiment, the free energy variation of the RDS (CO_2^* to $COOH^*$) was obviously reduced to promote the activity of a single-atom Ni catalyst for the CO_2 reduction reaction (CO_2RR).¹⁰ According to the free energy variation of RDS (N_2^* to N_2H^*), the activity of transition metal SACs for the nitrogen reduction reaction (NRR) was optimized through screening the transition metal type.¹³ In addition, the adsorption energy of gases, such as O_2 , NO , and NH_3 , can be tuned by changing the coordination structure composed of a central metal and coordination atoms.^{14,15} Therefore, based on the regulation of the coordination structure, the catalytic activity of SACs for different reactions can be well-tailored *via* tuning the energy variation of the RDS in thermodynamics.

However, in reality, the catalytic activity of the catalyst is determined not only by the energy variation in thermodynamics, but also the energy barrier in kinetics. It is important to understand the effects of structural regulation on catalytic activity in the perspective of energy barrier. To address the lack of kinetics factor in the activity regulation of SACs, an activity-based tuning in kinetics based on transition state theory¹⁶ was conducted in this work. Considering that the oxidation of SO_2 to SO_3 is a key step for both SO_2 removal in coal-fired power plant and for traditional sulfuric acid manufacture.¹⁷ Therefore, we take the catalytic oxidation of SO_2 to SO_3 by O_2 as an example to study the activity regulation in kinetics. In this work, the models of six transition metals (Cr, Mn, Fe, Co, Ni, and Cu) coordinated with four N atoms were constructed for the catalytic oxidation of SO_2 through DFT calculations. To build up the prediction model of catalytic activity, the

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adsorption energy of oxygen was selected as a descriptor to correlate the catalytic activity parameters including electronegativity, energy barriers, electron transfer, and so on. Based on the kinetic activity model and adsorption energies of oxygen, the activities of 132 SACs for the catalytic oxidation of SO₂ were studied.

Spin-polarized DFT calculations were performed using the Perdew–Burke–Ernzerhof functional with projector augmented wave basis set through the Vienna ab initio simulation package (VASP 5.4.1). The dipole and DFT-D3 corrections were considered to describe the interaction between the gas and surface accurately.¹⁸ According to the energy convergence test of kinetic energy cutoff (Fig. S1, ESI†), the kinetic energy cutoff of 450 eV with a Gaussian smearing width of 0.05 eV was selected to obtain accurate calculation results in minimum calculation time. Moreover, a *k*-point grid of 4 × 4 × 1 was adopted for the calculation of geometry optimization based on the energy convergence test of a *k*-point grid (Fig. S2, ESI†). In detail, the catalyst model and calculation settings can be found in the part of calculation method section of ESI.†

Consistent with our previous studies,^{7,19} the climbing-image nudged elastic band (CI-NEB)^{20,21} combined with an improved dimer method (IDM)²² was adopted to locate the transition state with the convergence criterion of 0.05 eV Å⁻¹. Next, the vibrational frequency with a finite displacement of ±0.02 Å^{23–25} was calculated to testify the transition states. Relative binding energy (*E*_{rb}) was defined to evaluate the stability of SACs, and its calculations depended on following equation:

$$E_{rb} = E_{cat} - E_{sub} - E_{metal} - E_{coh} \quad (1)$$

where *E*_{cat}, *E*_{sub}, *E*_{metal}, and *E*_{coh} are the energies of the catalysts, substrate, metal atoms, and experimental value of metal cohesive energy,²⁶ respectively. The adsorption energy (*E*_{ads}) of gas on the surface was calculated based on the following equation:²⁷

$$E_{ads} = E_{adsorb} - E_{cat} - E_{gas} \quad (2)$$

where *E*_{adsorb} and *E*_{gas} are the energies of the adsorption system and gases. The energy barrier (*E*_a) of the transition state in kinetics was calculated according to the following equation:²⁸

$$E_a = E_{TS} - E_{IS} \quad (3)$$

where *E*_{IS} and *E*_{TS} are the energies of the initial state and transition state, respectively. To evaluate the capability of attracting electrons for different SACs, system electronegativity (*X*) of SACs was calculated by the following equation:²⁶

$$X = (xE_C + yE_N - E_M) \times \theta_d/n_d \quad (4)$$

where *x* and *y* are the number of carbon and nitrogen atoms adjacent to the embedded metal atom; *E*_C, *E*_N and *E*_M are the electronegativity of the carbon, nitrogen and metal atoms, respectively; *θ*_d is the number of occupied electrons of the d orbitals of metal atoms; and *n*_d is the maximum number of electrons in the d orbitals.

Considering that four nitrogen atoms coordination is one of the most common types in experimental synthesis,^{28–30} double vacancy with four nitrogen atoms doping graphene was selected

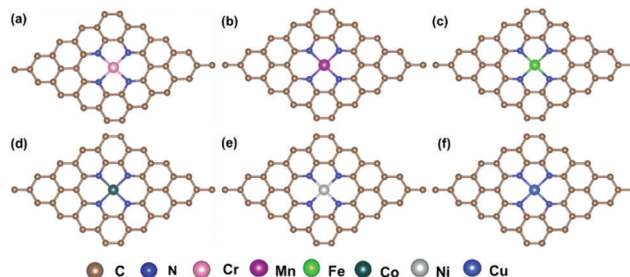


Fig. 1 Geometric configurations of the six SACs.

as the substrate of SACs (M/DV-N1234, M = Cr, Mn, Fe, Co, Ni, Cu). The geometric configurations of six different graphene-based SACs were optimized (Fig. 1), and some key properties of corresponding structures including bond length, Bader charge, electronegativity and binding energy were also summarized (Table S1, ESI†). Obviously, relative binding energies of six SACs are −3.08, −4.32, −3.53, −3.79, −3.82, and −2.04 eV, respectively, indicating that the binding strengths between transition atoms and graphene-based substrate are strong enough to guarantee the stability of SACs. In addition, our calculated results are similar to the literature,^{31,32} convincing that the calculated models of SACs are reasonable.

To discuss the activity of SACs for the catalytic oxidation of SO₂, we first study the reaction path of SO₂ oxidation with Fe/DV-N1234 as an example (Fig. 2(a)). The catalytic oxidation of SO₂ includes three reaction stages. In the first stage, an oxygen molecule is adsorbed on the catalytic surface and SO₂ attacks the first oxygen atom and then generates an SO₃ molecule, with an energy barrier denoted as *E*_{a1}. In the second stage, the residual oxygen is further consumed by another SO₂, with an energy barrier denoted as *E*_{a2}. In the last stage, the formed SO₃ molecule desorbs from the surface, with an energy barrier denoted as *E*_{a3}. Obviously, the overall RDS for catalytic oxidation of SO₂ is determined by those three steps, including IM1 to TS1 (*E*_{a1}), IM2 to TS2 (*E*_{a2}), and FS1 to IS0 (*E*_{a3}). In detail, *E*_{a1} and *E*_{a2} equal the transition state energy barrier calculated through eqn (3), and *E*_{a3} equals the opposite number of adsorption energy calculated through eqn (2). The detailed value of *E*_{a1}, *E*_{a2}, and *E*_{a3} for the six SACs were calculated (Fig. 2(b)–(d)).

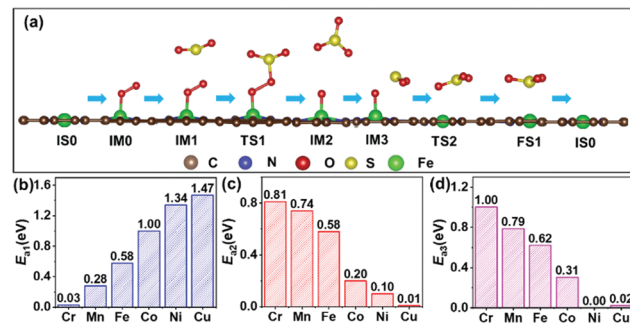


Fig. 2 (a) Key configurations along the reaction path of SO₂ oxidation. (b)–(d) Energy barriers of the two transition states and desorption process for different SACs.

With the increase of the atomic number, the variation of energy barrier shows different tendency. For the first reaction stage, the values of E_{a1} are gradually increasing from 0.03 eV to 1.47 eV, and Cr/DV-N1234 has the smallest energy barrier. However, for the last two stages, the values of E_{a2} and E_{a3} both decrease with increasing atomic numbers, and Cr/DV-N1234 has the largest energy barrier. This opposite energy barrier trends in three reaction stages indicate that the different SACs are suitable for different reaction stages in the catalytic oxidation of SO_2 .

With the advantages of low computational cost and relatively high prediction accuracy, adsorption energies of simple adsorbates, such as H, C, N, and O, were selected as a simple and effective descriptor of catalytic activity.^{33–38} Based on the liner relationship between the adsorption energy and other energy variation, we can make a large-scale screening towards similar catalytic systems to search potential catalysts. Therefore, we selected the adsorption energy of the oxygen atom $E_{\text{ads}}(\text{O})$ as a descriptor of catalytic activity. The relationships between $E_{\text{ads}}(\text{O})$ and some other important activity parameters of graphene-based SACs, including the adsorption energy of molecular oxygen ($E_{\text{ads}}(\text{O}_2)$), reaction energy barriers of different steps (E_{a1} , E_{a2} , E_{a3}), amounts of electron transfer from SACs to gas (Q), and electronegativity of SACs (X) are studied (Fig. 3).

Obviously, there is a significant positive correlation between $E_{\text{ads}}(\text{O})$ and $E_{\text{ads}}(\text{O}_2)$ (Fig. 3(a)). The stronger the $E_{\text{ads}}(\text{O})$, the lower the E_{a1} and the higher the E_{a2} (Fig. 3(b) and (c)), indicating that strong adsorption facilitates the formation of the first SO_3 and suppresses the formation of the second SO_3 . This phenomenon is consistent with Sabatier principle,³⁹ a moderate

adsorption of reactant is most favourable for the catalytic reaction.⁴⁰ Moreover, a strong adsorption energy corresponds to a high desorption energy barrier (Fig. 3(d)). Furthermore, the tendency of the adsorption energy and binding mechanism of the oxygen atom was discussed in the view of the electronic structure. There is an obvious liner relationship between electron transfer and $E_{\text{ads}}(\text{O})$, the more the amount of electron transfers the larger the $E_{\text{ads}}(\text{O})$ (Fig. 3(e)). System electronegativity (X) can represent the ability of SACs to obtain electrons in the bonding process,²⁶ so a higher X corresponds to a weaker binding interaction (Fig. 3(f)). Additionally, obvious electron transfer from SACs to the oxygen atom can be observed from the electron density difference (Fig. S3, ESI†). Moreover, from Cu to Cr, the electron distribution of the d orbital for M/DV-N1234 is gradually approaching the Fermi level, according to the projected density of states (Fig. S4, ESI†). This tendency of the d orbital electron distribution is consistent with the calculated value of the d-band center, specifically, a larger value of the d-band center corresponds to a stronger binding interaction (Fig. S5, ESI†). Therefore, based on the significant liner relationship and binding mechanism in the electronic structure, we can conclude that $E_{\text{ads}}(\text{O})$ can be a simple and effective descriptor for energy barriers.

Based on the liner relationship between the adsorption energy of an oxygen atom and three energy barriers with high square of correlation coefficients (R^2) of 0.97, 0.94 and 0.99, respectively, the energy barrier of RDS with different $E_{\text{ads}}(\text{O})$ was obtained (Fig. 4(a)). The energy barrier of RDS for the oxidation of SO_2 is dependent on the maximum energy barriers in three reaction stages. Taking the $E_{\text{ads}}(\text{O}) = -0.83$ eV as the boundary, there are two regions with different RDS. When $E_{\text{ads}}(\text{O})$ is located at the left of -0.83 eV, the RDS is the desorption process of SO_3 from the catalyst surface, indicating that too strong adsorption leads to the difficulty in the process of product desorption. When $E_{\text{ads}}(\text{O})$ is located at the right of -0.83 eV, the RDS is the formation process of the first SO_3 , indicating that too weak adsorption leads to the difficulty of the reactant activation process. Based on this activity model, Fe/DV-N1234 shows the highest activity among the calculated six SACs due to its moderate adsorption energy of O. Moreover, the catalytic activity of SACs can reach the highest when $E_{\text{ads}}(\text{O})$ reaches -0.83 eV.

To further expand the research scope, the activities of other 132 SACs (Fig. S6, ESI†) consisting of 12 metals and 11 substrates were explored based on this activity model (Fig. 4(a)) and

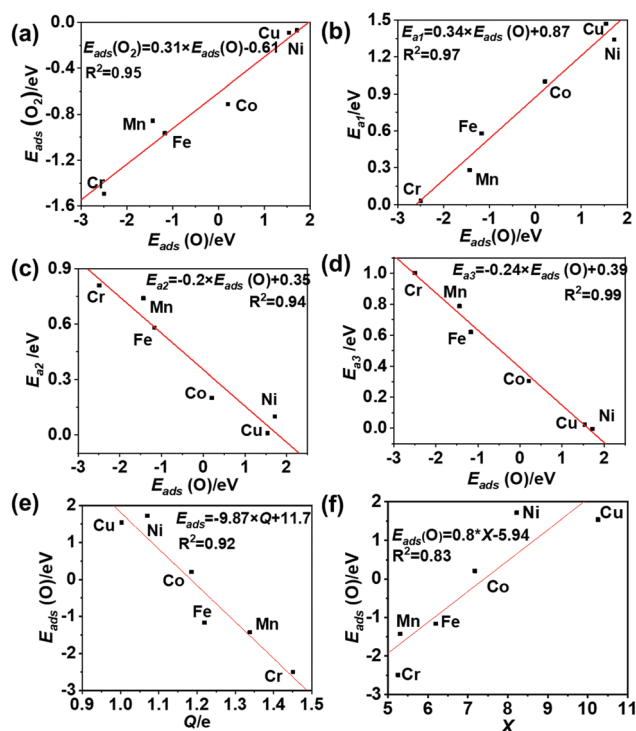


Fig. 3 Linear relationship between $E_{\text{ads}}(\text{O})$ and other catalytic activity parameters.

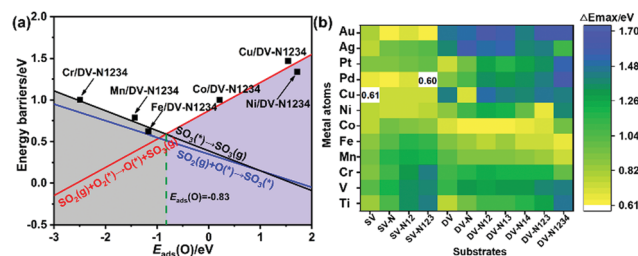


Fig. 4 Catalytic activity plots (a) energy barriers with different $E_{\text{ads}}(\text{O})$ (b) RDS energy barriers for 132 SACs in the catalytic oxidation of SO_2 .

adsorption energy of O.²⁶ Herein, we define the largest value among three energy barriers as the energy barrier of RDS (ΔE_{max}), and the value of ΔE_{max} was calculated (Fig. 4(b)). According to the different values of ΔE_{max} , it is marked in different colours. The blue and yellow regions represent poor and good catalytic activity for the catalytic oxidation of SO₂, respectively. The white regions indicate the highest catalytic activity, and they are a single-atom Cu catalyst supported on a single-vacancy graphene-based substrate (Cu/SV) and a single-atom Pd catalyst supported a single-vacancy graphene-based substrate with three doped nitrogen atoms (Pd/SV-N123). In detail, the energy barriers of RDS in Cu/SV and Pd/SV-N123 are 0.61 and 0.60 eV, respectively. In addition, the energy barrier range of RDS in 132 SACs is from 0.60 to ~1.71 eV, which is much lower than that of a non-saturated carbon catalyst (3.35)⁴¹ and C-doped boron nitride nanosheets (1.73 eV),⁴² indicating that SACs exhibit superior activity than other catalysts. Based on the difference analysis between thermodynamic and kinetic models (ESI[†]), it is necessary to use the activity model of kinetic to predict catalytic activity.

In this work, based on significant liner relationship between the adsorption energy of O and energy barriers, an exact prediction model based on kinetics was constructed to study the activity of SACs in catalytic oxidation of sulfur dioxide. Through the screening of 132 SACs in catalytic oxidation of sulfur dioxide, two candidate catalysts (Cu/SV and Pd/SV-N123) were obtained, which are worthy of further theoretical and experimental research. Comparing the difference between the kinetic activity model and the thermodynamic activity model, we can conclude that the kinetic activity model is more efficient in the catalytic oxidation of SO₂.

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Conflicts of interest

There are no conflicts to declare.

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