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**Potential of Transition Metal Atoms Embedded in Buckled Monolayer g-C₃N₄ as
Single-Atom Catalysts**

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ABSTRACT

We use first-principles calculations to systematically explore the potential of transition metal atoms (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt, and Au) embedded in buckled monolayer g-C₃N₄ as single-atom catalysts. We show that clustering of Sc and Ti on g-C₃N₄ is thermodynamically impeded and that V, Cr, Mn, and Cu are much less susceptible to clustering than the other TM atoms under investigation. Strong bonding of the transition metal atoms in the cavities of g-C₃N₄ and high diffusion barriers together are responsible for single-atom fixation. Analysis of the CO oxidation process indicates that embedding of Cr and Mn in g-C₃N₄ gives rise to promising single-atom catalysts at low temperature.

1. Introduction

Supported metal nanostructures as heterogeneous catalysts are used in many important reactions.¹⁻³ The size is a key factor for the performance due to the higher ratio of low-coordinated metal atoms as active sites in smaller nanostructures.^{4,5} Accordingly, approaches to reduce the size have drawn significant attention in order to improve the performance.⁶⁻⁹ Single atom catalysts (SACs) with well dispersed atoms on supports not only minimize the consumption of metals but also have great potential for high reactivity and selectivity.¹⁰⁻¹² However, strong interaction with the support is essential for anchoring the single metal atoms and, therefore, for achieving SACs. Metal oxides can effectively fixate single metal atoms through surface O atoms and thus have been widely investigated.¹³⁻¹⁵ However, the supported single atoms either suffer from partial oxidization, which may degrade the activity,^{16,17} or agglomerate rather rapidly.¹⁸⁻²⁰

It may be a fruitful compromise to select a support with *intrinsic cavities* that can firmly trap the catalytically active metal atoms. Monolayer carbon nitride (g-C₃N₄), similar to γ -graphyne,²¹ is a candidate material that combines the merits of high surface area and low cost with cavities able to capture single metal atoms.²² Recently, transition metal (TM) atoms have been successfully prepared on g-C₃N₄ (TM/g-C₃N₄) and have shown higher activity and better durability in hydrogen evolution and hydrogenation than commercial catalysts.²³⁻²⁵ Charge transfer between the TM atoms and g-C₃N₄ support has been claimed to play an important role for the superior performance.²³ A later study, however, has argued that the embedded TM atoms maintain neutral states which account for the enhanced activity.²⁶ It appears that both the electronic nature and role of the TM atoms are not finally settled.

In addition to the experimental interest in hydrogen evolution and selective hydrogenation,²⁷⁻³³ there have been pioneering theoretical studies to explore the potential of TM/g-C₃N₄ in CO₂ and O reduction.^{26,33,34} Although these reports have intensified the interest in g-C₃N₄ as host for SACs, a comprehensive understanding of the interaction between the TM atoms and g-C₃N₄ support is missing. The same applies to the behavior of TM/g-C₃N₄ in the presence of adsorbates. For this reason, we use first-principles calculations to systematically investigate the properties of TM (Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt, and Au) atoms embedded in the cavities of g-C₃N₄. We study 3d TM atoms due to the economic advantage of noble-metal-free catalysts³⁵ and selected 4d and 5d TM atoms that are frequently used in heterogeneous catalysis.³⁶ The

interaction of O₂, CO, and O with the hybrid materials is evaluated to explore the potential of g-C₃N₄ as SAC substrate for CO oxidation and to obtain hints for the design of novel SACs based on g-C₃N₄.

2. Computational details

We use the Vienna Ab-initio Simulation Package with projector augmented wave pseudopotentials.^{37,38} The Perdew-Burke-Ernzerhof³⁹ flavor of the spin-polarized generalized gradient approximation is chosen for the exchange-correlation potential, as it is known to be accurate for simulations in heterogeneous catalysis.^{33,34,40} Dispersion forces are not expected to affect the adsorption properties, as strong chemical bonds are formed. However, we have tested various cases of O adsorption considering dispersion forces^{41,42} and find that the relative stability does not change, see Fig. 1. The cutoff energy of the plane-wave expansion is set to 500 eV and the Brillouin zone is sampled on a Γ -centered $3 \times 3 \times 1$ **k**-mesh in the structure relaxations and on a Γ -centered $7 \times 7 \times 1$ **k**-mesh in the electronic structure calculations. $2 \times 2 \times 1$ supercells are used to model embedding of one or two TM atoms in g-C₃N₄, see Fig. 2, with 15 Å vacuum added in the *z*-direction to guarantee sufficient separation between periodic images. The structure relaxations are continued until all residual forces have declined below 0.02 eV/Å. The climbing image nudged elastic band method is applied to calculate minimum energy paths and transition states.⁴³ The crystal orbital overlap population is extracted from the projector augmented wave functions by projection onto Slater-type orbitals.^{44,45}

3. Results and discussion

3.1 TM atoms embedded in g-C₃N₄

Pristine g-C₃N₄ exhibits uniformly distributed cavities coordinated by six N atoms, see Fig. 2. A flat geometry results in a lattice constant of 7.14 Å and an in-direct band gap of 1.21 eV based on the Perdew-Burke-Ernzerhof functional. However, buckling reduces the total energy by 36 meV per atom, leading to a smaller lattice constant of 6.99 Å and a significantly enlarged band gap of 1.86 eV, which highlights the importance of this structural feature. Calculations on the Heyd-Scuseria-Ernzerhof hybrid functional level⁴⁶ for the buckled geometry yield an in-direct band gap of 2.94 eV. As a consequence of the buckling, the C-N bonds are no longer equivalent,

with bond lengths ranging from 1.32 to 1.46 Å. These results are consistent with previous studies.⁴⁷⁻⁴⁹ The cavities (surrounded by six lone pair electrons) are highly electron-rich⁵⁰ and thus ideal centers for fixation of TM atoms. In the following, we explore the stability and bonding of TM atoms embedded in buckled g-C₃N₄.

The $2 \times 2 \times 1$ supercell contains four evenly distributed cavities. However, because of the buckling, the C (and N) atoms are not all equivalent. To obtain the lowest energy configuration of TM/g-C₃N₄, we therefore consider adsorption at all top, bridge, and hollow sites, see Fig. 2, which highlights the hollow sites at the center (H1) and corners of the cavity (H2, H3, and H4) as well as those due to the C-N rings (h1, h2, and h3). We evaluate the binding energy as

$$E_{\text{bind}} = (E_{\text{TM/g-C}_3\text{N}_4} - E_{\text{g-C}_3\text{N}_4} - nE_{\text{TM}})/n, \quad (1)$$

where $E_{\text{TM/g-C}_3\text{N}_4}$, $E_{\text{g-C}_3\text{N}_4}$, and E_{TM} are the total energies of g-C₃N₄ (with and without TM atom) and a single TM atom, n being the number of these atoms. For all the considered TM atoms it is found that location in the cavity is energetically favorable. TM atoms initially placed at the H2-H4 sites relax toward the H1 site, while those placed at C-N rings relax either to the H1-H4 sites or to the C6 site. The TM atoms are likely to deviate from the center of the cavity.⁴⁰ This deviation can be characterized in terms of the difference between the longest and shortest TM-N bond lengths, see Fig. 3a. It turns out that Fe is subject to the most significant deviation, while Sc stays close to the H1 site. The average bond length, see Fig. 3b, gradually increases as the atomic number increases, reflecting protrusion from the cavity plane.

According to Fig. 3c, the binding energy is always negative (exothermic process). The bonding strength follows the trend $3d > 4d > 5d$ and decreases in each period as the atomic number increases, resembling the behavior of the average bond length (the shorter the bonds the stronger is the bonding). The Sc atom is subject to the strongest bonding of -6.38 eV with a short bond length of 2.38 Å, while the Au atom experiences the weakest bonding of -0.78 eV with the longest bond length of 2.53 Å. These values are comparable to those of 3d TM atoms in C₂N,⁴⁰ but remarkably higher than observed for TM adsorption on graphene.⁵¹ We note that our value for Ir embedded in buckled g-C₃N₄ (-3.70 eV) is lower than that obtained on planar g-C₃N₄ (-3.02 eV),⁵² demonstrating the importance of the buckling. Because of the large energy difference, it can be expected that the same applies to the other TM atoms. We investigate the effect of the

coverage by placing an additional TM atom in a neighboring cavity. Only minor modifications of the binding energy are obtained, see Fig. 3c. The same is true when the TM coverage is increased to a full monolayer using a $1 \times 1 \times 1$ supercell. The $2 \times 2 \times 1$ supercell (6.99 Å distance between embedded TM atoms) thus is sufficiently large for quantifying the interaction between the TM atoms.

A recent theoretical study has argued that the TM atoms in the cavities can maintain neutral states,²⁶ challenging previous experimental conclusions about the importance of charge transfer between the TM atoms and g-C₃N₄ in the catalytic processes.²³ To address this dispute and obtain insight into the valence states of the TM atoms, results of Bader charge analyses⁵⁴ are shown in Fig. 3d. It turns out that charge is transferred toward g-C₃N₄, leaving the TM atoms positively charged. The amount of charge transfer decreases as the atomic number increases, in agreement with the trend of the electronegativity.⁵⁵ Sc has the lowest electronegativity (1.36) and shows a charge transfer of 1.71 *e*, while Au has the highest electronegativity (2.54) and the charge transfer is reduced by more than a factor three to 0.52 *e*. These values are comparable to results for C₂N,⁴⁰ potentially equipping the hybrid materials under study with similar activities toward CO oxidation.

In order to understand the chemical bonding the crystal orbital overlap population^{44,45} is analyzed, see Fig. 4. Along each period the antibonding states turn out to gradually shift to lower energy, leading to increased occupation and thus weakened TM-N bonds. It is noted that they shift to higher energy from Cu to Ru and from Ag to Ir, which results in enhanced bonding. On the other hand, reduction of the charge transfer between the positively charged TM atoms and negatively charged N atoms from Sc to Au weakens the electrostatic attraction, so that the stability of a TM atom in a cavity is determined by both ionic (charge transfer) and covalent (orbital overlap) features.

For achieving SACs it is problematic that a high cohesive energy (E_{coh}) makes clustering of TM atoms likely.^{18-20,56,57} Clustering on the surface generally is not favorable if $|E_{\text{bind}}|$ approaches E_{coh} ($E_{\text{bind}} + E_{\text{coh}} \sim 0$) or exceeds it ($E_{\text{bind}} + E_{\text{coh}} < 0$).^{21,58} We obtain for $E_{\text{bind}} + E_{\text{coh}}$ values of -2.25 eV for Sc and -0.69 eV for Ti, indicating thermodynamically driven diffusion in the cavities of g-C₃N₄. In the case $E_{\text{bind}} + E_{\text{coh}} \sim 0$ clustering is to be expected when the diffusion is kinetically impeded by a large diffusion barrier (E_{barrier}). For this reason, we employ climbing image nudged elastic band

calculations to determine the diffusion paths of V, Cr, Mn, Cu, and Ag ($E_{\text{bind}} + E_{\text{coh}} < 1.5$ eV, see Fig. 5a). According to Fig. 5b, we obtain for E_{barrier} values of 3.94, 4.05, 2.79, 3.25, and 1.55 eV, respectively. The diffusion coefficient

$$D = a^2 \nu^* \exp(-E_{\text{barrier}}/k_B T), \quad (2)$$

where the hopping distance between neighboring sites is $a = 6.99$ Å and the hopping frequency is set to $\nu^* = 10^{13} \text{ s}^{-1}$, therefore is tiny for V, Cr, Mn, and Cu, so that these atoms will remain in the cavities and clustering cannot occur when the deposition is slow and the cavities are not saturated with TM atoms.²⁴ For Ag, on the other hand, E_{barrier} is low and diffusion thus is possible.

Embedded Sc transfers two s electrons to $g\text{-C}_3\text{N}_4$, see Fig. 6a, consistent with our Bader analysis. The unpaired d electron results in a magnetic moment of $1.0 \mu_B$. While the large charge transfer points to strong electrostatic attraction between the Sc and N atoms, most Sc-N hybridized states are located above the Fermi energy (vacant antibonding states). Thus, both the electrostatic interaction and covalent bonding fixate the Sc atom⁵⁹ in the cavities, the former preventing formation of Sc dimers. In contrast, Au donates only one s electron to $g\text{-C}_3\text{N}_4$, so that the electrostatic interaction is weaker, and the Au-N hybridized states are predominantly occupied (occupied antibonding states). This weak Au-N bonding is not able to fixate an Au atom. The reduced Au-Au repulsion is also not sufficient to prevent formation of Au dimers. As a result, Sc avoids clustering in contrast to Au even though its cohesive energy is higher (Sc: 3.90 eV/atom, Au: 3.81 eV/atom⁶⁰).

3.2 O₂, CO, and O adsorption on TM/ $g\text{-C}_3\text{N}_4$

CO oxidation is an environmentally important reaction in C-based energy cycles and regarded as a prototypical heterogeneous process for designing atomic-scale catalysts.⁶¹⁻⁶⁴ Therefore, we investigate O₂, CO, and O adsorption on TM/ $g\text{-C}_3\text{N}_4$ to preliminarily evaluate the activity toward CO oxidation. The adsorption energy is given by

$$E_{\text{ad}}(X) = E_{X@TM/g-C_3N_4} - E_{TM/g-C_3N_4} - E_X, \quad (3)$$

where $E_{X@TM/g-C_3N_4}$ is the total energy after adsorption of X and E_X is the total energy of the adsorbant (calculated by placing O₂ and CO inside 1000 Å³ cubic cells, taking for O half of the value of O₂). Negative values represent exothermic processes. Adsorption on pristine $g\text{-C}_3\text{N}_4$

turns out to be unfavorable with E_{ad} values of 0.06, -0.04, and 1.28 eV, respectively. Therefore, it is expected that O_2 , CO, and O will bond directly to the TM atoms, consistent with previous studies.^{26,33,34} CO adsorption on top of Ni, an adjacent N atom, the H2 site, and the h2 site of Ni/g- C_3N_4 results in adsorption energies of -1.81, -0.12, -1.75, and 0.07 eV, respectively, where we observe that CO shifts away from the H2 site to eventually bond to Ni, confirming that the TM atom is the active center to capture adsorbates. We thus consider only adsorption directly at the TM atoms, taking into account end-on and side-on geometries for O_2 and CO. The obtained values of E_{ad} are given in Fig. 7 and the structural properties are summarized in Table 1.

As O_2 activation is crucial in CO oxidation, it is investigated first. It turns out that O_2 prefers direct bonding to the TM atoms, see Fig. 8a. The bonding is strongest for Sc and Ti (< -3 eV) with remarkably elongated O-O bonds (≥ 0.23 Å). The O_2 magnetic moments almost disappear according to Bader charge analyses⁵⁴ due to large charge gains ($> 1 e$). The other extreme is given by Cu, Ag, and Au, which show exclusively end-on adsorption. The O-O bonds are hardly elongated and there remain substantial magnetic moments ($> 1 \mu_B$), as the charge transfers are very small ($< 0.5 e$). This implies molecular adsorption with only slight O_2 activation. An O_2 adsorption energy of only -0.18 eV points to physisorption on Au/g- C_3N_4 due to the closed d shell. CO also prefers direct bonding to the TM atoms (via C), see Fig. 8b. The strongest adsorption is found for Pt (-2.78 eV) and the weakest for Ag (-0.39 eV). The C-O bond is always slightly elongated (≤ 0.04 Å) with respect to the free molecule (1.14 Å), which can be ascribed to small charge gains from the support, see Table 1.

Examples of the charge redistribution upon adsorption are shown in Fig. 8. Remarkable accumulation of charge is found in both the side-on and end-on configurations for O_2 , mainly in its π^* states,^{26,65} while the σ -like bonding states lose charge. Together this gives rise to O-O bond activation. Interaction between O_2 and V is more evident than between O_2 and Cu, which rationalizes the observed adsorption energies. For the CO molecule we find a similar pattern of charge redistribution but reduced amplitude (0.62 e versus 1.00 e) and the orbital overlap with the support is less evident. The adsorption on V/g- C_3N_4 thus is weaker. The adsorbed O atom not only gains 0.96 e of charge but also hybridizes with the V atom, reflecting a strong V-O bond. The oxidation state of the TM atom, given by the charge transfer, is crucial in catalytic processes.^{23,26,59} To clarify the role of TM/g- C_3N_4 , we next analyze the variation of the oxidation

state during the adsorption, see Table 1. It turns out that the TM atom loses much less charge than gained by the adsorbate. According to Fig. 8 the difference is due to the g-C₃N₄ support, which reveals charge depletion especially for the N atoms around the cavity. As all the adsorbates favor bonding to the TM atom, the precise role of TM/g-C₃N₄ becomes clear: The embedded TM atom not only serves as active site to capture the adsorbate but also transmits charge from the support (which acts as charge reservoir).

3.3 CO oxidation on TM/g-C₃N₄

CO oxidation by O₂ can follow the Eley-Rideal⁶⁶ and Langmuir-Hinshelwood⁶⁷ mechanisms. Because of the reduced tendency to clustering, see above, we study V, Cr, and Mn embedded in g-C₃N₄, while Cu is expensive and therefore not considered. As CO adsorbs weaker on these TM atoms than O₂, in atmosphere most TM centers would be occupied by O₂. Thus, the CO oxidation process probably follows the Eley-Rideal mechanism: $\text{CO} + \text{O}_2^* \rightarrow \text{CO}_2 + \text{O}^*$ and $\text{CO} + \text{O}^* \rightarrow \text{CO}_2$. It turns out that CO₂ adsorbs weakly on V, Cr, and Mn embedded in g-C₃N₄ with E_{ad} values of -0.04, -0.04, and -0.10 eV, respectively.

Fig. 9 shows the atomic configurations of the initial (IS), transition (TS), and final (FS) states of climbing image nudged elastic band calculations for the CO oxidation process, including the structural parameters. From IS1 to TS1 the O_a-O_b bond is stretched in each case, while the C-O_b distance decreases. FS1 consists of a CO₂ molecule (weakly physisorbed due to the large C-O_a distance) and O_a bonded to the TM atom. The process is strongly exothermic (-3.69, -3.28, and -2.91 eV for V, Cr, and Mn, respectively) and needs to overcome only small energy barriers (0.18, 0.61, and 0.72 eV). Thus, the formation of the first CO₂ molecule is both thermodynamically and kinetically possible. Reaction of CO with the remaining O atom to form a second CO₂ molecule is also an exothermic process in each case. We obtain energy barriers of 0.90 eV on V/g-C₃N₄ (kinetically impeded process) and 0.52 eV on Cr/g-C₃N₄, while no energy barrier is found on Mn/g-C₃N₄.

The observed variations in the energy barrier can be qualitatively understood by the Sabatier principle.⁶⁸ According to Table 1, O₂ molecules are significantly activated on V embedded in g-C₃N₄, which lowers the energy barrier for breaking the O-O bond. On the other hand, much energy is required for breaking the V-O bond to form a second CO₂ molecule, see Fig. 7. The

same picture applies to Sc and Ti embedded in g-C₃N₄ with even higher energy barriers in the second step. Therefore, according to Refs. 69 and 70, only Cr/g-C₃N₄ and Mn/g-C₃N₄ are promising for CO oxidation at room temperature.

4. Conclusions

We have systematically studied the bonding behaviors of 16 types of TM atoms embedded in the cavity of g-C₃N₄. It turns out that clustering of Sc and V on g-C₃N₄ is thermodynamically impeded. Due to high diffusion barriers, V, Cr, Mn, and Cu are less susceptible to clustering than the other TM atoms under investigation. Single-atom configurations thus are likely to dominate in the case of slow deposition and low TM coverage. Cr and Mn embedded in g-C₃N₄ emerge as promising single-atom catalysts for low temperature CO oxidation. The TM atoms and g-C₃N₄ support turn out to play distinct roles for the high activity: Partially oxidized TM atoms at the same time serve as active sites for the CO oxidation and transfer charge from the g-C₃N₄ support, which acts as charge reservoir and, most importantly, ensures that clustering of the TM atoms is avoided.

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Table 1

X@TM/g-C₃N₄: O-adsorbate and TM-adsorbate bond lengths (bold numbers in parentheses indicating O₂ end-on adsorption), magnetic moments, and charge transfers.

	Bond length (Å)					Magnetic moment (μ_B)			Charge transfer (e)					
	O ₂		CO		O	O ₂	CO	O	O ₂		CO		O	
	O-O	TM-O _a (O _b)	C-O	TM-C	TM-O				O ₂	TM	CO	TM	O	TM
gas	1.23	--	1.14	--	--	2.00	0.00	2.00	--	--	--	--	--	--
Sc	1.47	1.93 (1.94)	1.16	2.20	1.72	0.00	0.11	0.01	1.07	-0.18	0.30	-0.08	1.02	-0.04
Ti	1.46	1.86 (1.86)	1.17	1.99	1.67	0.00	0.01	0.01	1.15	-0.70	0.58	-0.34	1.06	-0.74
V	1.42	1.84 (1.86)	1.18	1.83	1.62	0.01	0.02	0.10	1.00	-0.47	0.62	-0.28	0.96	-0.62
Cr	1.40	1.87 (1.88)	1.16	2.04	1.63	0.33	0.14	0.06	0.90	-0.38	0.31	-0.13	0.85	-0.55
Mn	1.42	1.85 (1.86)	1.16	1.98	1.66	0.06	0.07	0.37	0.98	-0.20	0.35	0.02	0.83	-0.21
Fe	1.43	1.81 (1.82)	1.18	1.80	1.69	0.16	0.14	0.67	0.89	-0.13	0.46	-0.04	0.85	-0.31
Co	1.38	1.80 (1.82)	1.17	1.75	1.66	0.38	0.05	0.75	0.74	-0.15	0.39	-0.03	0.75	-0.36
Ni	1.38	1.82 (1.82)	1.17	1.72	1.67	0.01	0.00	0.70	0.77	-0.21	0.38	0.09	0.76	-0.13
Cu	1.31	1.89 (2.69)	1.16	1.78	1.72	1.09	0.00	0.67	0.50	-0.15	0.14	-0.08	0.71	-0.10
Ru	1.41	1.94 (2.01)	1.18	1.83	1.75	0.36	0.01	0.00	0.82	-0.38	0.46	-0.36	0.83	-0.71
Rh	1.35	1.99 (2.01)	1.17	1.86	1.76	0.59	0.18	0.52	0.65	-0.12	0.32	-0.03	0.75	-0.38
Pd	1.37	2.00 (2.02)	1.16	1.87	2.01	0.01	0.00	0.00	0.66	-0.34	0.26	0.03	0.54	-0.08
Ag	1.28	2.75 (3.13)	1.15	2.09	2.21	1.29	0.00	0.00	0.33	-0.05	0.06	-0.06	0.56	0.01
Ir	1.39	1.98 (1.99)	1.17	1.84	1.75	0.51	0.00	0.31	0.73	-0.11	0.41	-0.12	0.92	-0.35
Pt	1.41	1.99 (1.99)	1.17	1.80	1.79	0.01	0.00	0.00	0.78	-0.47	0.29	0.14	0.79	-0.46
Au	1.25	3.33 (3.34)	1.15	1.88	2.09	1.41	0.01	0.00	0.28	-0.06	0.03	-0.08	0.54	0.01

Fig. 1. Adsorption energies of O@TM/g-C₃N₄ (3d TM atoms only) when the dispersion forces are neglected (full bars) or taken into account (striped bars).

Fig. 2. C-top, N-top, and hollow sites on buckled g-C₃N₄. Dashed lines indicate the unit cell. A side view is given at the bottom.

Fig. 3. (a) Deviations of the TM atoms from the H1 site. (b) Average TM-N bond lengths. (c) Binding energies of the TM atoms. (d) Charge transfers (blue) and electronegativities (red) of the TM atoms.

Fig. 4. Crystal orbital overlap populations for TM/g-C₃N₄. Bonding and anti-bonding states are colored red and blue, respectively.

Fig. 5. (a) Binding energies of TM atoms on g-C₃N₄ compared with corresponding cohesive energies. (b) Diffusion paths of V, Cr, Mn, Cu, and Ag between two cavities in g-C₃N₄.

Fig. 6. Densities of states projected on the TM *s* and *d* orbitals for (a) Sc/g-C₃N₄ and (b) Au/g-C₃N₄. The Fermi energy is set to zero.

Fig. 7. Adsorption energies of O₂, CO, and O on TM/g-C₃N₄.

Fig. 8. Charge differences (isosurface value $0.0015 \text{ e}/\text{\AA}^3$) for (a) $\text{O}_2@\text{V}/\text{g-C}_3\text{N}_4$, (b) $\text{O}_2@\text{Cu}/\text{g-C}_3\text{N}_4$, (c) $\text{CO}@\text{V}/\text{g-C}_3\text{N}_4$, and (d) $\text{O}@\text{V}/\text{g-C}_3\text{N}_4$. The red and green colors represent charge accumulation and depletion, respectively.

Fig. 9. Atomic configurations with structural parameters (in $\text{\AA}$) of the initial, transition, and final states of CO oxidation on (a) $\text{V}/\text{g-C}_3\text{N}_4$, (b) $\text{Cr}/\text{g-C}_3\text{N}_4$, and (c) $\text{Mn}/\text{g-C}_3\text{N}_4$. Energy barriers and reaction energies (in eV) are given in brackets.