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Simulation of perovskite structure materials in catalysis.
Computational Chemistry for Pollutants Mitigation - Paris 2017

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**Emissions Control**

**Without catalyst**

- **Gasoline engines**
  - CO₂
  - HC
  - CO
  - NOₓ
  - Particulates

- **Diesel engines**
  - CO₂

**Reactions to be catalysed:**
- CO oxidation (to CO₂)
- HC oxidation (to CO₂ and H₂O)
- NOₓ reduction (to N₂)

**Regulated:**
- CO, CO₂, HC, NOₓ, Particle Number, CH₄*, N₂O*
- US only

**Unregulated:**
- SOₓ, H₂S, NH₃

**Regulations getting tighter.**

Europe – different regulations between Gasoline and Diesel

US – same regulations for Gasoline and Diesel

Euro 6 – introduction of particulate numbers for Gasoline & Diesel (6 x 10¹¹ km⁻¹)

*US only
Perovskites

- ABX₃ structure.
- Wide range of ions for ‘A’ and ‘B’, ‘X’ usually O²⁻.
- ‘A’ and ‘B’ can be of the same or different charges. Can also be mixed.
- Defects, especially oxygen vacancies, are common.
- Many materials distorted from cubic by distortion or tilting of the octahedra.
- Generally moderate to good oxide conductors.
- Many LaMO₃ perovskites good for oxidation catalysis, LaFeO₃ widely reported with greatest NO reduction activity.*


Bulk Structure and Computational Methods

Many pure LaMO$_3$ materials are strongly distorted from the ideal cubic perovskite structure. Doped and defective structures often tend back towards cubic.

- DFT (CASTEP, VASP) and inter-atomic potentials (Gulp, Bush et al potentials) models are capable reproducing the experimental structures (not always good for electronic properties).

- Not all DFT functionals are equal. HSE06 > PBE ≈ PW91 > PBEsol for structural parameters of bulk LaFeO$_3$.

Surfaces & Active Sites
What can computational chemistry do?

• Which surfaces are likely to be present?
  → calculate surface energies.

• Which surface sites will adsorb gas phase molecules?
  → simulated adsorption on a range of sites.

• How active are the sites?
  → calculate sorption energies and electron transfer (activation).

• Will the sites be available?
  → energies to create sites and competitive adsorption.

• How can we modify the properties of sites
  → permute A- and B-site dopants in simulations.
Reactivity
What can computational chemistry do?

- Identify Active Site(s)
- Follow reactions between surface species (initially lead by literature)
- Calculate activation barriers
- Analyse effects of factors (i.e. dopants) on barriers

This can be extended to cover a wide range of interacting species, surface sites, possible competing mechanisms, material compositions, etc.

The goal is to provide both understanding and design guidance to experimental programs.
Oxygen Vacancy Creation
Effect of A-site dopants on $V_O$ creation.

Oxygen Reference:
$O^{2-}_{(lattice)} \rightarrow V^0_{o} + \frac{1}{2}O_2(g)$

Effect of A-site doping on $V_O$ creation energy LFO.

Figure shows effect of low concentration A-site dopants on the ‘top’ site oxygen vacancy creation energy on the [110] surface of lanthanum ferrite.
[110] Surface and Oxygen Vacancies

\[ 2\text{Fe}^x_{\text{Fe}} + O^x_{\text{O}} \rightarrow 2\text{Fe}'_{\text{Fe}} + V_{\text{O}}^\cdot + \frac{1}{2}\text{O}_2 \]

- Oxygen vacancies charge compensated by A-site 2+ doping or B-site metal ion reduction.
- Trends (above) show vacancies more stable as cross TMs.
- Oxygen vacancies required for significant activity towards gas phase NO and O\(_2\).
Vacancy Site Sorption Energy Trends

All results shown on subsequent slides for binding over ‘top’ oxygen vacancy on [110] surface.

Top site binds all species most strongly in LaFeO$_3$.

1$^{\text{st}}$ sub-surface layer oxygen vacancy more stable in vacuum but unfavourable with adsorbates present.

Sr dopant ion locations based on stability from previous screening study.

Detailed results on following slides.
Vacancy Site Sorption Energy Trends
Molecular Oxygen

- All B-site metals bind O$_2$ strongly (2.5 to 5eV) over the oxygen vacancy site.
- Significant transfer of electron density is seen, creating peroxide / superoxide species.
- From Cr onwards there is a uniform trend of decreasing binding strength.
- Rh in LaFeO$_3$ lattice shows weaker O$_2$ binding.
- Vanadium fully dissociates oxygen, vacancies unlikely to be present over V.
- Addition of Sr dopant weakens binding relative to uncompensated O vacancy (electron rich) system.

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Vacancy Site Sorption Energy Trends
Nitric Oxide

- All B-site metals bind NO fairly strongly.
- The binding energy forms a double humped trend centred on Co and Cr.
- When Sr doped, Fe and Mn bind NO with similar strength to Rh.
- Sr doping effects some B-site metals much more strongly than others and generally more so than in $O_2$ binding.
- There is substantial transfer of electron density on the NO, largely residing on the nitrogen.

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B-Site Ion Locations
Dilute dopants in LaFeO₃ lattice.

- Location of low concentration B-site metals hosted in LaFeO₃ lattice modelled.
- Allows prediction of likely surface presence and catalytic accessibility of these metals in low concentration mixed systems.
- Cu, Rh and Pd (cf. ‘intelligent catalyst’ *) have a preference for the surface and vacancy site. Others generally in bulk.


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CO oxidation by surface activated oxygen
In two steps

- Probed using LST/QST approach.
- 1st step is insertion of CO between O – O bond.
- Results in a meta-stable surface M-O-CO-O entity.
- Exothermic (-3.5eV) with a forwards barrier of ~1.2eV.
- Second step is release of CO₂, leaving O on surface.
- Very small barrier (~0.3eV).
Literature CO/NO Mechanism

- First step is binding and activation of NO.

- Bound CO can then acquire oxygen from the surface or abstract it from activated NO, resulting in surface CO$_2$ and N.

- Products are then formed and released.

- Activated molecular oxygen can also readily oxidise CO.

- These steps are being modelled, with activation barriers and electronic movements to be calculated.

\[
\begin{align*}
\text{NO}_\text{gas} & \rightarrow \text{NO}_\text{ads} \\
\text{NO}_\text{gas} & \rightarrow \text{N}_\text{ads} + \text{O}_\text{ads} \\
\text{CO}_\text{gas} & \rightarrow \text{CO}_\text{ads} \\
\text{CO}_\text{ads} + \text{O}_\text{ads} & \rightarrow \text{CO}_2\text{ads} \\
\text{NO}_\text{ads} + \text{N}_\text{ads} & \rightarrow \text{N}_2\text{O}_\text{ads} \\
\text{N}_2\text{O}_\text{ads} & \rightarrow \text{N}_2 + \text{O}_\text{ads} \\
2\text{O}_\text{ads} & \rightarrow \text{O}_2 \\
2\cdot\text{N}_\text{ads} & \rightarrow \text{N}_2
\end{align*}
\]

Adsorption & Dissociation (over surface oxygen vacancy site)

Surface Reactions

Product Release

CO / NO Reaction on LaFeO₃

• Only gas phase + surface species interactions being studied for now.
• CO(s) NO(g) does not readily go, but still being explored.
• NO(s) CO(g) has been explored and an activation barrier identified.
• Exothermic (-1.8eV) with a barrier of ~ 1.3eV.
For metal ion at active site in LaFeO$_3$ host lattice:

Fe (1.4eV) > Rh (1.8eV) > Cu (2.1eV) > Mn (2.3eV) > Ni (2.4eV) > Pd (3.0eV)

- In isolation results suggest pure lanthanum ferrate most active (followed by rhodium and copper) and Palladium should show extremely low activity.

- However, this is for monoatomic B-site substitution only! Not supported atoms, particles, multiple substitutions, etc.

- Does not consider subsequent steps, inc. product release.

- Importantly, must consider availability of sites;
  - Oxygen binding energies over these sites relative to NO varies significantly.
Competitive adsorption

- In presence of oxygen iron (and most of the TM) active sites occupied by activated O₂
- Unavailable to bind NO for CO / NO activity.

Only the rhodium containing material has an absolute preference for NO over O₂, while of the transition metals the energy difference is least on copper.

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Confidential
Reactivity Mechanisms
Isocyanate formation on lanthanum ferrate

Over all highly **exothermic**: -3.3eV
Moderate activation **barrier**: 0.95eV

- Isocyanates (R-NCO) widely speculated to be an important intermediate in NO reduction.
- Experimental evidence for their presence.
- Surface *-N resulting from direct CO /NO approached by further CO.
- C-O bond order reduces and OC-N bond forms.
- Resulting isocyanate is loosely bound, regenerating O vacancy.
- Isocyanate is both mobile and reactive.
- Experiment suggests reaction with water important.
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What Else?

Nitrogen proceeding via hydrogenation

Water Activation

Reactants
Mixed A/B dopants and activity

Nitrogen proceeding via isocyanate

Oxygen Mobility

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Conclusions

Availability of Active Sites

- Identity of active sites.
- Energetics of oxygen vacancy formation.
- A range of A-site dopant effects.
- Segregation of B-site dopants.
- Competition between NO and O₂ for available surface.

Behaviour of Active sites

- Adsorption strengths of gases of interest.
- Activation of adsorbed molecules.
- A and B site dopant effects on adsorption.
- Exploration of possible reaction mechanisms.
- Estimation of transition states and activation barriers.
- Effect of dopants on activation barriers.
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