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Toward better understanding of the support effect: test cases for CO dissociation on Fe_n/TiO₂(110), n=4,5

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ABSTRACT

The Fischer-Tropsch reaction is initiated by direct CO dissociation for Iron catalyst even though a H-assisted mechanism may be easier on other metals. In the gas phase, the CO dissociation is only favorable for Fe-clusters composed by more than 11 atoms. We show here the remarkable effect of the support TiO₂(110), making this dissociation exothermic for Fe₄ and Fe₅ clusters. The main factor for the CO activation is the electron transfer to the reducible support. The role of the TiO₂(110) support is to transform the neutral cluster into a positively charged one for which CO dissociation is easier

1. Introduction

Understanding the interaction between transition metal nanoparticles and metal-oxides is a challenging topic both for experimentalists in the prospect of improving catalytic properties and for theoreticians to rationalize and assist this improvement. In fact, the metal/metal-oxide interface can determine the overall behavior of a system in many industrially relevant areas, such as microelectronic or photovoltaic devices, coating, sensors devices [1,2] and information storage [3]. Focusing on heterogeneous catalysis, it is well accepted that the support strongly modifies the activity of a metal, an effect known as “strong metal support interaction”, SMSI. It has been reported that the interaction between metal aggregates and metal-oxide support depends largely on its reducibility [4,5]. Thus, oxides can be classified into two categories according to this character: “SMSI oxides” such as TiO_2 [4], Nb_2O_3 , V_2O_5 , Ta_2O_3 [4,6] and CeO_2 [7], where the metal cations could be reduced by the presence of oxygen vacancy or by adsorption of an electron donor species such as hydrogen, hydroxyl ions or metal atoms, and “non SMSI oxides” such as SiO_2 [8] and Al_2O_3 [9].

The SMSI effect has been shown to be crucial for the significant improvement of the hydrogenation rate of CO catalyzed by a transition metal supported on TiO_2 within the Fischer-Tropsch synthesis, FTS. This iconic process has recently received remarkable attention both in academy and in industry [1-3,10-12]. This reaction corresponds to the reduction of CO by H_2 in the presence of a metal cluster deposited on a support. The FTS is an attractive process for the production of middle-distillate and diesel fuels via surface polymerization from a syngas mixture ($\text{CO} + \text{H}_2$) [11]. The metal catalysts common for FTS are diverse, Co, Fe, Ni and Ru [13]; however, the Fe-based catalysts are those most used industrially, due to their low cost, high activity, flexible product distribution and also to their ability of working at low H_2/CO ratio [4,5]. Two possible reaction pathways for the first step of the FTS have been proposed: either a direct CO dissociation occurs at first (carbide mechanism) followed by hydrogenation of the carbon

(formation of CH_x), or the hydrogen activates the C-O bond cleavage through the formation of a formyl intermediate (H-assisted dissociation). In the case of the iron catalysts, the most probable mechanism initiates by the dissociation of CO [6,7,14]. This is the case when iron catalyst is supported on TiO_2 [15] even though the H-assisted dissociation is reported on Cu doped-iron surfaces [16,17].

This paper is devoted to modeling the effect of the support on the first step of the FTS, i.e. CO dissociation, taking the rutile- TiO_2 (110) surface as support (indeed a reducible metal oxide) and Fe_4 and Fe_5 clusters as catalyst. Previously, we have reported a study of CO dissociation on Fe_n clusters ($n=1$ to 65) on the gas phase that showed that dissociation was not exothermic for the case of Fe_n ($n<11$).

2. Computational details

We performed spin-polarized periodic calculations based on Density Functional Theory (DFT) in the generalized gradient approximation (using the PW91 exchange-correlation functional) as implemented in the VASP code [18-21]. Plane-wave basis sets (with a kinetic energy cutoff of 400 eV) describe the valence electrons: ten and six electrons for the surface atoms Ti and O, respectively, and eight electrons for including the 4s and 3d electrons for Fe atom. The core electrons were replaced by projector augmented wave (PAW) pseudopotentials [22,23]. The relaxation of the atomic positions in the supercell took place until energy differences are smaller than 0.02 eV/Å.

Our calculations are periodic in three dimensions and we imposed a vacuum distance of 13 Å, which is large enough to avoid any interaction between two successive slabs. The model consists of nine atomic layers slab (three Ti_2O_4 layers) of rutile oriented in the (110) direction, see Figure

5 [15,24,25]. We considered a double cell p(2x3) with $a = 13.12 \text{ \AA}$ and $b = 9.19 \text{ \AA}$. The closest distance between repeated metal clusters is therefore $6.95 \text{ \AA}$. At the surface, we found two kinds of Oxygen atoms: bridging atoms sticking out (O_{2c}) and ‘in-plane’ threefold-coordinated atoms (O_{3c}). Only the adsorbate (here in this work Fe_4 , Fe_5 , C, O and CO) and the top two tri-layers were relaxed, the bottom tri-layer was kept at bulk position.

The adsorption energy (E_{ads}) is calculated as:

$$E_{ads} = E_{sys} - E_{CO} - E_{Fe_n/TiO_2}$$

Where E_{sys} is the energy of the $TiO_2(110)$ supported Iron cluster including adsorbate. It is negative for exothermic adsorption.

The dissociation energy for CO is defined as the difference between adsorption energy in the dissociated (noted as C/O) and molecular (noted as C-O) states:

$$E_{diss} = E_{ads}(dissociated) - E_{ads}(molecular)$$

SD (total spin density) denotes the difference between the numbers of electrons of opposite spin $N_\alpha - N_\beta$. When considering local values under adsorption, unless specified, the spin magnetic moment per iron atom (μ_B/atom) is simply the average value, $(N_\alpha - N_\beta)/n$ ($= SD/n$).

In order to find the different saddle points, the minimum energy paths between different minima were optimized by use of the climbing image nudged elastic band (CI-NEB) method of Jónsson and co-workers [26,27], and the transition state structure characterized by appropriate frequency calculation ensuring that it exhibits one imaginary frequency only which indeed corresponds to CO dissociation.

3. Results and Discussion

Carbon monoxide dissociation has been extensively investigated on a series of iron clusters in our previous work.[28-30] We concluded that C-O is adsorbed on a hollow site, that dissociation is exothermic for clusters whose size exceed 10 atoms while for smaller clusters, it remains endothermic. Taking the small Fe_4 and Fe_5 clusters as an example of a system for which CO dissociation is thermodynamically favored, in this work we show that CO dissociation becomes exothermic when these small clusters are deposited on a support, here rutile TiO_2 (110).

3.1. CO dissociation on isolated Fe_4 and Fe_5

a. C-O adsorption and co-adsorption of C/O on Fe_4

As a benchmark for this study, we first summarize what we concluded for CO dissociation on a naked Fe_4 cluster. In agreement with previous work,[31-33] our GGA-PW91 DFT calculations allowed to conclude that the most stable structure is a tetrahedron, with a Fe-Fe distance close to 2.4 Å.[29] The magnetic moment is 3.5 μ_B /atom, in agreement with calculations made by Roy,[34] and slightly more than other calculations that found 3 μ_B /atom.[31-33] C-O adsorption takes place at a hollow site, see Figure 1, with calculated adsorption energy of -2.11 eV (Table S1, ESI). This is the configuration of lowest energy and the CO is slightly activated with an elongated distance (1.20 Å vs. 1.15 Å for bare CO). There is no quenching in the magnetic moment after adsorption (14 μ_B for the whole cluster). In ref [29], even though we do not see a decrease of SD between naked and C-O adsorbed clusters in many cases (Fe_4 , Fe_5 , Fe_9 , Fe_{10} , Fe_{12} ,...etc), a quenching of SD by $\pm 2 \mu_B$ happen for some cluster sizes. However, a quenching of SD by $\pm 2 \mu_B$ is more generally observed once a Hubbard correction is applied (DFT+U). This change is due to the naked clusters that have then higher spin states.

Figure 1: Lowest energy structures for C-O adsorption (left side) and co-adsorption of C/O on Fe_4 (right side)

The co-adsorption of separated C and O represents the product of the CO dissociation. O is capping a triangular face while C may be bridging or capping. Different configurations for C and O have been investigated: In that of lowest energy, C and O are bound to one Fe common atom as shown in Figure 1 with an adsorption energy -1.8 eV (Table S1, ESI). The global magnetization is $12 \mu_B$ (a quenching of $2 \mu_B$ with respect to the clean Fe_4 cluster).

b. Elementary steps for CO dissociation on Fe_4

We study the dissociation of a CO molecule initially adsorbed at the hollow position. We have calculated the minimum energy path (MEP) using the climbing image nudged elastic band method (CI-NEB) between the hollow site and the nearest structure of the dissociative form shown in the Figure 2. In this geometry, C and O are vicinal; however, migration of O leads to the most stable geometry shown in Figure 1. The dissociation step implies a crossing between two electronic states with different multiplicity. However, the energy difference between the two electronic states is small (less than 0.1 eV) and the energy barrier calculated imposing both multiplicities or removing the constraint of a fixed multiplicity leads to the same value, 2.38 eV. This value is large as compared to those for larger clusters, 1.80 eV for Fe_{13} , [30] and it is also larger than that calculated for dissociation on the Fe(100) surface (Jiang and Carter reported an energy barrier of 1.52 eV [35]).

Figure 2: Minimum energy path (MEP) of the CO dissociation on Fe_4 .

c C-O adsorption and co-adsorption of C/O on Fe_5

The most stable Fe_5 structure is a trigonal bipyramid [31], the magnetic moment per atom ($3.2 \mu_B/\text{atom}$) agrees with calculations made by Roy et al. [34] and is larger than previous results [31]. GGA + U gives a more symmetric structure and a magnetic moment of $18 \mu_B$ ($3.6 \mu_B/\text{atom}$). The best adsorption mode, that taking place over a triangular facet, corresponds to an adsorption energy of -2.09 eV (Table S2, ESI). This is comparable to the adsorption on the Fe_4 tetrahedron and the dissociation energy is the same, $+0.31 \text{ eV}$.

We also made the adsorption of the Fe_5 cluster with square pyramid structure. The clean structure is higher in energy than the trigonal bipyramid by 0.20 eV , the C-O adsorption is also higher by 0.48 eV , which leads to an adsorption energy of -1.81 eV . However, the co-adsorption of C/O gives a similar energy compared to the one on the trigonal bipyramid structure.

3.2. CO dissociation on TiO₂ (110) supported Fe₄ and Fe₅

In this part, the surface of the rutile TiO₂ (110) has been considered as a support for CO dissociation on adsorbed Fe₄ cluster. We choose a p(2x3) cell which provides a surface large enough to avoid any interaction between repeated clusters. We started by searching the most stable configuration for four adsorbed iron atoms. The Fe₄ cluster tends to flatten on the surface making a rectangle with Fe-Fe distances of 2.25-2.60 Å, see Figure 3. Other low energy configurations also correspond to flat structures (Table S3, ESI). The tetrahedron structure (found in vacuum) was also optimized but lead to a flat structure as well. We tested other geometries such as zigzag, linear and dispersed atoms; they all lead to higher energies.

Figure 3: Most stable configurations for Fe₄ deposited on TiO₂ (110). Relative energies are presented. Structure (a) is a cyclic Fe₄ cluster with Fe-Fe=2.25-2.60 Å; structure (b) may be viewed as two dimers with Fe-Fe=2.24 Å or as a Fe₄ chain, counting the central Fe-Fe distance (2.88 Å) as a bond while structure (c) is the most stable adsorption of four Fe atoms at the same coverage ($d_{\text{Fe-Fe}} > 3.4$ Å).

The structure of lowest energy for adsorption of Fe₅ is a square pyramid, the four basal atoms bound to the oxygen atoms of the support and the vertex maintaining the cluster structure and prefiguring an atom from a new surface layer. For both sizes, there is a large distortion relative to the naked structure; two edge sharing triangle flattening on the support surface. The distance in

Fe_4 and the relative energy show that we do not have four Fe individual atoms (see figure 3), however the tendency to dispersion exists. The vertex of the square pyramid, maintains more integrity in Fe_5 structure, see figure 4.

Figure 4: Most stable configurations for Fe_5 deposited on TiO_2 (110). Relative energies are presented. Structure (a) is a square pyramid cluster; structure (b) is the trigonal bipyramid cluster.

a. C-O adsorption on supported Fe_4 and Fe_5

Several modes for C-O adsorption on the lowest energy configuration of the Fe_4 cluster adsorbed on the TiO_2 surface (Figure 3a) were investigated, see Figure 5. We showed that adsorption at the on-top position is more exothermic than at hollow position by 0.14 eV. Tilting the CO molecule from the on-top position has been investigated but it is less favorable than the vertical position, and its geometry is not reported here. Similarly, tilting the O atom of the hollow coordinated CO towards a Fe atom, structure $\text{C}_{4f}\text{-O}_{1f}$, is not energetically favored. Differently, tilting the O atom of the hollow coordinated CO between two Fe atoms to form a bridge between them, structure $\text{C}_{4f}\text{-O}_{2f}$ (Figure 4d), corresponds to the most stable adsorption mode. Hence, the hollow site, $\text{C}_{4f}\text{-O}_{2f}$, becomes more exothermic than on-top site consistently with the gas-phase cluster study. Comparison of the CO distances at different positions reveals a

clear activation of CO when coordination on the hollow site, from 1.17 Å for the isolated molecule up to 1.31 Å for $C_{4f}-O_{2f}$.

Figure 5: Most relevant C-O adsorption modes on supported Fe_4/TiO_2 (110). 1f, 2f and 4f refer to the coordination of C or O to Fe atoms, respectively. For clarity, C and O atoms of the CO molecule are presented in green and pink colors.

For Fe_5 , we tested the three possible lowest energy structures namely on-top, bridge and hollow sites (Table S7, ESI). The hollow site was again that of lowest with an adsorption energy -2.06 eV. This is significantly less than the value for Fe_4 . This is clearly due to the shape of the four members ring that allows easy adsorption in the absence of capping atom.

b. C/O co-adsorption on supported Fe

A prerequisite to study the mechanism of CO dissociation with the CI-NEB method is defining the initial and final geometry. To characterize the final geometry, we investigated the co-adsorption of C and O on the supported Fe_4 that are accessible from the geometry of lowest energy for molecular CO adsorption; structure $C_{4f}-O_{2f}$ in Figure 5d. Two possible scenarios were considered for CO dissociation, see Figure 6: the first one corresponds to the C atom at the hollow site while the O atom moves to a bridging site pointing down toward a Ti atom, leading

to structure $C_{2f}-O_{2f}$ (Position A). In the second one, the C and O atoms move toward opposite Fe bridges, leading to structure $C_{4f}-O_{2f}$ (Position B).

Figure 6: Most relevant C/O co-adsorption modes on supported $Fe_4/TiO_2(110)$ with respect to the lowest energy C-O adsorption ($C_{4f}-O_{2f}$). For clarity, C and O atoms of the CO molecule are presented in green and pink colors, respectively.

While dissociation of CO to structure C_{2f}/O_{2f} is endothermic by 0.1 eV, we were pleased to find that CO dissociation to structure C_{4f}/O_{2f} is exothermic by 0.37 eV. The corresponding value for the naked Fe_4 cluster was endothermic by 0.31 eV. The iron supported catalyst becomes closer to the naked Fe_{13} cluster which was found favorable to CO dissociation (dissociation exothermic by 0.53 eV). [30] This is a first indication of the contribution of the support. Note that this process involves a motion of the C atom at variance to what occurs for naked cluster. The C atom ends bound to two iron atoms and to two surface oxygen atoms.

We also performed the adsorption of dissociated CO on the Fe_5 cluster supported over a $TiO_2(110)$ surface. As for the molecular adsorption, the adsorption energy, -2.52 eV, is smaller than that on the Fe_5 cluster. The main result is however that the dissociation energy goes from endothermic (by 0.30 eV) for the naked cluster to exothermic (by 0.46 eV) for the supported Fe_5 cluster. This is again a huge effect revealing the support effect.

c. Elementary steps for CO dissociation on Fe₄/TiO₂ (110)

In this part, we present the energy profile for the dissociation of CO to structure C_{4f}/O_{2f}, see Figure 7. As a result from the section above, the path A defines the initial and final positions to calculate the MEP using again the CI-NEB method. Contrary to the case of the naked cluster, there is no crossing spin problem since both molecular and dissociated CO adsorptions have a global spin of 10 μ_B .

Figure 7: Minimum energy path (MEP) of the CO dissociation on Fe₄ cluster supported by the rutile TiO₂ (110) surface

The energy barrier calculation (see Figure 7) shows, surprisingly, a net decrease of the value from gas phase calculation of the Fe₄, 2.38 eV, or even the Fe(100) surface, 1.52 eV,[33,35] to that of the supported cluster, 0.57 eV. The latter value is lower than those obtained for the naked

larger clusters also, as for Fe_{13} cluster (1.8 eV) and Fe_{55} cluster (0.99 eV).[36,37] Two main reasons may explain this interesting improvement:

First, molecular adsorption of CO in the $\text{C}_{4f}\text{-O}_{2f}$ position on the supported cluster activates CO more than similar adsorption on an iron cluster (Fe_4 or even larger clusters up to 65 atoms). This hypothesis is supported by the fact that the C-O distance (originally 1.17 Å) is clearly longer when CO adsorbs on the supported cluster, 1.31 Å, compared with adsorption on the gas phase cluster, where the C-O bond elongates to only the maximum value of 1.24 Å (1.21 Å and 1.19 Å for Fe_{13} and Fe_{55} , respectively). Second, CO dissociation energy, which is endothermic for the small gas phase cluster, becomes exothermic considering the support. The dissociative configuration is stabilized on the supported cluster. Atomic migration on the surface may improve the overall energetic.

d. Electron transfer

The remarkable result is that the TiO_2 support offers the possibility of CO dissociation, an event not possible on the isolated Fe_4 cluster. The reason cannot be the tendency to the dispersion of the Fe atoms, considering that the cohesion of the cluster is diminished. It is true that the Fe_4 cluster is distorted flattened with elongated Fe-Fe distances. However, deformation of the most stable structure remains limited (compare structure a with structure c in figure 3) and CO dissociation is not possible on a single iron atom [29] and thus dispersion should not help. The reason must be electronic. In order to make clear this effect, we made a Bader charge analysis of the Fe_4 cluster supported on TiO_2 (without CO). In presence of the support, $2e^-$ have been transferred to the surface oxidizing 2 Ti^{4+} into Ti^{3+} and hence Fe_4 becomes positively charged (Fe_4^{2+}). CO adsorption and dissociation is therefore occurring on a charged metal cluster. The reducibility of the support is then a key-factor. In Table 1 we show that the dissociation energy

of CO decreases from the neutral to the charged iron cluster by 0.68 eV. This result explains the improvement of the dissociation energy when the iron cluster is supported by a reducible surface as the rutile TiO_2 .

	Neutral (Fe_4^0)		Charged (Fe_4^{2+})	
	Energy (eV)	SD (μ_B)	Energy (eV)	SD (μ_B)
$\text{CO}_{\text{mol}}/\text{Fe}_4$	-37.858	14	-22.774	12
$\text{CO}_{\text{diss}}/\text{Fe}_4$	-38.067	12	-23.665	12
E_{diss} (eV)	-0.21	-	-0.89	-

Table 1: Dissociation energy of CO on a neutral (Fe_4^0) and charged (Fe_4^{2+}) iron cluster. SD is the spin density.

e. Remark on the cluster size

The aim of this article was to compare the dissociation of CO on two clusters (Fe_4 and Fe_5) naked or supported. When supported, these clusters distort but do not fragment. This stability was necessary for the comparison. However, differences exist between the two clusters. The structure of the Fe_4 cluster on the support has changed when flattened and there is a hollow site at the center of the four-member ring allowing a strong interaction with CO. The capping atom of the Fe_5 cluster maintains more cohesion in the adsorbed species that is closer to the initial form. It is then less active and the adsorption energies are smaller. The supported systems have to be also discussed in terms of increasing coverage. The capping iron atom of the Fe_5 pyramid is not directly bound to the support, appearing as a premise for the generation of a new layer. Contrary to the basal atoms, it is not charged and thus not very different from an atom of a naked cluster.

Conclusion for the dissociation and the support effect are not changed; however, Fe_4 is more active and low coverage should be better if activity is searched.

4. Conclusion

In this study, we presented DFT calculations to investigate the role of a support for CO dissociation promoted by a transition metal cluster adsorbed on the support surface. As test case we chose to investigate CO dissociation on a Fe_4 cluster. Previous work indicated that CO dissociation on isolated and relatively small Fe clusters is not energetically favorable. We considered the (110) surface of rutile- TiO_2 as a support, its reducibility was thought to be essential for the CO dissociation.

Our results indicate that the Fe-cluster we investigated has a tendency to flatten on the support surface. Further, our calculations indicated a noticeable effect of the support that renders CO dissociation kinetically easy in the case of the Fe_4 cluster. A longer C-O bond on a free Fe_4 cluster as compared to CO adsorbed evidences activation of the adsorbed CO species. More fundamentally, our analysis indicates that a transfer of electron density from the cluster to the support is the key factor promoting CO dissociation. Indeed, analysis of the Bader charges indicated that after adsorption on the TiO_2 (110) surface, the Fe_4 cluster can be formally described as a charged Fe_4^{2+} cluster, with a transfer of $2e^-$ to the surface. This transfer of electrons results in a kinetically and thermodynamically favored CO dissociation. Calculations on the Fe_5 cluster confirms the role of the support for CO dissociation. Adsorption energies are then small due to the topology adopted by this cluster on the surface suggesting the coverage of the support by the metal should remain small.

ASSOCIATED CONTENT

Supporting Information.

This material is available free of charge via the Internet at <http://pubs.acs.org>.

Geometries of the different structures, tables of the adsorption energies of Fe_n on TiO_2 and CO on the supported Fe_n/TiO_2 , and tables of the dissociation energies of CO on the supported Fe_n/TiO_2 ($n=4,5$).

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

‘**VASP**’ Vienna Ab-initio Simulation Package, ‘**PAW**’ Pseudopotential Augmented-Wave, ‘**DFT**’ Density Functional Theory, ‘**GGA**’ Generalized Gradient Approximation, ‘**PW91**’ Perdew-Wang 1991, ‘**SD**’ Total Spin Density, ‘**CI-NEB**’ Climbing Image Nudged Elastic Band, ‘**MEP**’ Minimum Energy Pathway.

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KEYWORDS

Metallic clusters, phase transition, spin magnetic moment, iron.

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Graphical Abstract