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Phase diagrams of the terminating oxygen layer on MXenes M_2CO sheets ($M = Ti, V, Nb$)

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Abstract. In this work we have studied the behavior of oxygen adsorbed on the MXenes M_2CO ($M=Ti, V, Nb$) surface by the density functional theory and Monte Carlo methods. An approximation for the lateral interactions potential has been constructed that has the form of a pair potential. We have carried out the quantitative assessment of the errors of the pair potential. Using SuSMoST program we have constructed isotherms of adsorption. The results showed a non-trivial phase behavior of the adlayer: we observed three phases characterized by the 1/3, 1/2 and 2/3 coverage. It has been predicted that complete oxygen removal from the MXenes surface is possible at temperatures above 500 K.

1. Introduction

In recent times, two-dimensional nitrides, carbides and carbonitrides, the so-called MXenes, are of great interest to many scientists. This interest is prompted by the unique properties of MXene, namely, universal composition and structure, stability under certain conditions, high surface area [1], surface functionality [2]. MXenes have the general formula $M_{n+1}X_nT_{x-1}$ ($n = 1 - 3$), where M corresponds to a transition metal, X is carbon and/or nitrogen and T – termination of the surface. The majority of MXenes can be obtained using the selective etching of atomic layers from MAX-phases [3-4]. Selective etching of transition metals from MAX-phases occurs by adding a solution of hydrofluoric acid. The process takes place at room temperature. Due to their unique properties MXenes are widely used as Mg-ion and Li-ion batteries [5-6], sensors, as catalysts for the hydrogen production reaction, water dissociation process, ammonia synthesis, nitrogen reduction reactions, etc. [7].

During the synthesis of MXenes, functional groups T = (OH, O, F) are adsorbed onto the surface. Functional groups contribute greatly to the properties of MXenes. Terminating functional groups have an impact on thermodynamics, stability in applications related to the MXenes surface [8-9]. Therefore, understanding MXenes surface finishes and their stability is critical to adapting these materials to specific applications. Therefore, the structure of the MXenes surface is of great interest.

To date, there is no exact understanding of the terminated structure of the MXenes surface. This is due to the fact that during the experiment the mechanism of surface functionalization is unknown, that is, how it depends on the preparation conditions, etc. [10]. It is important to understand the surface chemistry of these compounds for future use in applications. The term "surface chemistry" includes the formation of various phases on the surface, interactions, and thermal stability. Different types of surface groups have different thermal stability. For example, fluorine is desorbed from the titanium surface at 750 °C. Oxygen, on the other hand, has a higher thermal stability. We have already



investigated this effect on vanadium, but only one-sided adsorption of oxygen was considered there. We investigated of surface terminator -O. The surface can be cleaned of termination groups by heating. To clean the surface from the most stable functional group -O, a very high temperature is required [12]. In [13], we investigated the one-sided adsorption of oxygen on V_2C -O. We obtained a completely empty surface without oxygen at a temperature of 2900 K. Therefore, oxygen is always present on the surface, since it is very difficult to create such conditions under which it will not be present on the surface. Therefore, it is interesting how oxygen will behave during two-sided adsorption on MXenes M_2CO ($M = Ti, V, Nb$). Three popular representatives of this class of compounds were taken as MXene; these are M_2CO ($M = Ti, V, Nb$), which are currently being synthesized.

2. Computation details

The energies of lateral interactions of O_2 on the MXenes M_2CO surface ($M = Ti, V, Nb$) was calculated using quantum methods, namely, quantum chemical methods and using the pair potential approximation. Next, we created a lattice model of the adlayer [14]. The model was calculated using Monte Carlo method. We calculated the equilibrium degrees of O_2 coverage at temperatures of 100-2000 K and the chemical potential in the gas phase from -1 to 1 eV. Quantum calculations were performed in the Quantum Espresso program [15], and statistical calculations in the SuSMoST program [16]. We used the PBE functional (Perdew-Burke-Ernzerhof) and corrections for the Van der Waals interactions Grimme-D3 [17]. The cutoff energies were 802 eV for V_2CO_2 , 707 eV for Ti_2CO_2 , and 775 eV for Nb_2CO_2 . The size of the k-point grid and the cutoff energy was performed with an accuracy of 0.001 eV. To avoid periodic interactions, the distance between the layers was 12 Å. Equilibrium coverage rates were calculated by Parallel Tempering Monte Carlo simulations in SuSMoST at temperatures from 100 K to 2000 K. Simulations were performed on lattices with a linear size $L = 60$. A 100,000 Monte Carlo steps were used to bring the system into equilibrium followed by another 50,000 steps to calculate the averaged characteristics. In the Parallel Tempering calculations were used 14 replicas of the system.

3. Result and Discussion

Figure 1 shows the surface of MXenes M_2CO ($M = Ti, V, Nb$) with O_2 terminated at full coverage. In Figure 1, titanium atoms are shown in gray, vanadium atoms in yellow, niobium atoms in green, and oxygen atoms in red. Also, in the pictures there are atoms of the middle layer of carbon in the structure, they are indicated in dark gray.

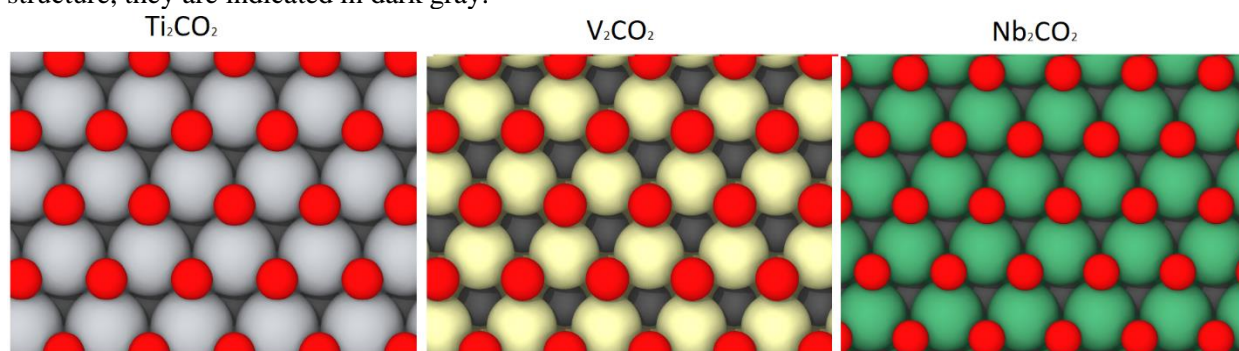


Figure 1. O_2 on the MXenes M_2CO sheets ($M = Ti, V, Nb$) at full coverage.

The oxygen adsorption energy μ in the ground state at zero temperature is 4.56 eV. As the temperature rises, the value of μ changes primarily by cause of the entropy component of the free energy of the gas phase. The selected function of the lateral interactions in tabular form is shown in Table 1. The lateral interactions of O_2 in different coordination spheres, as well as the maximum error are presented in

Table 1. As can be seen, after the fourth coordination sphere, the values of the interaction energies become insignificant. Interactions beyond 3 angstroms were not considered as they are minor. The values of the maximum mean error are also within the normal range. Errors do not exceed 0.003 eV for titanium and vanadium, and for niobium, no more than 0.007 eV. This indicates that the model is stable and sustainable.

Table 1. Parameters of the Hamiltonian of O₂ adlayer on M₂CO₂ MXenes of density calculations.

Structure		r/a_0	Total DFT
Ti ₂ CO-O	ϕ , eV	1	0.1190
		$\sqrt{3}$	-0.0049
		2	0.0552
		$\sqrt{7}$	0.0015
		3	-0.00002
		MaxAE, eV	0.0027
V ₂ CO-O	ϕ , eV	1	0.1353
		$\sqrt{3}$	0.0059
		2	0.0429
		$\sqrt{7}$	-0.0251
		3	0.00008
		MaxAE, eV	0.0022
Nb ₂ CO-O	ϕ , eV	1	-0.00001
		$\sqrt{3}$	0.0076
		2	-0.0036
		$\sqrt{7}$	-0.00007
		3	-0.0002
		MaxAE, eV	0.0062

The isotherms obtained in the course of statistical modelling are shown in Figure 2. The isotherms show the change in coverage from 0 to 1 ML in the chemical potential range from -1 to 1 eV at temperatures from 100 to 2000 K.

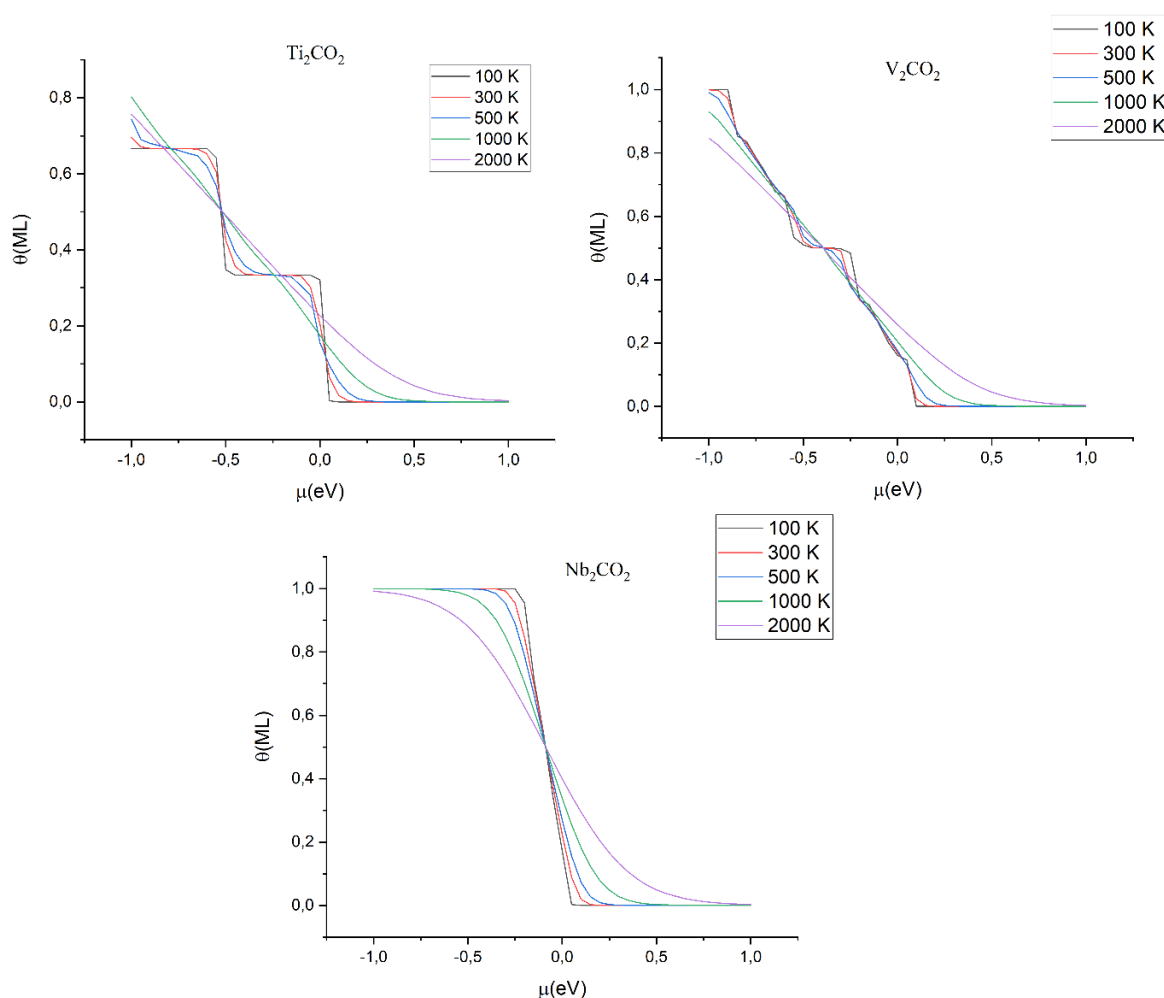


Figure 2. Isotherms of adsorption of terminated O_2 on the MXenes M_2CO sheets ($M = Ti, V, Nb$).

The isotherms show phases at zero and full coverage for Nb_2CO_2 and V_2CO_2 . Intermediate phases are also observed when $1/3$ ML and $2/3$ ML of the surface are filled with oxygen. In the V_2CO_2 structure, the $1/3$ ML and $2/3$ ML phases are not as pronounced as in Ti_2CO_2 , but the $1/2$ ML phase is present. However, intermediate phases are observed at temperatures no higher than 500 K. At higher temperatures, these phases are not observed. However, it is difficult to talk about thermal stability, phase resolution temperature, and the like. The difficulty lies in the fact that we consider the coating not only at different temperatures, but also at different chemical potentials. At different values of the chemical potential, there can be different temperatures, and therefore, speaking about thermal stability, we have temperature values in the range of chemical potential from -0.5 to 0 eV. At chemical potentials above 0 eV, no intermediate phases are observed. Phases with coatings $1/3$ and $2/3$ ML are characteristic of adlayers with repulsive interactions of the nearest neighbours on a triangular lattice. Phases $1/3$ and $2/3$ ML of the Nb_2CO_2 structure are not observed in the isotherms; this may probably be due to the low energies of lateral interactions of this structure, relative to others.

The phase of V_2CO_2 $1/2$ ML is of great interest. This is due to the fact that it we can obtain it if we take into account only the nearest interactions. Its symmetry is lower than that of a clean surface or other phases, which raises the likelihood of the presence of specific features of the physicochemical properties of the surface with such a coating.

4. Conclusion

We investigated the behavior of the O₂ layer on MXenes M₂CO sheets (M = Ti, V, Nb). We have obtained the phases which are characterized by the intermediate coverage of 1/3, 1/2 and 2/3 ML that persist up to a temperature of 500 K. The phase with 1/2 ML coverage is interesting, since it has a lower symmetry than the other phases in V₂CO₂. Intermediate phases in the Nb₂CO₂ structure are not observed in the isotherms; this may probably be due to the low energies of lateral interactions of this structure, relative to others.

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