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Final Report for Period Beginning 31-Jul-2020 and Ending 30-Nov-2021

Title: Design of atomically dispersed metals on oxides as catalysts for oxidative decomposition of chemical warfare agents

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Major Goals: Facile decomposition and neutralization of chemical warfare agents (CWAs) under ambient conditions is a major challenge in the modern world. Recent events have demonstrated that there is an unmet need to better protect soldiers using personal protective ensembles that neutralize or destroy CWAs under ambient conditions. To achieve the goal of efficient CWA destruction under ambient conditions, new highly efficient catalysts are required.

Our aim is to develop principles for designing new materials comprised of highly dispersed metal atoms, including single atoms, supported on metal oxides as catalysts for efficient oxidative decomposition of CWAs under ambient conditions. Our objective is to develop principles for predicting which metal/metal oxide combinations form stable and reactive catalysts. The role of charge transfer from the oxide to the dispersed metal centers on stability, oxophilicity and activity will specifically be studied. This strategy has the potential for development of catalysts with high reactivity under moderate, ambient conditions by exploiting the high reactivity of open coordination sites on highly dispersed metal centers.

A combination of experiment and theory is being used to investigate the decomposition of CWAs (sarin and mustard) and their simulants (DMMP and CEES) (Scheme 1). This combination will yield design principles for predicting stability and reactivity of catalysts. Experimental studies of well-defined materials are being performed on simulants and compared to density functional theory (DFT) calculations to assure the accuracy of the calculations. DFT can also be used to model actual CWAs to assess how well simulant studies predict CWA behavior. The understanding gained in this work can be applied in the future to design and synthesize active and cost-effective catalysts for efficient CWA decomposition.

Accomplishments: Report Summary, July 31, 2020-November 30, 2021

Project Title: Design of atomically dispersed metals on oxides as catalysts for oxidative decomposition of chemical warfare agents

Principal Investigators: Cynthia Friend, Harvard, and Philippe Sautet, UCLA

Overview. Facile decomposition and neutralization of chemical warfare agents (CWAs) under ambient conditions is

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a major challenge in the modern world and new highly efficient catalysts are required. Our aim was to develop principles for designing new materials comprised of highly dispersed metal atoms, including single atoms, supported on metal oxides as catalysts for efficient oxidative decomposition of CWAs under ambient conditions. A combination of experiment and theory has been used to investigate the decomposition of CWAs (sarin and mustard) and their simulants (DMMP and CEES). Experimental studies of well-defined materials have been performed on simulants and combined with density functional theory (DFT) calculations. DFT has been used to model actual CWAs to assess how well simulant studies predict CWA behavior.

Decomposition of DMMP on pristine and defective r-TiO₂(110)

The decomposition of DMMP (P=O(OCH₃)₂(CH₃)) was studied on both pristine and oxygen vacancies containing rutile TiO₂(110). These studies provide a basis for understanding the reactivity of DMMP on titania as the first step towards determining the efficacy of highly dispersed metal centers—especially single atoms—for promoting decomposition of DMMP and ultimately CWAs.

A combination of temperature-programmed desorption and density functional theory (DFT) calculations showed that rutile TiO₂(110) present a low reactivity at room temperature for DMMP decomposition. The temperature programmed experiments show that molecular DMMP desorbs over a broad temperature range, up to 550K. Small amounts of methanol and formaldehyde form at 650K with the product yield correlating with the number of O vacancies on the surface. Reaction pathway using DFT calculations showed that the C-O bond in DMMP is the easiest to cleave, but nevertheless with barriers of 1.2 eV, that can be passed only at a temperature of about 600K. However, that decomposition channel cannot lead to gas phase products. P-O bond cleavage shows a very high barrier (barrier of 2.18 eV).

On the defective surface, molecular adsorption of DMMP happens via the P=O group occupying the oxygen vacancy site. The decomposition via C-O bond cleavage still has the lowest barrier of 1.25 eV, however, the oxygen vacancy helps reduce the barrier of the P-O bond cleavage (1.41 eV), leading to gas phase products at 650 °C. The TPD and DFT results agree well and show that oxygen vacancies may act as a reaction center, helping the transfer of methoxy species to surface Ti5c.

Theoretical studies of sarin decomposition on r-TiO₂(110)

Theoretical investigation of sarin (P=OF(OCH(CH₃)₂)(CH₃)) decomposition in comparison with DMMP provides a means of evaluating the efficacy of DMMP as a simulant for Sarin. There is a very high energy barrier for P-O bond dissociation of Sarin on pristine r-TiO₂(110) (2.27 eV), similar to DMMP. The P-F bond is easier to cleave although the barrier remains high (1.74 eV). The C-O bond cleavage is the easiest to cleave with a barrier of 1.17 eV. The reactivity of sarin is modified on the surface with oxygen vacancies. Specifically, the barriers for both P-F and P-O bond dissociation are substantially reduced to 0.85 eV and 1.05 eV, respectively, rendering reaction possible at ~400 K, although P-F bond dissociation is still favored. This indicates a high reactivity for the defective TiO₂(110) surface for sarin decomposition. Therefore, sarin is significantly more reactive than DMMP, especially on defective TiO₂(110), due to the more reactive P-F bond in sarin. The role of oxygen vacancies in facilitating the decomposition of Sarin is to favor transfer of fluorine to surface Ti5c.

Systematic theoretical studies of Ag and Ir single atoms on TiO₂(110)

A systematic exploration of the structure and stability of highly dispersed Ag and Ir species (monomers and dimers) has been performed on rutile TiO₂(110) in ambient conditions (under a pressure of oxygen). The main question addressed is whether single atoms species are stable, both in the absence and presence of dioxygen.

Metallic species Ag and Ag₂ units on TiO₂(110) are not very stable with respect to bulk Ag (+1.3 or +1 eV per Ag atom for Ag and Ag₂ respectively) which would indicate a strong trend for sintering into large particles, in agreement with STM experiments that show large Ag particles. However, additional O atoms can strongly stabilize the highly dispersed Ag species. The most stable one in a large region of O chemical potential is Ag₂O, being 0.15 eV more stable than Ag bulk. This implies that highly dispersed Ag on TiO₂ becomes stable in the presence of oxygen.

For Ir, two major differences occur compared to Ag. First, Ir can substitute Ti in the TiO₂ surface, and this appears to be the most stable species for Ir in oxygen rich conditions. This requires however displacement of Ti atoms on the surface and should only happen after high temperature calcination. The next most stable species is a single IrO₂ unit on TiO₂, hence a Ir(IV) species.

Highly Dispersed Pt species on TiO₂(110): Theoretical studies of Pt single atoms and dimers

We have studied the stability of Pt₁ and Pt₂ cluster on TiO₂ in an oxygen atmosphere. One structure is clearly more stable in the entire range, where a single PtIV atom is substituting a 5 coordinated Ti atom. Its formation would however require a calcination treatment to enable the substitution. Slightly less stable, (+0.41 eV per Pt atom) we find a Pt₂O₄ structure and just above two monomer structures of composition PtO₂/TiO₂. CO is calculated to bind strongly on the Pt atoms of these single atom structures and the calculated CO stretching frequencies (2172 cm⁻¹ on Pt_{sub}Ti and 2140 cm⁻¹ on PtO₂/TiO₂) agree well with experimental data.

Highly dispersed Pt species on TiO₂(110): experiment

Atomically-resolved images of highly dispersed Pt species on r-TiO₂(110) have been obtained on a slightly reduced

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surface. A combination of Pt atoms and small clusters were observed with preferred nucleation at step edges or near oxygen vacancies. The Pt clusters have an apparent height of 0.15 nm. Atomically-resolved images of highly dispersed Pt species on an oxygen pre-covered r-TiO₂(110) surface have also been obtained. The TiO₂ surface is first prepared by sequential sputter-anneal cycles, then O₂ is dosed creating a 8% coverage of O adatoms. Pt is then evaporated in vacuum. The image shows two types of Pt species: highly dispersed Pt (atoms or small clusters) and large particles. By combining with our computational results, we propose that initially, at low dose, Pt will interact with the O adatoms to form PtO₂ single species or small clusters with the same stoichiometry. These highly dispersed species are very stable and do not sinter with time.

Pt SA species on TiO₂: influence on the oxygen removal energy

In order to have a general idea on the activity of our calculated structures for Pt SA on TiO₂ for oxidation reaction, we calculated the oxygen removal energy, which is the energy to remove one O atom from the surface and form ½ O₂ in the gas phase. O atoms on the bare TiO₂ surface are strongly bound to the Ti cations and their removal energy is high (3.38 eV). The substitution of one surface Ti⁴⁺ by a Pt⁴⁺ strongly decreases the O removal energy (by 1.8 eV). The supported PtO₂ results in a much smaller decrease of the removal energy for the bridge-bonded O (0.4 eV) but brings two additional oxygen atoms, that present a low removal energy. As a result, both structures for the Pt SA have a potential high activity for oxidation reactions.

Training Opportunities: Celine Tesvara, PhD student, was trained in DFT calculations and exploration of reaction pathways using the VASP code.

Results Dissemination: Participation in monthly meetings and also preparation of publications.

Honors and Awards: Nothing to Report

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Co PD/PI

Participant: Philippe Sautet

Person Months Worked: 1.00

Project Contribution:

National Academy Member: N

Funding Support:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

Participant: William de Benedetti

Person Months Worked: 6.00

Project Contribution:

National Academy Member: N

Funding Support:

Participant Type: Graduate Student (research assistant)

Participant: Celine Tesvara

Person Months Worked: 15.00

Project Contribution:

National Academy Member: N

Funding Support:

Participant Type: Co PD/PI

Participant: Cynthia Friend

Person Months Worked: 1.00

Funding Support:

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Project Contribution:
National Academy Member: N

Partners

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I certify that the information in the report is complete and accurate:
Signature: Cynthia M Friend
Signature Date: 2/28/22 4:19PM

Annual Report, July 31, 2021-Nov 30, 2021

Project Title: Design of atomically dispersed metals on oxides as catalysts for oxidative decomposition of chemical warfare agents

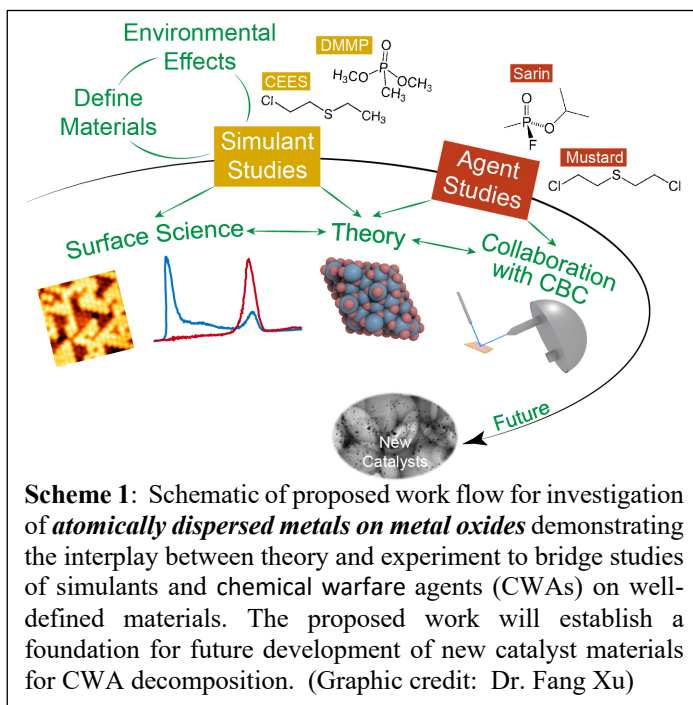
Principal Investigators: Cynthia Friend, Harvard, and Philippe Sautet, UCLA

Overview. Facile decomposition and neutralization of chemical warfare agents (CWAs) under ambient conditions is a major challenge in the modern world. Recent events have demonstrated that there is an unmet need to better protect soldiers using personal protective ensembles that neutralize or destroy CWAs under ambient conditions. To achieve the goal of efficient CWA destruction under ambient conditions, new highly efficient catalysts are required.

Our aim is to develop principles for designing new materials comprised of highly dispersed metal atoms, including single atoms, supported on metal oxides as catalysts for efficient oxidative decomposition of CWAs under ambient conditions. Our

objective is to develop principles for predicting which metal/metal oxide combinations form stable and reactive catalysts. The role of charge transfer from the oxide to the dispersed metal centers on stability, oxophilicity and activity will specifically be studied. This strategy has the potential for development of catalysts with high reactivity under moderate, ambient conditions by exploiting the high reactivity of open coordination sites on highly dispersed metal centers.

A combination of experiment and theory is being used to investigate the decomposition of CWAs (sarin and mustard) and their simulants (DMMP and CEES) (Scheme 1). This combination will yield design principles for predicting stability and reactivity of catalysts. Experimental studies of well-defined materials are being performed on simulants and compared to density functional theory (DFT) calculations to assure the accuracy of the calculations. DFT can also be used to model actual CWAs to assess how well simulant studies predict CWA behavior. The understanding gained in this work can be applied in the future to design and synthesize active and cost-effective catalysts for efficient CWA decomposition.



Highly dispersed Pt species on partially oxygen covered TiO₂(110)

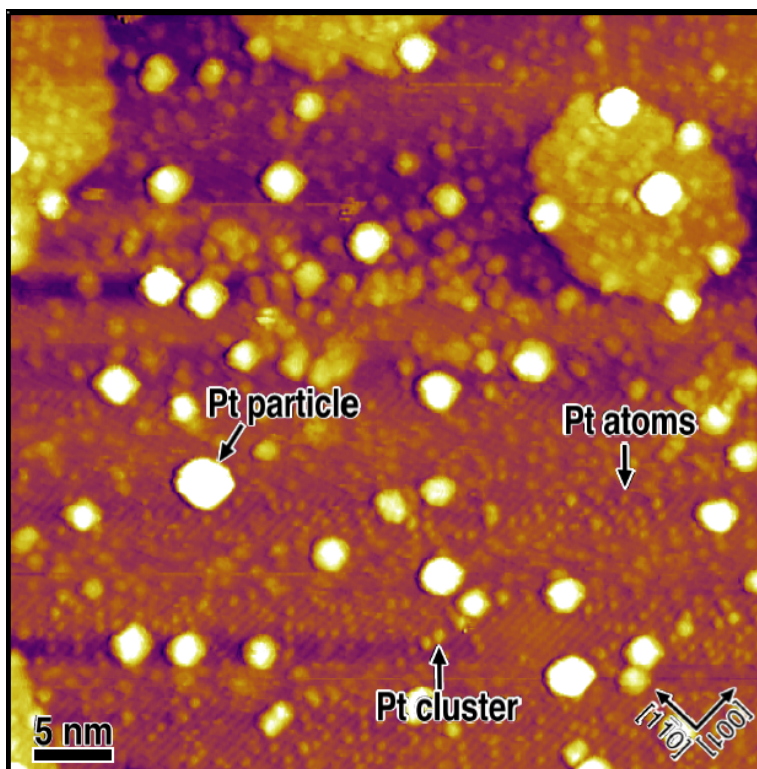


Figure 1: STM image of highly dispersed Pt on *r*-TiO₂(110) with 8% O-adatoms

Following the previous study of highly dispersed Pt species on the slightly reduced *r*-TiO₂(110) surface, atomically-resolved images of highly dispersed Pt species on an oxygen pre-covered *r*-TiO₂(110) surface have been obtained (Fig. 1). The TiO₂ surface is first prepared by sequential sputter-anneal cycles, then O₂ is dosed creating a 8% coverage of O adatoms. Pt is then evaporated in vacuum. The image shows two types of Pt species: highly dispersed Pt (atoms or small clusters) and large particles. By combining with our computational results, we propose that initially, at low dose, Pt will interact with the O adatoms to form PtO₂ single species or small clusters with the same stoichiometry. These highly dispersed species are very stable and do not sinter with time. Our simulated STM images with PtO₂ species deposited on TiO₂ match the experimental image.

However, additional Pt atoms beyond 4% of coverage cannot find O atoms, and they form metallic species, which are much less stable and sinter into Pt particles of size 3 to 5 nm. Hence a smaller dose of Pt should be able to selectively produce highly dispersed stable PtO₂ species and clusters.

Pt SA species on TiO₂: influence on the oxygen removal energy

In order to have a general idea on the activity of our calculated structures for Pt SA on TiO₂ for oxidation reaction, we calculated the oxygen removal energy, which is the energy to remove one O atom from the surface and form $\frac{1}{2}$ O₂ in the gas phase (figure 2). Surfaces with low O removal energy should be very active for oxidation reaction.

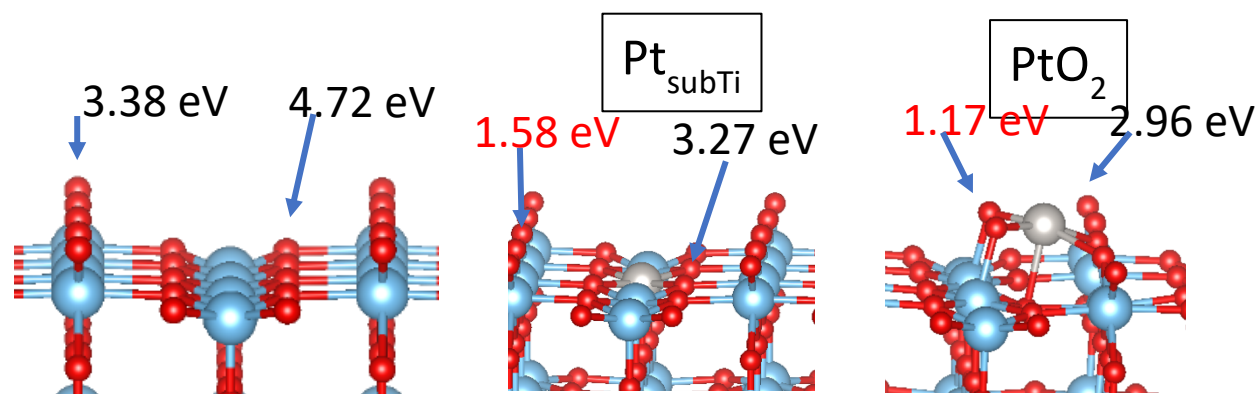


Figure 2: oxygen removal energy (eV) for the bare r-TiO₂(110) surface (left), the substitutional Pt single atom (middle), and the supported PtO₂ species (right).

O atoms on the bare TiO₂ surface are strongly bound to the Ti cations and their removal energy is high, the lowest energy (3.38 eV) corresponding to the bridge bonded O atom as already known (Figure 2, left). The main difficulty is that the O atoms (formally O²⁻ in the crystal) leaves two electrons behind on the surface, that need to relocate on high lying Ti levels. The substitution of one surface Ti⁴⁺ by a Pt⁴⁺ strongly decreases the O removal energy (by 1.8 eV) because now the electrons can reduce the Pt instead to Pt²⁺ (Figure 2, middle). The supported PtO₂ (Figure 2, right) results in a much smaller decrease of the removal energy for the bridge-bonded O (0.4 eV) but brings two additional oxygen atoms, that present a low removal energy. As a result, both structures for the Pt SA have a potential high activity for oxidation reactions. Our DFT calculations indicate that thermodynamically the Pt SA structures are able to oxidize DMMP and sarin. This is a necessary but not sufficient condition, since pathways and kinetic aspect are not yet included.

Pt SA species on TiO₂: CO oxidation

We completed the exploration of the CO oxidation pathway on Pt atom in substitution of Ti, by including the pathways for the formation of carbonate.

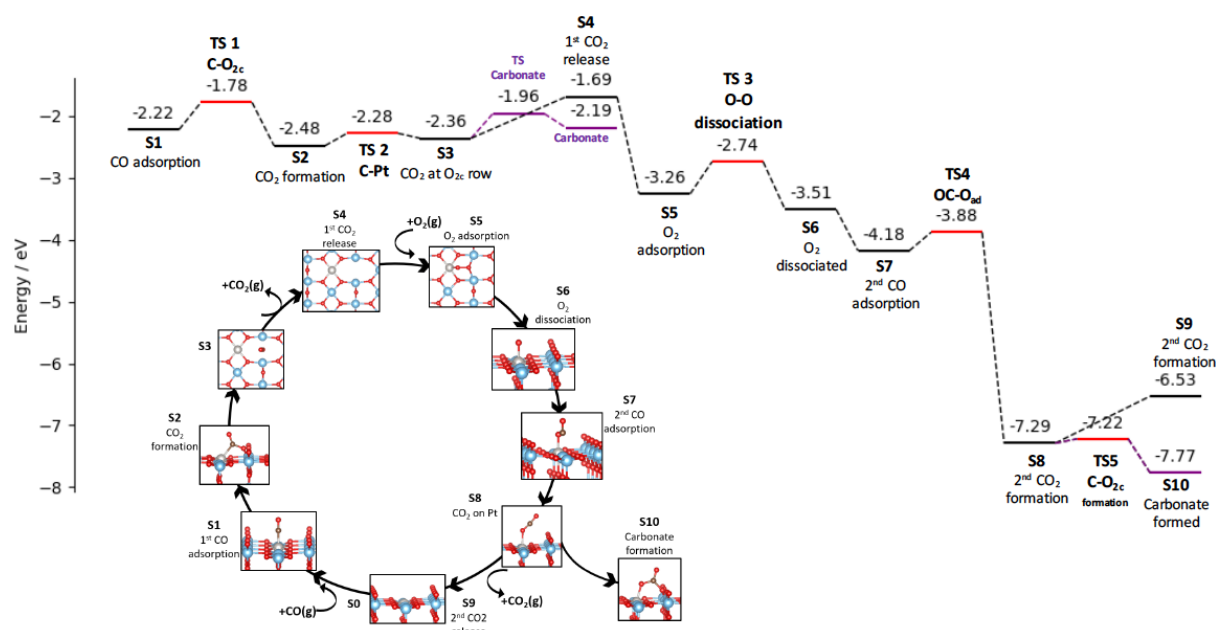


Figure 3. Calculated CO oxidation pathway on $\text{Pt}_{\text{sub}}/\text{TiO}_2$, including carbonate formation

After the first oxidation step (S3), the formation of the carbonate is moderately stable, so that CO desorption should still be favored by entropy. This is not the same after the second oxidation step, where the carbonate species is 1.24 eV more stable than gas phase CO_2 . A favored desorption of CO_2 would therefore require an elevated temperature (~ 550 K) and hence the formation of carbonate is a serious problem here, that could poison the catalyst.

We initiated the exploration of the reaction pathway on the PtO_2 species supported on $\text{r-TiO}_2(110)$. The first oxidation step, generating CO_2 and a surface O vacancy is shown on figure 4. The mechanism is similar to the previous case, but involving one O atom of the PtO_2 species. The barrier for the CO-O bond formation through the transition state TS1 is higher (1.08 eV) and the CO_2 desorption step more endothermic, so that a slightly elevated temperature would be required for a high activity.

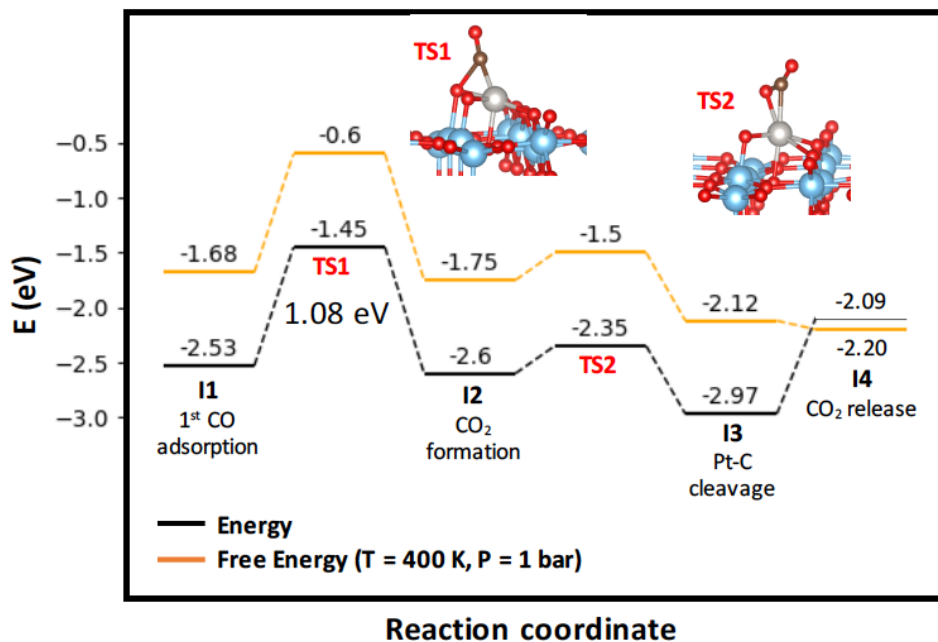


Figure 4: Calculated CO oxidation pathway on PtO₂/TiO₂