

First-Principles Investigation of the Reactivity of Ceria and Ceria-Supported Metal Clusters

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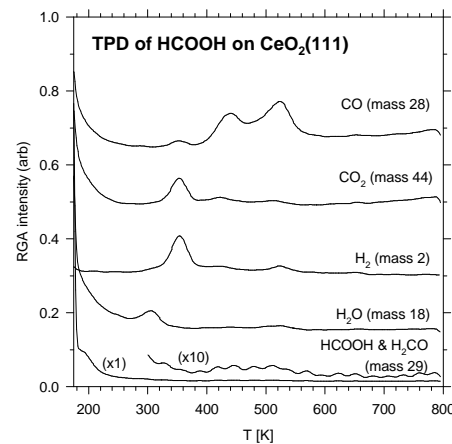
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Adsorption and Reactivity of Formic Acid on CeO₂(111)

Formate is the simplest carboxylate and a frequent intermediate in C1 chemistry, including the WGS. The goal of this study is to elucidate the nature of surface intermediates and the mechanism of formate decomposition.



B` Ht K sdc ur-Q@HQR1 d rt qdc
uhaq` slmmi keqpt dnbtr

Formic acid on CeO ₂ (111)	Formate* (Ce-Ce)	Formate* (Ce-Ce)+H*	Formate* in O_vacancy
Expt'l (250 K)	Expt'l (400 K)	Calc'd	Calc'd
3575			3565
2845	2848	2860	2914
1560	1592	1554	1533
		1291	1360
			1355
1375, 1360, 1330	1380, 1330, 1317	1242	1326
			1283

) Rdm m x' j d % L t lhm+rmoqtrr-

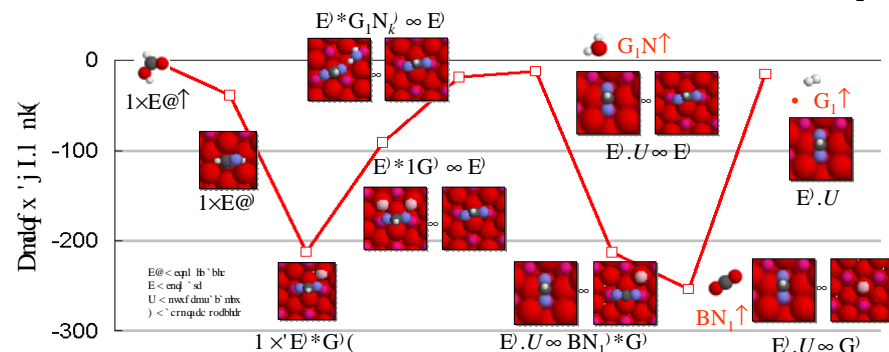
TPD results suggest the following steps:

- $2\text{HCOOH} + 2\text{O}_i \rightarrow 2\text{HCOO}^* + 2\text{HO}_i^*$
 $\rightarrow 2\text{HCOO}^* + \text{H}_2\text{O} \uparrow + \text{O}_i + \text{V}$
- $\text{HCOO}^* + \text{H}^* \rightarrow \text{CO}_2 \uparrow + \text{H}_2 \uparrow$
- $\text{HCOO}^* + \text{V} \rightarrow \text{CO} \uparrow + \frac{1}{2}\text{H}_2 \uparrow + \text{O}_i$

Experimental data appear to match a combination of isolated formate and formate+H at 250 K and isolated formate and formate in O_vac at 400 K (see Wesley Gordon's poster for more detail).

In addition, sXPS and EXAFS results suggest formate to be the only C1 surface species.

Calculated Reaction Energy Profile for Formic Acid Decomposition on CeO₂(111)



The calculated reaction energy profile suggests that the reaction should be desorption-limited, thus raising several questions about the reaction mechanism:

- Reduction via H₂O is costly due to mutual stabilization of formate/H and formate/H₂O; yet TPD indicates desorption at 300 K
- H adsorption energy is over 140 kJ/mol vs. H_{2(g)}; yet it desorbs simultaneously with CO₂ at 360 K
- RAIRS suggests some formate states persisted after others decomposed at ca. 360 K. Why were they stable? Where did their hydrogen go eventually?

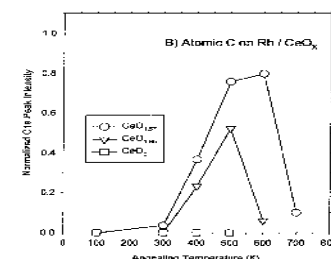
Synopsis: Atomic-level insights provided by density functional theory (DFT) calculations have proven valuable in an ever growing number of studies in surface science and heterogeneous catalysis. We are applying DFT calculations to several fundamental problems encountered during this research program in order to generate new mechanistic insights. Topics currently under investigation include:

- The adsorption and reactivity of formic acid on CeO₂;
- The promotion of CO dissociation on CeO_x-supported Rh particles;
- The interaction of Rh clusters with oxygen vacancies on CeO₂.

Methods: Periodic, spin-polarized total energy calculations performed with Vienna Ab Initio Program (VASP) using projector augmented wave (PAW) pseudopotentials in GGA-PW91. DFT+U formulation used to treat the localization of *f* electrons in cerium.

Our earlier experiments found:

- CO adsorbs molecularly (mainly on Rh) at low T
- On Rh/CeO₂: CO desorbs completely by 500 K without dissociation
- On Rh/CeO_x: CO dissociates to an extent that is dependent on the extent of reduction of ceria
- Rh loading or particle morphology have been ruled out as factors; later experiments on Pd/CeO_x found isotopic scrambling of C¹⁶O/C¹⁸O
- The mechanism of CO dissociation on Rh/CeO_x remains unclear



Previous DFT results indicate:

*Mavrikakis et al, Catal. Lett. 81 (2002) 153.

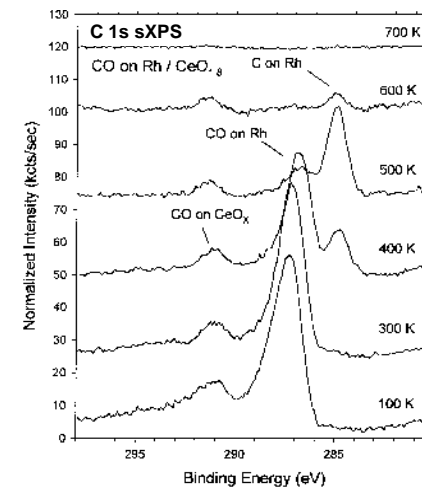
- CO adsorption energy on Rh is -170~-180 kJ/mol; relatively insensitive to surface geometry
- CO dissociation barriers are > 300 kJ/mol on Rh(111); ~ 200 kJ/mol on Rh step edge
- CO essentially desorbs without dissociation on Rh; consistent with earlier experiments by Yates et al. and Rebholz et al.

Possible locations of CO dissociation:

- Rh (modified in some ways);
- Rh-ceria interface;
- ceria

Promotion of CO Dissociation on Rh/CeO_x

CO does not dissociate on Rh particles supported on fully oxidized ceria but readily dissociates on Rh supported on partially reduced ceria. The reason remains unclear.



* Mullins & Overbury, J. Catal. 188 (1999) 340.

Promotion of CO dissociation on Rh(111) by Ce/CeO

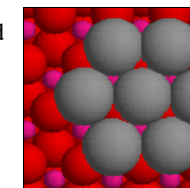
Encapsulation of metal particles by oxide supports (SMSI) has been observed or inferred for several systems, including Pt, Pd, Rh, and Ru supported on VO_x, TiO_x and CeO_x.

A small amount of mobile Ce/CeO species may be present on the surface of Rh particles.

Preliminary calculations (see right) show that co-adsorbed CeO_x species can stabilize CO, weaken the CO bond, and significantly lower the dissociation barrier.

Interaction of Rh clusters with oxygen vacancies

CO dissociation on Rh/CeO_x may on the other hand involve surface oxygen vacancies (V's). Since V's on ceria do not promote CO dissociation, the Rh-ceria interface may be the reaction locus. We are investigating how V's interact with Rh particles as a first step toward elucidating the Rh-ceria interfacial structure and its relevance to CO dissociation as well as potentially other reactions.

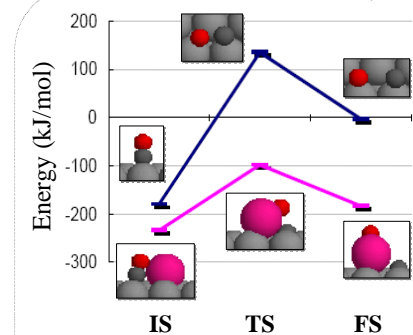


Additional experiments can help clarify the preferred adsorption sites for CO

Adsorption of CO on Ce-/CeO-Rh(111)

CO state	Rh(111)	Ce-Rh(111)	CeO-Rh(111)
<i>atop</i>	B.E. = -169 kJ/mol ν _{C-O} = 2000 cm ⁻¹	-189 kJ/mol 1820 cm ⁻¹	-148 kJ/mol
<i>fcc</i>	B.E. = -180 kJ/mol ν _{C-O} = 1762 cm ⁻¹	-234 kJ/mol 1375 cm ⁻¹	-211 kJ/mol 1484 cm ⁻¹

Dissociation of CO enhanced by Ce



A lowering of the activation barrier by ca. 180 kJ/mol essentially increases dissociation probability from zero to unity at 500 K.

Some Future Directions

- Adsorption of small organic molecules on CeO₂
- effect of crystalline facets
- Surface structure of highly reduced ceria
- Mixed oxide structures
- as catalysts or functional supports