FeO₂ / MgO(100) Supported Cluster: Computational Pursual for a Low-Cost CO and Low-Temperature Nanocatalyst

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ABSTRACT

We study the electronic and catalytic properties of FeO₂ adsorbed on a MgO(100) surface which shows potential as a novel low-cost and low-temperature CO nanocatalyst in an overall exothermic reaction. The CO oxidation may be separated into two steps, namely (1) oxidation of CO by the metal oxide leaving a reduced metal oxide and (2) oxidation of the reduced metal by oxygen to regenerate the active metal oxide. It is found that CO and O₂ adsorption energies are the driving force for the CO oxidation by providing the energy required to surmount the activation energies along the reaction path.

1. Introduction

Efficient carbon monoxide (CO) oxidation into more benign CO₂ is a very important and active research area aimed to solve serious environmental, and health protection problems caused by this pollutant (CO is a colorless and odorless poisonous gas). The scientific interest in CO oxidation is of immense technological importance, and the current research is focused on finding efficient ways to reduce CO emissions.¹⁻⁷ One example is the three-way catalytic converter (TWC) used for emission control of gasoline fueled vehicles. In this application, platinum (Pt_x) is often used for oxidation of carbon monoxide and unburned hydrocarbons. One severe limitation of the TWC, however, is the reduced activity at low temperatures (below 100°C), generally referred to as the cold-start problem.⁸ In theory, a catalytic converter can eliminate 99% of the toxic CO gas; in reality, the converter is inefficient as long as it is not very hot.^{7,9}

The cold start problem is inherent to the nature of the catalytic converter and its interaction with the CO and O₂ gases, as recently discussed in a review by Royer and Duprez.¹⁰ CO has a higher sticking probability than O₂ on the noble metal active sites of the TWC. Furthermore, the desorption rate of CO is moderate at low temperatures because the CO-metal chemisorption energy is too high, ranging from 1.13 to 1.43 eV for different faces of Ru, Ni, Ir, Pd, Rh, and Pt.⁸ At low temperatures, CO blocks all active metal sites in the TWC and poisons the catalyst. Catalyst ignition does not occur until the metal particles have been heated to sufficiently high temperatures by the exhaust gas, part of the CO molecules have been desorbed, and O₂ has been adsorbed on the catalyst. Based on experiments in ultrahigh vacuum conditions,¹¹ the reaction in the TWC has been found to proceed via a Langmuir-Hinshelwood (LH) mechanism where adsorbed CO reacts with adsorbed and dissociated O₂ to form CO₂. At higher partial pressures of O₂, it has been suggested that formation of surface oxides may also be of importance at certain reaction conditions.¹²⁻¹³

Seeking for a low-cost CO catalyst, iron oxides have been investigated by Walker *et al.* to evaluate the possible use of iron catalysts for automobile-emission control.¹⁴ Unsupported Fe₂O₃ surfaces and several supported catalysts were investigated and the authors reported the following order of activity in CO oxidation at 300°C: Fe₂O₃/Al₂O₃ > Fe₂O₃/TiO₂ ≈ Fe₂O₃ » FeSbO₄ > FePO₄ > Fe₂(MoO₄)₃. Although the results were encouraging, the high activation barriers involved in the CO oxidation (more than 0.84 eV), limited the ability of the studied catalysts to work at low temperatures. Therefore, low-temperature oxidation aimed to increase the conversion efficiency of CO continues to be an unsolved problem, and scientists continuously seek suitable catalysts to realize this task.¹⁵⁻²⁰ In general, the ability of a catalyst to promote the CO oxidation at low temperatures depends on two relevant factors:

1. A low CO chemisorption binding energy (of the order of 0.4 eV) that avoids the blocking of the active metal sites (CO poisoning) for processes following the LH reaction mechanism, and,
2. Low energy barriers (around 0.6 eV) along the reaction path that enable the reaction to occur at low temperatures (~100°C).

Examples of catalyst formulations that fulfill the above requirements and remain stable under moisture, are Au_x nanoparticles adsorbed on base transition metal oxides,²¹ and Co₃O₄ nanorods.¹³ In a recent report, Li *et al.* proposed Fe-anchored graphene oxide²² as a low-cost CO catalyst. Having found that the LH mechanism presents a large energy barrier of 2 eV, Li *et al.* proposed an Eley-Rideal mechanism, in which CO reacted with an adsorbed and activated O₂ molecule to form a carbonate-like intermediate with an energy barrier of only 0.6 eV. Martynova *et al.*²³ studied the low-temperature CO oxidation of Ruthenium oxide films, finding that the reaction sets in only when the oxygen coverage exceeded 1 monolayer (1ML) and presents a low energy barrier of 0.6 eV in the range of 127-197 °C. Xie. *et al.*¹³ experimentally studied the low-temperature oxidation of CO catalyzed by Co₃O₄ nanorods. It was found that the nanorods preferentially exposed the {110} planes, favoring the presence of active Co³⁺ species at the surface and with an activating energy toward CO oxidation of only 0.23 eV.

Regarding the CO catalytic activity of iron oxide species at low-temperatures, it has been experimentally observed that thin oxide films on metals may indeed exhibit greatly enhanced catalytic activity compared to the underlying metal substrate under the same conditions.²⁴ In addition to the above studies, low temperature CO oxidation over Ag supported ultrathin MgO films was recently reported.¹⁷ In this case, the activation barrier (0.7 eV) resulted lower than the corresponding barrier of CO oxidation on Pt(111) of 0.9 eV. The gas phase reaction ($\frac{1}{2}\text{O}_2 + \text{CO} \rightarrow \text{CO}_2$) was calculated to present an overall exothermicity of 3.2 eV. Importantly, this study showed the possibility to generate a catalyst in which the **CO adsorption energy of only 0.4 eV is low enough to prevent CO poisoning**, therefore enabling a low temperature CO oxidation route, and addressing the cold start problem.²⁵

Despite the above mentioned studies, the development of active and stable catalysts, without noble metals, for low-temperature CO oxidation under an ambient atmosphere remains a significant challenge. Earlier reports, as mentioned above, indicate that the Fe₂O₃ is the most active iron oxide surface toward CO oxidation at high

temperatures (~ 300 °C).⁸ Furthermore, a number of theoretical and experimental cluster studies have also shown that selected iron oxide compositions and charge states are the most reactive toward CO oxidation, i.e. FeO_2 , Fe_2O_3 , FeO_2^- , Fe_2O_3^- , FeO^+ , FeO_2^+ , Fe_2O^+ , Fe_2O_2^+ and Fe_2O_3^+ .²⁶⁻²⁷

The aim of the proposed work is to carry out a detailed investigation that will provide information about the electronic, geometrical, and catalytic properties of the iron oxide FeO_2 cluster adsorbed on defect-free $\text{MgO}(100)$ surfaces on the quest for a low-cost and low-temperature CO nano-catalysts. Note that thin oxide films have been found more active at low temperature²⁴ as compared to the iron oxide surfaces.¹⁴ Our objective is to show that iron oxide adsorbed clusters are indeed the next natural step towards the design of a CO catalysts. Within the scope of the present project, we address the complete CO catalytic process, namely, the oxidation of CO by the $\text{MgO}(100)$ adsorbed FeO_2 cluster, further oxidation of a second CO molecule with the release of CO_2 leaving a reduced $\text{Fe/MgO}(100)$ species, and then the oxidation of the reduced metal by O_2 that regenerates the nano-catalyst in an overall exothermic reaction.

As discussed in the introduction, in some cases the energy gained in the initial steps of the CO oxidation is insufficient to complete the catalysis due to high barrier energies, in others, low-temperature catalysis cannot be achieved and high temperatures are required to start the reaction by promoting the desorption of species that poisoned the active sites. For us, it is expected to start the cycle at low temperature, and despite the energy needed to overcome the barriers for the transition states like in MgO-FeO-O-CO (0.97 eV) it is shown to be possible to complete the catalysis because of the large CO and O_2 adsorption energies of 2.0 and 3.8 eV respectively that prove to be the driving force for the catalytic CO oxidation. Note that after an exothermic step like CO or O_2 adsorption there are a large number of competing processes that may take place and it is statistically unlikely that all of the energy of adsorption will be channeled only into the reaction pathway containing the required activation barrier. These processes may include uni-molecular fragmentation (RRKM), collisional dampening, radiative decay, and any reaction pathways leading to other products. The calculated reaction pathway however shows one energetically favorable mechanism by which the reaction can take place. Other potential pathways leading to the same product or other products were not fully explored.

2. Computational Method

All calculations are performed within the generalized gradient DFT formalism, employing the exchange-correlation functional proposed by Perdew, Burke, and Ernzerhof (PBE) approximation³¹ and the deMon2k software.³²⁻³³ The electronic orbitals and eigenstates are determined by using a linear combination of Gaussian atomic type orbital molecular orbital (LCGTO) approach. To speed up the calculations we use a variational fitting of the Coulomb potential to avoid the calculation of four-center electron repulsion integrals.³⁴ The exchange correlation potential is calculated via a numerical integration from the auxiliary function density.³⁵ All electrons of the MgO cluster and of the Fe and O atoms are treated explicitly using the double zeta valence plus polarization (DZVP) basis sets.³⁶ The GEN-A2 auxiliary function set³⁷ is employed for the calculation of the auxiliary density for all the atoms. Different spin multiplicities were

tested and it was found the most stable spin states correspond to triplets and these are the reported results as we conclude that the reaction occurs in this potential energy surface. For the geometry optimization, a quasi-Newton method in internal delocalized coordinates was used.³⁸⁻³⁹ To analyze the charge transfer between the MgO(100) surface and the adsorbed species a Natural bond orbital (NBO) analysis⁴⁰ was performed. The transition state search and the determination of the energy barriers were performed in two steps. The approximate transition states were determined via constrained optimizations and the saddle method⁴¹ and further refined by a local uphill walking algorithm employing the eigenvector following method in redundant coordinates. Finally, a local vibrational analysis was performed to discriminate between minima and transition states. This methodology has been successfully implemented and tested in the deMon2k program and has been used in our previous studies.²⁶⁻³⁰

To further eliminate any uncertainty associated with the choice of basis set or the numerical procedure, we carried out supplementary calculations by the Naval Research Laboratory Molecular Orbital Library (NRLMOL) set of codes which allow efficient calculations using large basis sets calculations.⁴²⁻⁴⁴ For these calculations a generalized gradient approximation as in the deMon2k code was employed.³¹ A 5s, 4p, and 3d basis set for the C and O atoms, and a 7s, 5p, and 4d basis for the Fe atom was used. In each case, the basis set was supplemented by a diffuse Gaussian. We found excellent agreement in the cluster calculations between deMon2k and NRLMOL calculations. Both methods predicted the same ground-state multiplicities and geometries with differences in the range 1-3 pm in the bond lengths. Calculations in deMon2k however allowed to include embedded charges in our cluster models as described below and we report the results from these calculations.

3. Results and Discussion

3.1 Cluster model and O₂, CO and FeO₂ absorption on the MgO surface.

The essential features of the cluster embedding technique used in this study are illustrated in **Figure 1**. The active cluster that is treated by all electron DFT calculations is the Mg₃₀O₃₀ moiety shown in red and grey. To provide a proper electrostatic environment and boundary conditions, an Evjen array⁴⁵ of 1740 point charges surrounds the active cluster so as to form an MgO(100) surface with the adsorbed species on top. Details of the development of the method can be found in previous works by Reveles et al.^{39,46-48} in which the rumpling and relaxation of the surface were studied through structure optimizations with equivalent and constrained delocalized internal coordinates.

In our recent joint experimental and theoretical study of the reactivity of anionic transition metal oxide clusters it was found that the changes in the elemental composition of the cluster from Fe to Co, Ni, and Cu, resulted in variations of the experimentally measured rate constant for oxygen transfer to CO. Theoretical calculations indicated that the variation in reactivity results primarily from a combination of two factors: i) differences in the CO binding energy to the clusters, the overall change in energy, ii) the spin multiplicity change from reactants to products.³⁰ Our studies on the gas-phase clusters have shown that **specific stoichiometries present enhanced reactivity toward CO oxidation**, and that reactivity is linked to the stoichiometry,

charge state, initial CO binding energy, and oxygen bond strength on the transition metal oxides. We, hence, begin by considering the adsorption of O₂, CO and FeO₂ on the MgO(100) cluster model. The most preferential adsorption site was identified by considering all possible adsorption sites such as on top of O, on top of Mg, bridge (above a Mg-O bond) and on hollow sites of the surface. The results for the most stable geometries are shown in **Figure 2**. We calculated the energy gained during the absorption (E_a) to investigate the stability of the adsorbed species by using the equation:

$$E_a = E[X] + E[\text{MgO}(100)] - E[\text{XMgO}(100)], \text{ with } X = \text{O}_2, \text{CO, and FeO}_2.$$

Here, E[X] represents the energy of the gas phase species, E[MgO(100)] is the energy of the MgO(100) cluster model and E[XMgO(100)] is the energy of the surface model with the adsorbed species. Note that according to this definition, a positive E_a corresponds to a bound structure and a larger E_a value implies a more stable structure.

Earlier studies have shown that a CO adsorption energy (E_a) of the order of 0.4 eV is insufficient (low) to prevent CO poisoning on Ag supported ultrathin MgO films.¹⁷ In the present study, we also find that O₂ and CO to have small adsorption energies of 0.36 and 0.55 eV, respectively (Cf. **Figure 2**). These small values of E_a prevent the blocking of the surface and the need of high temperatures to start the reaction. The FeO₂ adsorption, on the other hand, results in a large E_a of 2.82 eV. This larger adsorption energy, as determined by the NPA analysis, is a result of stronger interaction with 0.34 electrons being transferred from the MgO surface. The large E_a allows the FeO₂ cluster to remain attached to the MgO surface working as an active site for the low temperature CO oxidation during the whole process as described in the next section.

3.2 Oxidation of CO and formation of reduced MgO(100)-FeO and MgO(100)-Fe species

We also studied the Langmuir-Hinshelwood (LH) and Eley-Rideal (ER) mechanisms for the reaction of O₂ and CO. In the ER mechanism, O₂ is adsorbed and activated onto surface and reacts with a gas phase CO molecule to form a carbonate intermediate that releases the oxidation product. In the LH mechanism, both O₂ and CO absorb at the active site and react to form a CO₂ molecule that is desorbed.

Eley-Rideal (ER) Mechanism: In order to examine the reaction of O₂ and CO by the ER mechanism we started with several co-adsorption configurations by placing CO and O₂ into close distance. Such configurations have been previously investigated in similar studies on Fe anchored graphene by Li et al.²² In our study, we did not find any CO₂ formation primarily because the carbon atom of CO inevitably favored a stronger interaction with the Fe metal. After several optimization attempts in various configuration, we concluded that the CO oxidation reaction process via ER mechanism is not favorable by thermodynamic reasons.

Langmuir-Hinshelwood (LH) Mechanism: Our previous experimental and theoretical studies on gas-phase clusters have shown that CO is readily oxidized by gas phase FeO₂⁻ at ambient temperature via LH mechanism and that the conversion efficiency increases with increase in the CO pressure. The calculated energy profile for the CO oxidation by FeO₂⁻ showed a large energy gain of 1.7 eV for the initial CO

binding on the Fe atom. This energy may be sufficiently large to overcome the energy barrier of 0.3 eV toward the formation of the intermediate OFeOCO^- species which, in turn, results in energy gain of 0.9 eV. The intermediate subsequently releases CO_2 in an overall exothermic reaction. The initial CO binding energy should also be sufficient enough to overcome the energy barriers at higher reaction pressures in which the rate of collision with additional gas molecules may be large enough to remove some of the CO association energy through collisional cooling and damping vibrations.

We now consider the CO oxidation on the MgO-FeO_2 cluster model. The optimized structure geometry of MgO adsorbed FeO_2 species is shown in [Figure 2](#). Here we propose a catalytic cycle for the CO oxidation. FeO_2 shows a strong interaction with the MgO surface ($E_a = 2.82$ eV) and with two separated O atoms freely available for CO oxidation. The absorption of CO on the Fe site results in a large energy gain of 0.83 eV. Additional cluster calculations on the entropic and Gibbs free energy changes for this step gave an estimated loss of around 0.5 eV mainly related to the translational contribution to the partition function of the gas-phase CO molecule. The resulting energy gain for the CO absorption is then just enough to overcome the energy barrier (0.34 eV) towards the formation of the intermediate (MgO-FeO-CO_2) with an energy gain of 1.21 eV. The formation of a possible Fe- CO_3 carbonate complex was studied at this point, however, it showed to require a large energy barrier of 1.41 eV due to the needed rearrangement of the FeO-CO_2 complex. We also explored the release a CO_2 molecule which requires 1.51 eV to proceed. Finally, a more favored path with the absorption of a second CO molecule leading to an energy gain on 0.68 eV (0.18 eV considering Gibbs free energy changes) resulted the most favorable option. After a second energy barrier of 0.28 eV an intermediate with two CO_2 attached molecules $\text{MgO-Fe-CO}_2\text{-CO}_2$ is formed. It is at this step where the release of a first CO_2 with a cost of only 0.68 eV proceeds leaving a MgO-Fe-CO_2 species. [This barrier is only slightly larger than the desired value of 0.6 eV necessary to make the catalyst work at low temperature; thanks to the final entropic gain due to the translational freedom of \$\text{CO}_2\$ molecule released, it is expected that the barrier of 0.68 eV could be easily overcome.](#) Note how the co-adsorption of two CO molecules into the active site significantly reduces the energy required for the CO_2 release.

3.3 Oxidation of the reduced species to regenerate the active nano-catalyst.

At this step we study the O_2 oxidation of the reduced species to regenerate the nanocatalyst. As discussed in the introduction, experimental studies have shown that under reaction conditions, at oxygen partial pressure in the millibar range, a FeO bilayer film restructures to give an OFeO trilayer.³² The formation of the oxygen enriched film requires overcoming a **small energy barrier of 0.3 eV**, where the required energy is provided by oxygen pressure. Based on these results, we calculate the reaction path that involves the oxidation of the reduced MgO-Fe-CO_2 species to determine the intermediate species, transition states and the energy barriers involved in the regeneration of the nanocatalyst.

Oxygen absorption on the MgO-Fe-CO_2 model resulted in an activated O_2 molecule with a O-O bond length of 1.4 Angstroms and a large energy gain of 1.99 eV (1.49 eV considering entropic contributions to the Gibbs free energy). The breaking of the activated O-O bond in this intermediate required our largest calculated energy

barrier of 0.97 eV that lead to the regeneration of the active species after a second CO₂ molecule is released with an energy cost of 0.39 eV. Similar to the release of the first CO₂ molecule discussed above, due to the entropic gain by the translational freedom of the CO₂ released this barrier could be easily overcome. On the other hand, the energy barrier for the O-O breaking is a little larger than the calculated range of around 0.6 eV needed to promote the CO oxidation at low temperatures for surfaces and thin films. *Note that only a direct activation path has been investigated, but other paths with lower barrier are likely to exist, but they have not been investigated in the present paper.* Furthermore, the system has already released around 6.0 eV (see Fig. 3) when reaching this step of the process which may help surmounting this energy barrier.

We have further analyzed in detail this barrier which is the third transition state shown in **Figure 3** to certainly prove that the barrier is correct. For instance, we calculated the transition state in the FeO-O cluster without MgO surface to later compare with the final calculated molecule results. Our calculated energy barrier was of **1.3 eV** for the cluster and resulted indeed a little larger. This additional study showed that the calculated transition state for the MgO surface was correct and that this was indeed stabilized by its interaction with the surface reducing the energy barrier.

In order to obtain better understanding of the results, we compiled the results in a **Table 1**. The energy diagram, illustrating the energy changes for every step (ΔE) in the catalytic cycle for CO oxidation is shown in **Figure 3**. The reaction is calculated to be overall exothermic and the full catalytic cycle is presented in **Figure 4** corresponding to the following equation:

The bond lengths of the optimized species are summarized in **Table 2**. The distances for FeO are given for the two O atoms near to Fe, the following entry correspond to the O that binds to CO. We found that the Fe-O bond distance increases systematically until the CO₂ is formed. Likewise, the carbon-iron and oxygen-oxygen bond distances also increases during the reaction path, and the CO₂ is released when the Fe-C bond length reaches 1.86 Å. The Fe to the surface bond length varies in a small range from 1.76 - 1.99 Å. The calculated FeO distance for the gas phase cluster is 1.61 Å.²⁶ Thus it is concluded that the cluster remains firmly attached to the surface during the whole catalytic process.

Conclusions

To summarize, we have examined the catalytic process of CO oxidation using a cluster model supported on a MgO surface. We studied the adsorption energies, barrier heights, geometrical parameters and binding energies. Thin oxide films have been found more active at low temperature as compared to the iron oxide surfaces in previous reports. Our results show that the iron oxide adsorbed clusters are indeed the next natural step towards the design of a CO catalyst and that the iron oxide FeO₂ cluster adsorbed on MgO(100) may work as a low temperature and low-cost nano-

catalyst. We found small energy barriers of **0.28 to 0.34 eV** for the formation of the C-O-O transition states and a larger energy barrier of **0.97 eV** for the O-O breaking in the MgO-FeO-O-CO transition state. These energy barriers are expected to be surmounted, given that the system gains energy by the CO (0.7 to 2.00 eV) and O₂ absorption (2.00 eV) resulting in an overall exothermic reaction. The iron oxide FeO₂ cluster adsorbed on MgO(100) is predicted to have a good catalytic activity for CO oxidation via the Langmuir-Hinshelwood (LH) mechanism in an overall exothermic reaction proving to be an excellent candidate for a low cost and low temperature nano-catalyst.

The added caveat of the studied Nanocatalyst will be to also adjust the number of MgO layers for the optimal CO oxidation. Likewise, the introduction of defects (charged and neutral oxygen vacancies) in the surface. We expect that by introducing oxygen vacancies, and with that enhancing the charge transfer from the surface to the adsorbed clusters the energy barriers may be lowered. These studies are currently underway and will be reported in a future work. Finally, the results of the proposed project provides a template to guide the future studies of other MgO adsorbed transition metal oxide clusters, i.e. Fe₂O₃, Co_xO_y, Cu_xO_y and Ni_xO_y, (which have shown enhanced activity toward CO oxidation in our previous cluster studies⁶⁻⁸), in the quest for affordable and low-temperature CO nano-catalysts. We hope that our investigation motivates future experimental studies.

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Table 1. Calculated Energies for the Reaction of Adsorbed FeO₂ Cluster with CO. Superscripts indicate the molecular spin multiplicities.

			ΔE(eV)
¹ MgO + ⁵ FeO ₂	→	¹ MgO-FeO-O	-2.82
¹ MgO-FeO-O + ¹ CO	→	³ MgO-FeO-O-CO	-0.83
³ MgO-FeO-O-CO	→	³ MgO-FeO-O-CO_TS	0.34
³ MgO-FeO-O-CO_TS	→	³ MgO-FeO-CO ₂	-1.21
³ MgO-FeO-CO ₂ + ¹ CO	→	³ MgO-FeO-CO-CO ₂	-0.68
³ MgO-FeO-CO-CO ₂	→	³ MgO-FeO-CO-CO ₂ _TS	0.28
³ MgO-FeO-CO-CO ₂ _TS	→	³ MgO-Fe-CO ₂ -CO ₂	-0.65
³ MgO-Fe-CO ₂ -CO ₂	→	³ MgO-Fe-CO ₂ + ¹ CO ₂	0.68
³ MgO-Fe-CO ₂ + ³ O ₂	→	³ MgO-Fe-O ₂ -CO ₂	-1.99
³ MgO-Fe-O ₂ -CO ₂	→	³ MgO-Fe-O ₂ + ¹ CO ₂	0.39
³ MgO-Fe-O ₂ + ¹ CO	→	³ MgO-Fe-O ₂ -CO	-2.00
³ MgO-Fe-O ₂ -CO	→	³ MgO-Fe-O-O-CO_TS	0.97
³ MgO-Fe-O-O-CO_TS	→	³ MgO-FeO-O-CO	-2.07
³ MgO-FeO-O-CO	→	³ MgO-FeO-O-CO_TS	0.34
³ MgO-FeO-O-CO_TS	→	³ MgO-FeO-CO ₂	-1.21

Table 2. Bond lengths in Angstroms for the optimized structures along the reaction path.

	R (FeO)	R (FeC)	R (OO)	R (CO)	R (FeO_s)
MgO-FeO-O	1.63, 1.63		2.98		1.76
MgO-FeO-O-CO	1.65, 1.65	1.77	2.69	1.17, 2.12	1.99
MgO-FeO-O-CO_TS	1.65, 1.75	1.82	3.27	1.17, 1.93	1.91
MgO-FeO-CO ₂	1.61, 1.84	1.87	3.08	1.21, 1.33	1.83
MgO-FeO-CO-CO ₂	1.67, 2.11	1.83, 1.94	3.72	1.21, 1.29	1.92
MgO-FeO-CO-CO ₂ _TS	1.70, 2.02	1.86, 1.94	3.70	1.20, 1.30 1.16, 2.00	1.90
MgO-Fe-CO ₂ -CO ₂	1.93, 2.20	1.87, 1.98	3.44	1.27, 1.21 1.29, 1.23	1.85
MgO-Fe-CO ₂	1.90	1.86		1.22, 1.32	1.84
MgO-Fe-O ₂ -CO ₂	1.75, 2.07	1.91	1.40	1.23, 1.28	1.88
MgO-Fe-O-O-CO_TS	1.86, 1.66	1.82	1.99	1.17	1.93

Figure Captions

Figure 1. MgO(100) cluster embedded surface model. The full surface is given in (a), whereas the quantum region is highlighted in (b). The $\text{Mg}_{30}\text{O}_{30}$ cluster with the two sets of equivalent coordinates is depicted in (c), and the fixed substrate is given in (d). Oxygen and magnesium atoms correspond to grey and red circles respectively.

Figure 2. Calculated lowest energy structures, adsorption energies (E_a) and atomic charges (q) for O_2 a), CO b) and FeO_2 c) on the MgO(100) surface models. Oxygen, magnesium, iron and carbon atoms correspond to red, grey, cyan and brown circles respectively. Selected bond lengths are given in units of Angstroms.

Figure 3. Plot of the calculated change in energy (ΔE) for each step of the reaction pathway of the CO oxidation with MgO- FeO_2 . The top layer of the MgO cluster model is only shown for clarity. Oxygen, magnesium, iron and carbon atoms correspond to red, grey, cyan and brown circles respectively.

Figure 4. Catalytic cycle for the CO oxidation on the MgO-FeO species. Oxygen, magnesium, iron and carbon atoms correspond to red, grey, cyan, and brown circles respectively.

Figure 1.

Figure 2.

Figure 3

Figure 4.

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