Ab initio computational study: Adsorption of CO molecule on various base metal oxide surfaces

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Abstract. The use of some base metal oxide already widely studied for having beneficial properties in CO oxidation catalytic system. The properties of these base metals such as lower working temperature, high CO affinity, and economically cheaper would be beneficial for this solid system catalyst. The study of various base metal oxides shown these kinds of characteristics, but there still a few analyses of comparison among the various base oxide metals used as the support system for the oxidation reaction catalytic system. This study would give a comparison in the difference of the adsorption energy of various base oxide metals. This adsorption energy is one factor that promoting the activity of the catalytic system due to its affinity to the reactant on their surfaces. The DFT ab initio calculation for this comparison shows that NiO is the base metal oxide that having the highest CO adsorption energy. This oxide could be a potential support system combined with potential solid oxidative catalytic system.

1. Introduction
Carbon monoxide (CO) is a kind of gas that is formed as a product of incomplete carbon combustion reaction, which is a common process found in the environment [1]. Despite the common happening of this gas, the presence of this compound is extremely increasing since the age of industrial revolution, contributing to the high level of this gas in the atmosphere beyond the tolerated limit in some regions. By the knowledge of the hazard of CO gas, efforts have been conducted to minimalize the CO emission from some artificial combustion processes. The incomplete combustion, which is actually an oxidation process of carbon, giving a formula to this problem. The common simple and widespread idea is to complete those oxidation process of unfinished CO, by oxidizing this CO gas to become less hazardous CO$_2$ gas [2]. This conversion scheme is commonly done by the use of catalytic system, and some of those best known so far are the use of noble metals such as Ag and Pt which giving a good conversion yield [3]. Although these catalysts are considered as good enough, the exploration for catalyst of this process is still widely done, to meet the better conversion and efficiency. Another improvement aspects searched are the activity in lower temperature, selectivity, stability, and also the economic aspect on making those catalyst [1].

Several oxides known for having support properties for this catalytic process. Some of them are Al$_2$O$_3$, SiO$_2$, and MgO known as inert support, and some are considerable active support such as CeO$_2$, Fe$_2$O$_3$, MnO$_2$, and TiO$_2$, especially with the ability to facilitate the oxidation-reduction reaction and facilitating the oxygen mobility which are important parameters in the redox reaction [4].
classification is based on the observation in which Au nanoparticles are exhibiting lower intrinsic activities when supported on inert oxides, but exhibiting higher intrinsic activities when supported on active oxides that could contribute to the activation and supply of oxygen for the reaction. Some cheaper base transition metals such as Mn, Fe, Co, Ni, and Cu have been studied as well, known for potential activity as a redox catalyst by the combination of those metals with CeO₂ [3,5,6]. The variation of the metals with CeO₂ giving different results, depends on the interaction of the metals particle with CO molecule. Stronger metal-CO interaction would give the increase of adsorption of the CO molecule on the surface particle, which directly influence the higher oxidation process [3].

The previous studies show that various base metal oxides are having potential activity as a support for this CO oxidation catalyst systems. One of the parameters supporting this activity is that the interaction of the bases metals and the CO molecules in the surface of the solid system. However, there has not been any comparative study to show the difference of the activity of these potential base metals by using the exactly same method. Thus, in this study it will compare those base metals activity, by using the parameters of their interaction with CO molecule on the surface of their metal oxide.

The ab-initio term means “from first principle” which means the total wave function, orbital, and energy are calculated respectively without any empirical parameters. This research used DFT ab-initio computational method, to determine the stable structure and interaction energy of each modelled surface systems. The model used are basic metals oxides lattice, respectively used are TiO₂, Cr₂O₃, MnO₂, Fe₂O₃, CO₂O₄, NiO, Cu₂O, and ZnO which are common base metal oxides, with the interaction of CO molecules on each of their surfaces. All those base metal oxides are modelled to compare the interaction energy with CO molecules on their surfaces, in which this adsorption is one of the parameters directly influencing the activity of the support system for CO oxidation catalytic process.

2. Computational methods
All calculations are performed using Linux-based Quantum ESPRESSO 6.5 machine [7,8]. The input files are created by using notepad++ 7.7 and all modelled interactions are visualized using BURAI 1.3. The calculations of all the models are using first principle Density Functional Theory. The model was created as a slab in 2x2x2 supercell, with a vacuum space gap between lattice. This vacuum was purposed as the mimic of the interphase over the surface of solid system. The vacuum are set to be 15Å to ensure there is no interaction between each of slab surface [9]. The second process is that to model the interaction of CO molecules adsorbed in the surfaces of each oxide systems, with C atom bond to the surface metal atom. All the cell parameters and models are set as the same with the first calculation process [5].

The metals oxides modelled in this study were the commonly found structure of those base metals. TiO₂ crystal was known to be able to use as a support system for catalytic CO oxidation system [4]. This structure modelled as rutile structured and crystallizes in the tetragonal P4_2/mmm space group which then turn to be slab model. While Cr₂O₃ crystal is also known to have ability as an active support for oxidative catalytic system, with the modelled common Cr₂O₃ structure of orthorhombic, Pbcn, 60 space group [10]. The oxide chosen for Mn was MnO₂ that exhibiting catalytic activity in oxidation reaction better than other oxides of Mn [11]. The structure of modelled MnO₂ was rutile structured and crystallizes in the tetragonal P4_2/mmm space group. Then for Fe the structure is Fe₂O₃ which also generating activity in CO oxidation [5]. The next is CO₂O₄ which already wide studied as a support in CO oxidation [12,13]. The modelled structure was cubic lattice with Fd-3m space group. For Ni oxide, it is chosen NiO for calculation with cubic structure with Fm-3m space group [14]. Cu is also widely studied for CO oxidation support system, and in this study the modelled structure was cubic structure of Cu₂O with Pn-3m space group [14,15]. Then the last is ZnO modelled in Wurtzite structure in the hexagonal P6_3mc space group to be calculated [15].
3. Results and discussion

3.1. Optimization of the metal oxide slabs

Before studying the interaction, computational calculation was done to the metal oxide slabs structure first to determine the energy of each of the oxide structure so that it can be used to calculate the interaction energy with CO in the following part. The calculated structure of metal oxides are TiO$_2$, Cr$_2$O$_3$, MnO$_2$, Fe$_2$O$_3$, CO$_3$O$_4$, NiO, Cu$_2$O, and ZnO, while there is no oxide of Sc and V since there is no relevant reference saying their application for CO oxidation catalyst for both of the elements.

All these structures were then modelled as 2x2x2 supercell and turned become slab structure, to mimic the surface condition of each of the oxide systems [9]. This kind of slab surface is shown in figure 1.

![Diagram of slab models](image)

**Figure 1.** The slab modelled structure of each base metal oxides.
Those structure are created to model and mimic the surface part of a solid system. These models are computationally calculated in pw relax scf with DFT basis to optimize the slab structure and to gained the final self-consistent lattice energy for each of the structure. The calculation translates the three bottom atom of each structure in fixed position, while the above atoms are mobile during the optimization to get the relaxed optimized structure and the lowest energy of the oxides. The calculation giving the final result of optimized energy for each oxide slabs as in table 1.

These energies are the result of the convergence structure for each system, as the most stabilized relaxed structure. The result shows unpattern number of energies for these base metal oxides. This wide gap of crystal energy reaches 2000 Ry for some oxides indicate that the energy doesn’t simply depend on the periodicity of the element oxide. There is no sign of linear correlation of metals atomic number of each oxide to the resulted energies. This result can be as a result of further variables such as the difference in the structure and also the electronic properties of each oxide as well.
This optimized structure is the final calculated structure of the slab with the lowest energies of each oxide slab. These slab structures and energies are studied for further analysis in the interaction of these structures with the adsorbed CO molecules on their surfaces.

Table 1. The optimized energy of each slab metal oxide

| Oxide slab | Optimized energy (Ry)       |
|------------|----------------------------|
| TiO₂       | -2891.369625               |
| Cr₂O₃      | -1775.37291                |
| MnO₂       | -4367.846306               |
| Fe₂O₃      | -828.575096                |
| CO₃O₄      | -2095.995745               |
| NiO        | -1883.14872                |
| Cu₂O       | -2197.515964               |
| ZnO        | -1266.583221               |

3.2. Calculation of adsorbed CO models

The adsorption of CO molecules in the surface of each oxide slabs are modelled so that it will generate the adsorption energy of CO in each of the surfaces. The position of CO in all of the surface was set to be directly above the outermost metal atom, as it known to be the active site of the adsorption [3]. The distance of the CO molecules to the outermost metal atoms was set to be 2Å, regarding that it will be calculated to its optimized structure. Here shown the visualization of adsorbed CO in every oxide surfaces.

Figure 2. Visualization of adsorbed CO on base metal oxide slab surfaces.
Table 2. Adsorption energy of CO on each base metal oxide surfaces

| Oxide slab | - CO Adsorption energy (Ry) | - CO Adsorption energy (kcal/mol) |
|------------|-----------------------------|----------------------------------|
| TiO$_2$    | -7.51508464                 | -2357.05483                      |
| Cr$_2$O$_3$| -7.61239045                 | -2387.57413                      |
| MnO$_2$    | -7.55402713                 | -2369.2687                       |
| Fe$_2$O$_3$| -7.62020367                 | -2390.02469                      |
| CO$_3$O$_4$| -7.63996909                 | -2396.22398                      |
| NiO        | -7.65798318                 | -2401.87398                      |
| Cu$_2$O    | -7.61570149                 | -2388.61261                      |
| ZnO        | -7.58351789                 | -2378.51845                      |

The adsorbed CO was then calculated and the generated optimum energy used further for the calculation of the adsorption energy. The calculated parameters including the distance interaction and the lattice system energies which will be used further calculation of the adsorption energies. The adsorption energy is correlated to the interaction energy between the two components of each system, which are the metal oxide slab and the CO molecules.
The adsorption energy is calculated based on the difference of energies of the slab from the first calculation with the energies of the slab while adsorbing CO in the surface as follow [9], and the resulted adsorption energy of CO in each of the surfaces shown down below.

\[-E_{\text{ads}} = E(\text{adCO slab}) - E(\text{oxide slab}) - E(\text{CO})\]

The data shows the differences of CO adsorption energies on each metal oxide surfaces. It doesn’t show any linear trends, and can be said that the adsorption energy of CO doesn’t seems to change periodically. The interaction of CO with metals doesn’t simply follow the periodicity of the periodic system; thus, it cannot be predicted based only the periodicity of the element. The difference of the adsorption energy might be influenced by the specific structure of the surface. It can be seen that for TiO$_2$ and MnO$_2$ both are having rutile crystal structure and both are considered among the lowest adsorption energy for CO molecule. In contrast, crystals in cubic structure such as CO$_2$O$_4$, NiO, and Cu$_2$O are among the highest adsorption energy for CO molecule on their surfaces. Thus, the probability of CO adsorption is varied on different structure, in which the kind of the structure is one of determining factors affecting to the CO affinity. The other factor could be the specific electronical properties for each base metal, which are not studied further in this work.

![Comparison of CO adsorption energy](image)

**Figure 3.** The comparison of CO adsorption energies among the base metal oxide surfaces.

The focus is that from the data we get that NiO surface is having the highest adsorption energy for CO molecules, while TiO$_2$ have the least CO adsorption energy. Here we can say that some base metal oxides could have better affinity to CO rather than the others, which could lead to higher CO oxidation activity. Some base metals having higher CO adsorption energy such as Cr$_2$O$_3$, Fe$_2$O$_3$, CO$_2$O$_4$, NiO, and Cu$_2$O would become a better active support for CO oxidation catalytic system rather than that the other base metal oxides, regarding that they are easier to adsorb CO on their surfaces. From this adsorption step it can be drawn that for system with better adsorption capability, it will lead to a better catalytic performance due to the efficiency of interphase interaction on the surface [3]. This trend could be brought to the consideration for NiO rather than other oxides with its strong adsorption energies that could led to a better catalytic performance. This oxide can be an optional support system for CO oxidation catalytic system combined with other conventional active system.

4. **Conclusion**

The conducted calculation giving result that some base metal oxides are having relatively higher adsorption energy for CO adsorption process on their solid surfaces system, while the rest base metal oxide tends to have lower adsorption energy. This result shows that NiO surface having the higher affinity to CO molecules, which could led to a better efficiency for the catalytic system. Then it could
probably become potential support metal oxide for CO oxidation catalytic system which would bring the beneficial properties of this oxide, which are relatively cheaper and also lower working temperature for solid CO catalytic system.

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