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Optimum Cu nanoparticle catalysts for CO$_2$ hydrogenation towards methanol

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Abstract

Understanding the mechanism of CO$_2$ hydrogenation to methanol is important in the context of renewable energy storage from societal and technological point of view. We use density functional theory calculations to study systematically the effect of the size of Cu clusters on the binding strengths of reactants and reaction intermediates as well as the activation barriers for the elementary reaction steps underlying CO$_2$ hydrogenation. All the elementary reaction barriers exhibit linear scaling relationships with CO and O adsorption energies. Used in microkinetics simulations, we predict that medium-sized Cu$_{19}$ clusters exhibit the highest CO$_2$ hydrogenation activity which can be ascribed to a moderate CO$_2$ coverage and a low CO$_2$ dissociation barrier. The nanoscale effect is evident from the strong variation of CO and O adsorption energies for clusters with 55 or less Cu atoms. The reactivity of larger clusters and nanoparticles is predicted to depend on surface atoms with low coordination number. Optimum activity is correlated with the bond strength of reaction intermediates determined by the d-band center location of the Cu clusters and the extended surfaces. The presented size-activity relations provide useful insight for the design of better Cu catalysts with maximum mass-specific reactivity for CO$_2$ hydrogenation performance.

1. Introduction

The problem of rising atmospheric CO$_2$ levels originating from anthropogenic sources mainly through combustion of fossil fuel resources raises global concern. Renewable energy sources such as wind and solar power are increasingly regarded as important contributors to a low-carbon sustainable economy. While many activities in our society such as transportation can be electrified to a significant extent, there will remain a need of liquid transportation fuels for heavy duty transport and aviation and carbon-based chemicals for the production of materials. In the latter context, electro-reduction of CO$_2$ would constitute a direct way to combine CO$_2$ utilization with energy storage, but this desirable reaction is met with significant challenges [1,2]. Alternatively, CO$_2$ can be hydrogenated with renewable hydrogen into more valuable products such as carbon monoxide, hydrocarbons and alcohols [3,5-13]. For instance, CO$_2$ can already be converted into methanol (CO$_2$ + 3H$_2$ $\rightarrow$ CH$_3$OH + H$_2$O) using mixed CO$_2$/CO/H$_2$ feedstock [4].

Owing to the complexity of practical catalytic systems, it is increasingly important to understand in detail the kinetics and mechanism of catalyzed reactions in order to design novel or improved catalysts. Another great technological challenge relates to the dependence of activity and selectivity of catalytic nanoparticles on their size. As for many heterogeneous reactions, it remains unclear what is the optimum particle size for the catalytic hydrogenation of CO$_2$.

Catalytic performance is closely associated with the electronic structure of the active site [14-16], which depends strongly on the size and the local surface topology of the metal cluster or nanoparticle. Understanding how performance depends on surface topology remains a topic of significant interest to the catalysis community [12,16-23]. The exact mechanism of CO$_2$ hydrogenation mechanism may also depend on the transition metal [24]. Surface morphology effects in CO$_2$ electro-reduction were explored by Tang and Hori et al. [25,26]: steps

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on roughened Cu surfaces show a significant influence on the selectivity for CO$_2$ reduction. Small nanoparticles, especially clusters, may differ from larger ones, as they expose a higher fraction of coordinatively unsaturated surface atoms in the form of corner and edge atoms. The lower coordinative unsaturation leads to narrowing of the d-band, which results in an upward shift of the band's energy and, consequently, in stronger adsorption of reaction intermediates [14,16,26–30].

Copper has been widely used as catalyst for CO hydrogenation to methanol and also exhibits extraordinary activity and selectivity in low-temperature methanol synthesis by CO$_2$ hydrogenation [31,32]. In recent years, many efforts have focused on understanding the structure sensitivity of Cu surfaces towards CO$_2$ reduction [26,33–50]. Density functional theory (DFT) calculations show that the stepped Cu(211) surface is the most active facet for obtaining CH$_4$ from CO$_2$ [51]. It has been demonstrated that CO$_2$ hydrogenation for ZnO-supported Cu catalysts is nearly independent of Cu size for particles between 8 nm and 40 nm [52]. Well-developed facets disappear when the Cu particles become smaller than 1–2 nm. Then, the undercoordinated sites, local surface topology and, for very small particles below 1 nm, also quantum effects will determine the catalytic performance. Such structure sensitivity of Cu catalysts has been discussed for O$_2$ dissociation, CO oxidation in excess of H$_2$ and the catalytic degradation of CO$_2$ [53–55]. It has been mentioned that CO and H$_2$ selectivity strongly increases for particles smaller than 5 nm, which was attributed to low-coordinated surface sites that chemisorb reaction intermediates stronger [56]. CO$_2$ hydrogenation to CH$_4$OH on small Cu clusters has also attracted attention, as it is nowadays possible to synthesize stable Cu$_n$ (n = 3, 4, 8, 20, and so forth) clusters [48,57–60]. DFT calculations show that CO$_2$ adsorption and activation depend strongly on the position of the d-band for small-sized Cu$_n$ clusters (n = 7, 13 and 19) [60]. Another DFT study showed that a Cu$_{19}$ cluster displays higher activity in CO hydrogenation to methanol than a Cu(111) surface [61]. Methanol synthesis from CO$_2$ over size-selected Cu$_n$ (n = 3, 4 and 20) catalysts supported on hydrotreated amorphous Al$_2$O$_3$ has recently been experimentally investigated [57]. A small Cu$_4$ cluster deposited on Al$_2$O$_3$ exhibited a very high turnover rate for catalytic CO$_2$ hydrogenation [48,57]. It indicates that methanol synthesis over ultra-small Cu clusters is very sensitive to cluster size. Despite these relevant studies, there is a lack of systematic investigation of the dependence of CO$_2$ hydrogenation on cluster size.

In the present work, we explore the hydrogenation of CO$_2$ towards methanol on Cu particles smaller than 2 nm and follow up earlier work in the direction of particle size dependence by also including Cu clusters. Predictions can be made for larger particles on the basis of the results for the extended (111) and (211) surface of Cu. Specifically, we will demonstrate strong size-dependent activity in CO$_2$ reduction towards CH$_4$OH for Cu$_n$ clusters with n = 13, 15, 19, 55 and 79 and extended periodic surfaces. We employ DFT at the GGA level to compute stable adsorption geometries and activation barriers for elementary reaction steps associated with CO$_2$ hydrogenation by adsorbed H atoms. Structure dependence manifests itself in the form of size-dependent adsorption behavior. The activation barriers involved in methanol formation exhibit linear scaling relationship with the adsorption energies of CO and O, which are found to be suitable reactivity descriptors for methanol formation. Microkinetics simulations were then conducted to predict reaction rates based on these linear scaling relationships. On the basis of volcano curves, we can speculate about optimum Cu catalysts for CO$_2$ hydrogenation to methanol.

2. Methodology

2.1. DFT calculations

All spin-polarized DFT calculations were performed by using projector augmented wave (PAW) potentials [62] and the Perdew–Burke–Ernzerhof (PBE) functional [63] as implemented in the Vienna ab initio simulation package (VASP) code [64,65]. The p(1 × 1) slab models used here have a thickness of at least 20 Å Cu atomic layers and are separated by a vacuum of 15 Å for calculate of accurate surface energies. All the atoms in the slab are fully relaxed with the force convergence criterion of 0.02 eV/Å. A Monkhorst-Pack k-point 8 × 8 × 1 mesh [66] was used for the (111) surface. The surface energy was determined by $E_{\text{surf}} = (E_{\text{slab}} - NE_{\text{bulk}})/2\Gamma$, where $E_{\text{slab}}$ and $E_{\text{bulk}}$ are the total energies of the slab and one bulk Cu atom, respectively, $N$ the number of Cu atoms in the slab and $\Gamma$ the surface area. The structure of CO$_2$ cluster is obtained by Wulff construction based on the calculated surface energies.

For the study of the reaction mechanism, the clusters were placed in a large cubic box with a volume of 20 × 20 × 20 Å$^3$ for structure optimization. The p(4 × 3) and (1 × 4) periodic slab models were used for transition-state calculations on Cu(111) and Cu(211) surfaces, respectively. Both periodic surfaces were simulated by using four equivalent (111) atomic layers. Neighboring slabs were separated by a vacuum of 20 Å to avoid self-interactions. All the atoms in the cluster as well as the top two equivalent (111) layers for the periodic surfaces were fully relaxed. Brillouin zone sampling was restricted to the $\Gamma$-point for the clusters and a Monkhorst-Pack k-point meshes of 5 × 3 × 1 were used for the periodic surfaces. An energy cutoff of 400 eV was employed for the plane-wave basis set. The convergence threshold for ionic steps in geometry optimization was 1 × 10$^{-4}$ eV. Geometry optimization was deemed converged when the forces on each atom were below 0.02 eV/Å. The geometry optimization was followed by a frequency analysis to make sure that the optimized structures are genuine minima.

The improved force reversed method [67] was used to determine transition states (TSs). A force tolerance of 0.02 eV/Å was used. Several TSs were verified by the climbing-image nudged elastic band (CI-NEB) method [68,69]. A frequency analysis was performed to confirm the validity of each TS. The reaction barriers are reported with respect to the most stable adsorption energies of the reaction intermediates at infinite distance. All the reaction barriers were corrected for the zero-point-energy (ZPE) contribution.

2.2. Microkinetics simulations

The calculated activation barriers were used to compute forward and backward rate constants for CO$_2$ reduction. For surface reactions, the rate constants for the forward and backward elementary reactions were determined by the Eyring equation:

\[ k = Ae^{-\frac{E_a}{RT}} \]

where \( k \) is the reaction rate constant in s$^{-1}$ and the prefactor \( A = k_b T \frac{Q^5}{h} \), \( k_b \), \( T \), \( h \) and \( E_a \) are the Boltzmann constant, temperature, Planck's constant and the activation barrier, respectively. \( Q^5 \) and \( Q \) refer the partition functions of the transition and ground states, respectively. As an approximation, the pre-factor \( A \) was set to 10$^{13}$ s$^{-1}$ for all the elementary surface reactions.

For non-activated molecular adsorption, the rate of adsorption is determined by the rate of surface impingement of gas-phase molecules. The flux of incident molecules is given by the Hertz–Knudsen equation [70]:

\[ F = \frac{P}{\sqrt{2\pi m k_b T}} \]

Therefore, the molecular adsorption rate constant can be written as:

\[ k_{\text{ads}} = \frac{PA'}{\sqrt{2\pi m k_b T}} S \]

with \( P \) the partial pressure of the adsorbate in the gas phase, \( A' \) the surface area of the adsorption site, \( m \) the mass of the adsorbate and \( S \) is the sticking coefficient.

For desorption, it is assumed that there are three rotational degrees
of freedom and two translational degrees of freedom in the transition state. Accordingly, the rate of desorption is given by

$$k_{des} = \frac{k_T T^3}{h^4} \frac{1}{\sigma \theta} e^{-\frac{E_{des}}{kT}}$$  \hspace{1cm} (4)$$

where $\sigma$ and $\theta$ are the symmetry number and the characteristic temperature for rotation, respectively. $E_{des}$ is the desorption energy.

The approach to microkinetics simulations has been presented in detail elsewhere [71]. Differential equations for all the surface reaction intermediates were constructed using the rate constants and the set of elementary reaction steps. For each of the $M$ components in the kinetic network, a single differential equation in the form

$$\frac{d\theta_i}{dt} = \sum_{j=1}^{N} \left( k_{ji} \prod_{k=1}^{M} c_k^{j_k} \right)$$  \hspace{1cm} (5)$$

is obtained. In this equation, $k_i$ is the elementary reaction rate constant (see Eq. (1)), is the stoichiometric coefficient of component $i$ in elementary reaction step $k$ and $c_i$ is the concentration of component $k$ on the catalytic surface.

The CO$_2$ reduction rate is determined by the in-house developed MKMXX program [71]. Steady-state coverages were calculated by integrating the ordinary differential equations in time until the changes in the surface coverages were very small. Because chemical systems typically give rise to stiff sets of ODEs, we have used the backward differentiation formula method for the time integration [71]. The rates of the individual elementary reaction steps can be obtained based on the calculated steady-state surface coverages. In our simulations, the initial gas phase contained a mixture of CO$_2$ and H$_2$ in 1:5 M ratio at a total pressure of 6 atm.

The rate limiting step can be determined via the “degree of rate control (DRC)” method as introduced by Campbell et al. [72–74]. For elementary step $i$, the degree of rate control $X_{RC}$, $i$ can be defined as

$$X_{RC,i} = \frac{k_i \frac{\partial \theta_i}{\partial r}}{k_{r,i} \theta_i} = \left( \frac{\delta \ln r}{\delta \ln k_i} \right)_{k_{r,i},k_i}$$  \hspace{1cm} (6)$$

where $k_i$, $k_{r,i}$ and $r$ are the rate constants, the equilibrium constant for step $i$ and the reaction rate, respectively. Furthermore, the DRC coefficients have to obey the sum rule over all steps $i$ in the mechanism in such a way that [73]

$$\sum_i X_{RC,i} = 1$$  \hspace{1cm} (7)$$

3. Results and discussions

3.1. Structure of Cu clusters

The mechanism and energetics of methanol formation by CO$_2$ hydrogenation are explored for odd-numbered Cu$_n$ ($n = 13$, 15, 19, 55 and 79) clusters as they have singly occupied highest occupied molecular orbitals (HOMO), making them chemically more reactive than the even-numbered Cu clusters with a doubly occupied HOMO [60]. The structure of all of these clusters except the one with 79 atoms were optimized by energy minimization using reported Lennard-Jones potentials [75]. The resulting structures are given in Fig. 1. The structure of the larger Cu$_{79}$ particle was obtained by employing the Wulff theorem using computed energies of a range of periodic surfaces (Table S1). Finally, two typical Cu facets, i.e. (111) and (211), were used to represent terrace surfaces and step-edge sites on larger nanoparticles.

3.2. Adsorption of reaction intermediates

We first investigated the adsorption of the reactants and reaction intermediates relevant to CO$_2$ reduction towards methanol on all of the considered nanoparticles and extended surfaces at low coverage. Representative adsorption structures of key components and the adsorption energies on several of the explored models are displayed in Fig. 1. A complete overview of the stable adsorption configurations and adsorption energies are collected in Figs. S1 and S2. Generally, smaller Cu nanoparticles bind the reactants and reaction intermediates stronger than the larger ones, which can be understood by the principle of bond-order conservation.

The data in Fig. 1 indicate that adsorption of the key intermediates CO, OH and O is structure- and particle-size dependent. With increasing Cu particle size, CO, OH and O adsorption energies decrease significantly. OH and O prefer to adsorb on the 3-fold site, while the top site is the preferred site for CO adsorption. Less coordinatively saturated adsorbates bind to more Cu atoms with a higher adsorption strength than a more saturated compound like CO. H$_2$O, H and especially CO$_2$ adsorb weakly on the various Cu surface models and are affected less by surface structure than the other adsorbates. However, we still observe that small Cu clusters bind CO$_2$, H$_2$O and H species more strongly than larger ones. The adsorption energy of CO$_2$ is below 0.10 eV, suggesting that CO$_2$ adsorption is the most difficult step in CO$_2$ reduction. H$_2$O prefers to bind to a single Cu atom, while H tends to adsorb in high coordination sites like 3-fold and bridge sites.

The adsorption of CH$_3$O (n = 1–4) is strongly structure-sensitive (Figs. 1 and S2). The variation in the binding energies of HCO, CH$_2$O, CH$_3$O and CH$_4$OH intermediates among differently sized Cu clusters are 1.35 eV, 1.22 eV, 0.76 eV and 0.49 eV, respectively. We can see that the variation with cluster is size becomes larger for more coordinatively unsaturated adsorbates. It should be mentioned that CH$_3$O and CH$_2$OH bind to Cu only via the O atom, while both C and O atoms are involved in coordination of HCO and CH$_2$O to Cu. These variations in binding strength and adsorption mode will lead to different catalytic activity of CO$_2$ reduction towards methanol. Interestingly, these favorable adsorption sites are all edge sites on these Cu clusters, which are similar to the stepped surfaces, suggesting that the edge sites will be the most active sites on the surface.

As adsorption strengths of reactants and reaction intermediates linearly depend on the cluster size, we can describe the adsorption energies with a limited number of parameters. Careful analysis shows that the adsorption energies of CO$_2$ and the CH$_3$O (n = 1–4) intermediates scale linearly with CO and O adsorption energies (Fig. 2). The adsorption energies of H, OH and H$_2$O present linear scaling relations with the adsorption energy of O. These kind of linear activation energy relations or scaling laws have been formulated before for important catalyzed reactions [15,46,76–78]. These relations can be used in microkinetics simulations to explore a significantly larger fraction of configurational space than based on the available DFT data.

3.3. Reaction mechanism

In this section, we present DFT-computed energy barriers for the reaction mechanism for CO$_2$ hydrogenation on Cu surfaces. For the reaction mechanism, we follow the elementary reaction steps shown in Scheme 1. This mechanism is well accepted in recent literature [42]. It involves direct CO$_2$ dissociation to CO and O instead of CO$_2$ hydrogenation to COOH, because it has been demonstrated that the former pathway has a lower barrier than the latter on Cu(111) and Cu(211) (Fig. S3). CO$_2$ reduction towards methanol via HCOO intermediate is not taken into account in the present work, because HCOO is considered to be a spectator species. For instance, in CO$_2$ electroreduction, formate and CO are the products obtained at low over-potential, while more reduced products are obtained at higher over-potential. This is consistent with the pervading view that CO and formate have the lowest kinetic barriers to formation but CO is the intermediate that leads to further reduction [41]. Adsorbed CO has also been confirmed as an important intermediate in CO$_2$ electroreduction [79].

The resulting potential energy diagrams and the geometries of the transition states are shown in Figs. 3 and 4, respectively. The variation
for adsorption energies of reaction intermediates has a significant influence on the kinetics of CO$_2$ hydrogenation. As expected, stronger adsorption of CO$_2$ results in more facile CO$_2$ dissociation to CO and O. The associated TS involves CO located at top or bridge sites with the O atom moving to an adjacent bridge or three-fold site. CO$_2$ dissociation is highly structure-sensitive: the activation barrier is only 0.16 eV for the Cu$_{13}$ cluster, while it amounts to 1.45 eV for the Cu(111) surface. Clearly, small Cu clusters with under-coordinated surface atoms are more favorable for CO$_2$ dissociation than larger particles. This trend is consistent with Brønsted-Evans-Polanyi (BEP) principle, as lower activation barriers go together with more exothermic nature of the CO$_2$ dissociation reaction.

From Fig. 3 it also follows that stronger adsorption of CH$_n$O (n = 0–3) intermediates and of H atoms results in a higher barrier for hydrogenation of the CH$_n$O adsorbate. Overall, the hydrogenation of CH$_3$O (n = 0–3) is less structure-sensitive than CO$_2$ dissociation. Formation of HCO intermediate has a relatively high barrier in the 1.06–1.39 eV range, while formation of CH$_2$O and CH$_3$O is much easier with barriers in the 0.50–0.89 eV and 0.21–0.69 eV range, respectively. The step that forms methanol from CH$_3$O has the highest barrier (1.08–1.60 eV). As expected, the Cu(111) terrace presents the lowest barriers for CH$_n$O (n = 0–3) hydrogenation, whereas those barriers are highest for the Cu$_{13}$ and Cu$_{15}$ clusters.

For the removal of adsorbed O, the O + H $\rightarrow$ OH elementary reaction step is endothermic on small Cu$_{13}$ and Cu$_{15}$ clusters. For larger clusters and on the periodic surfaces, this reaction is exothermic. Accordingly, OH formation barriers decrease from 1.73 eV for Cu$_{13}$ to 0.97 eV for Cu (111) surface. The variation of the reaction barrier for H$_2$O formation via OH + H $\rightarrow$ H$_2$O is much smaller than for OH formation with barriers ranging from 1.26 eV to 1.41 eV. The difference in structure sensitivity of OH and H$_2$O formation steps originates from the different transition states as can be appreciated from Fig. 4. At the

| $E_{\text{ads}}$ (eV) | Cu$_{13}$ | Cu$_{15}$ | Cu$_{19}$ | Cu$_{55}$ | Cu$_{79}$ | Cu(111) | Cu(211) |
|----------------------|----------|----------|----------|----------|----------|---------|---------|
| CO                   | -1.30    | -1.24    | -1.22    | -1.08    | -1.07    | -0.78   | -0.95   |
| O                    | -5.68    | -5.42    | -4.98    | -4.89    | -4.85    | -4.50   | -4.79   |
| OH                   | -4.26    | -4.34    | -4.29    | -3.96    | -4.07    | -3.68   | -4.07   |
| CHO                  | -1.38    | -1.15    | -0.75    | -0.60    | -0.60    | -0.03   | -0.31   |
| CH$_2$O              | -1.47    | -1.41    | -0.78    | -0.82    | -0.91    | -0.24   | -0.64   |
| CH$_3$O              | -1.99    | -2.00    | -1.50    | -1.61    | -1.75    | -1.25   | -1.61   |

Fig. 1. Optimized geometries of key intermediates adsorbed on the Cu$_n$ (n = 13, 15, 19, 55 and 79) clusters and the extended surfaces.
transition state for OH formation, the O atom is located on a three-fold site with the H atom moving top or bridge sites. For the H2O-forming reaction, OH and H are located at bridge or three-fold site in the transition states.

Comparing the overall reaction energy diagrams, we note the following. For the periodic Cu(111) and Cu(211) surfaces, CH3O formation is very facile with barriers of 0.21 eV and 0.27 eV, respectively. For Cu(111), CO2 dissociation and OH hydrogenation are the most difficult steps. The barriers are ~ 0.4 eV higher than those of the other elementary reactions. For the stepped Cu(211) surface, water formation by OH hydrogenation is the most difficult step. For the small Cu13 and Cu15 clusters, CO2 dissociation is the most favorable reaction. However, O hydrogenation and CH3O hydrogenation are the most difficult steps for these clusters. For the intermediate-sized clusters, CH3O formation is facile with almost a similar barrier of ~ 0.4 eV. The OH hydrogenation, CH3O hydrogenation and CHO formation reactions are more difficult on these clusters with reaction barriers in the 1.12–1.36 eV range.

In order to properly compare these different clusters in CO2 hydrogenation, we performed microkinetics simulations that not only take into account the activation barriers but also the steady-state coverages of the reaction intermediates. We will present the catalytic performance as a function of the CO and O binding strengths as the two main activity descriptors. For this purpose, we first determined BEP correlations for the elementary reaction steps involved in CO2 hydrogenation.

### 3.4. BEP relations in CO2 hydrogenation

The BEP principle relates the activation barrier to the enthalpy of an elementary reaction step [77,80–84]. It is widely used to predict reactivity on the basis of easily accessible adsorption energies from which reaction enthalpies can be obtained in a computationally less
demanding manner than computing transition states. In heterogeneous catalysis, it has been widely used in computational studies to predict periodic activity trends [15,86–90]. Fig. 5 shows BEP relations for the forward activation barriers for all elementary reaction steps involved in CO₂ hydrogenation. For CO₂ dissociation, CHO, CH₂O, CH₃O and O hydrogenation reactions, the barrier increases with increasing reaction enthalpy. The reverse holds for CO and OH hydrogenation steps. These opposite trends derive from the specific transition state configuration involved in CO and OH hydrogenation (Fig. 4).

From our DFT calculations, it follows that CO₂ reduction to methanol is structure-sensitive. All the adsorption energies of reactants, intermediates and products exhibit linear scaling relationship with CO and O adsorption energies (E_CO + E_O). Therefore, all the forward and backward reaction barriers involved in CO₂ reduction can be correlated.
The predicted CO₂ reduction rates for di-clusters show lower performance. Since it was found that for all considered models CO₂ dissociation is the rate-determining step, the reason that the Cu₁₉ model shows the highest activity is that smaller or larger Cu nanoparticles have a less optimal surface composition of CO₂ and vacant sites. The CO₂ hydrogenation rate for the periodic surfaces is much lower, with the Cu(111) surface exhibiting the lowest reaction rate. Our calculations underpin the earlier made observation that CO₂ hydrogenation to methanol reaction is a highly structure-sensitive reaction [48,57]. Our data show that small clusters with proper CO and O adsorption energies are preferred. The maximum CO₂ hydrogenation rate can be achieved for CO and O adsorption energies of ~ −1.5 eV and ~ −4.5 eV, respectively. Meanwhile, we can also appreciate that there is still plenty of room to further improve CO₂ hydrogenation rate by modifying the CO and O binding energies. In general, strong CO adsorption would increase the catalytic performance. As the main reactivity descriptors, CO and O adsorption energies can be tuned by changing the particle size or structure.

3.5. Microkinetics simulations for CO₂ reduction to methanol

Microkinetics simulations are useful to predict activity on the basis of complex reaction mechanism [90–93]. Combining the DFT-based BEP relationships and the mechanism shown in Scheme 1, a volcano curve of the CO₂ reduction rate as a function of the CO and O binding strength descriptors can be constructed (Fig. 7). This heat map also shows the location of the Cu clusters and surfaces considered in this work. In the current work, we carried out microkinetics simulations for a temperature 500 K, which is close to experimental conditions [47,48,57,94,95]. The Cu₁₉ particle has the highest predicted CO₂ hydrogenation rate. Smaller and larger Cuₙ (n = 13, 15, 55 and 79) clusters show lower performance. Since it was found that for all considered models CO₂ dissociation is the rate-determining step, the reason that the Cu₁₉ model shows the highest activity is that smaller or larger Cu nanoparticles have a less optimal surface composition of CO₂ and vacant sites. The CO₂ hydrogenation rate for the periodic surfaces is much lower, with the Cu(111) surface exhibiting the lowest reaction rate. Our calculations underpin the earlier made observation that CO₂ hydrogenation to methanol reaction is a highly structure-sensitive reaction [48,57]. Our data show that small clusters with proper CO and O adsorption energies are preferred. The maximum CO₂ hydrogenation rate can be achieved for CO and O adsorption energies of ~ −1.5 eV and ~ −4.5 eV, respectively. Meanwhile, we can also appreciate that there is still plenty of room to further improve CO₂ hydrogenation rate by modifying the CO and O binding energies. In general, strong CO adsorption would increase the catalytic performance. As the main reactivity descriptors, CO and O adsorption energies can be tuned by changing the particle size or structure.

Fig. 8 shows how surface coverage of the intermediates depends on the reactivity descriptors (E_CO and E_O). A corresponding plot for the DRC values [73,96,97] is provided in Fig. S5. The coverages of the CH₄O (n = 0, 1, 2, 3, 4) intermediates increase going from the smallest to optimum Cu₁₉ cluster and then decreases going to larger sizes. These coverages are lowest for Cu(111). Regardless of the CO adsorption energy, CO₂ dissociation is the rate-determining step for CO₂ hydrogenation. When the O adsorption energy decreases to ~ −3.09 eV, the Cu surface will be poisoned by O atoms and H₂O formation controls CO₂ hydrogenation. When CO and O adsorb strongly on very small Cu clusters, such as Cu₁₃ and Cu₁₅, the low coverage of CO₂ limits methanol formation rate by CO₂ hydrogenation. However, if CO and O bond weakly on Cu clusters or surfaces, the higher CO₂ dissociation barrier will hinder CO₂ hydrogenation. Therefore, there will be a volcano curve for CO₂ reduction towards methanol. The Cu₁₉ cluster exhibits a suitable binding strength of CO and O for optimum CO₂ hydrogenation activity. This results in a low CO₂ dissociation reaction barrier at an intermediate CO₂ coverage. The latter is important to a high CO₂ hydrogenation rate, because CO₂ dissociation requires vacant sites. While we have explicitly computed adsorption energies and activation barriers for a set of clusters, we can use the data of the periodic surfaces to predict the performance of nanoparticles larger than 1–2 nm. With increasing size, the contribution of corner and edge atoms becomes smaller, implying that the surface of large nanoparticles and therefore also catalytic performance will be dominated by close-packed (111) and step-edge sites. Our microkinetics simulations show that the catalytic performance of step-edge sites is higher than that of terrace sites. Therefore, we predict that the CO₂ hydrogenation activity of nanometer-sized Cu particles will be dominated by the activity on step-
edge sites. A recent work of Van Helden et al. discusses the relation between step-edge site density and particle size for FCC metals [98]. It is also worthwhile to point out that a support that is typically used to stabilize small Cu clusters may affect the morphology and electronic structure. These effects, which will be more pronounced for smaller clusters than for large particles, need to be taken into account in future studies.

It is interesting to mention that the different clusters expose Cu atoms with different coordination numbers. For Cuₙ clusters with n = 13, 19, 55, 79, the coordination number of surface atoms is 6, for Cu₁₅ and the Cu(211) surface 7 and for the Cu(111) surface 9. Thus, the Cu(211) surface is more active than Cu(111) due to presence of more reactive surface Cu atoms. The dependence of CO and O adsorption energies on small Cu clusters is less dependent on coordination number than on size (Fig. 56). A molecule-like electronic structure consisting of discrete electronic levels in the very small clusters are key to understanding the catalytic behavior [99]. Also, the d-band center model provides a useful means to understand binding strength and reactivity trends across the transition metal block in the periodic table. The energy of the d states (the center of the d states) relative to the Fermi level is a good indicator of the bond strength [100,101]. Our data shows that the energy of the d-band center increases with decreasing Cu particle size (Fig. 9, corresponding density of states were shown in Fig. S5). CO and O atom adsorption energies on Cu clusters and surfaces scale linearly with the energy of d-band center location. This shift is due to the narrowing of d-bands when clusters become smaller (less Cu neighbors) and results in enhanced adsorption of CO, atomic O and other intermediates, essentially controlling the CO₂ hydrogenation activity.

4. Conclusions

The effect of Cu cluster size on Cu-catalyzed hydrogenation of CO₂ to methanol was studied by DFT calculations. All the reaction barriers involved in CO₂ reduction to methanol display linear scaling relationships with CO and O adsorption energies, thereby serving as catalytic reactivity descriptors for CO₂ hydrogenation. By microkinetics simulations, it is found that intermediate sized Cu₁₉ clusters are optimal for CO₂ hydrogenation. The Cu particle size effect originates from changes in the adsorption energies of the reaction intermediates which can be correlated to the location of the d-band of the Cu clusters. The up shift of the d-band center usually strengthens the bonding interaction between metal and intermediates, thereby influencing CO₂ reduction activity. The presented size-activity relations provide useful insight for the design of better Cu catalysts with maximum mass-specific reactivity for CO₂ hydrogenation performance.
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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.naone.2017.11.021.

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