

Probing Formate Structure on Cerium Oxide Thin Films: Reflection-Infrared and DFT Results

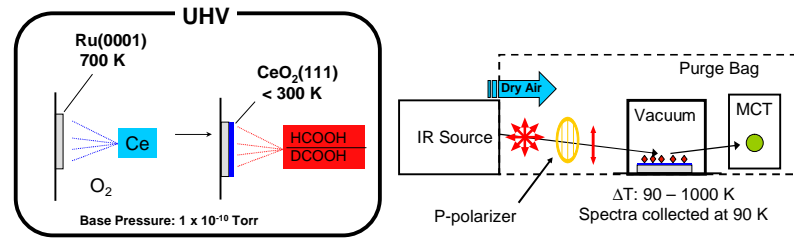


FWP KCC053 Fundamentals of Heterogeneous Catalysis on Surfaces and Nanostructures

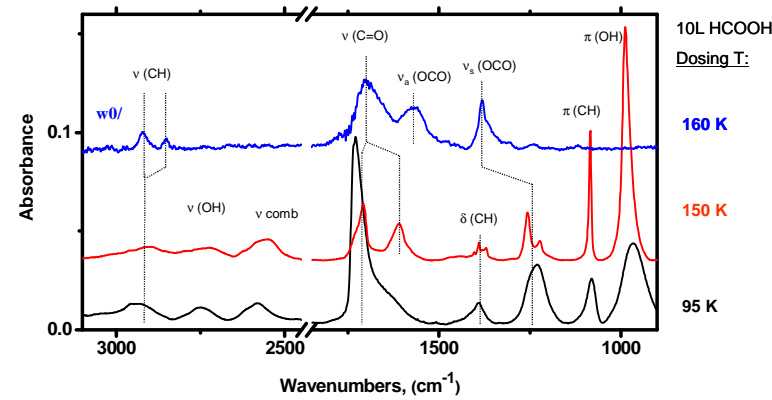
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Synopsis: Formate species have been proposed as intermediates in the water-gas-shift reaction on oxygen-storage materials such as ceria. The structure of formates on the common (111) face of ceria may therefore be important in understanding this catalytic reaction. In this study, formic acid adsorption and dissociation is studied using reflection-absorption infrared spectroscopy (RAIRS) and compared with DFT calculations. Bridging bidentate formates appear to be the most stable species, but higher temperatures and oxygen defects lead to a lower symmetry species.

Experimental

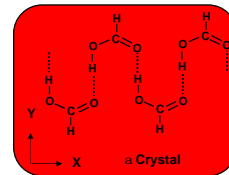


HCOOH exposure to ceria (111) at low temperatures



HCOOH structures on $\text{CeO}_2(111)$ varies with temperature:
 Ø 95 K: Disordered Ice (some α -polymorph)
 Ø 140-150 K: Crystalline α -polymorph determined by the ν (C=O) splitting, π (OH) position, and relative peak intensities
 Ø 160 K: Monolayer remains containing mostly formic acid along with some dissociated formate

Structure	π (OH)
Monomer	636
Dimer	917
b Crystal	947
a Crystal	974



J. Phys. Chem. 1996, 100, 12509-12516

Formate Structure and Orientation with RAIRS

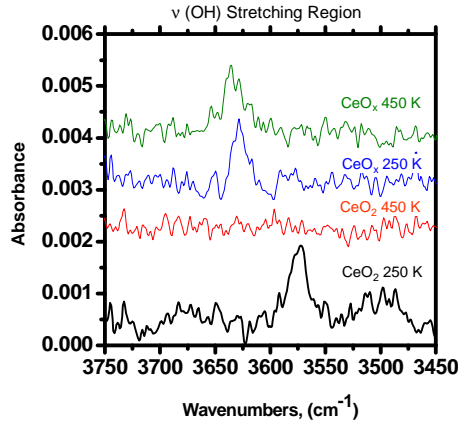
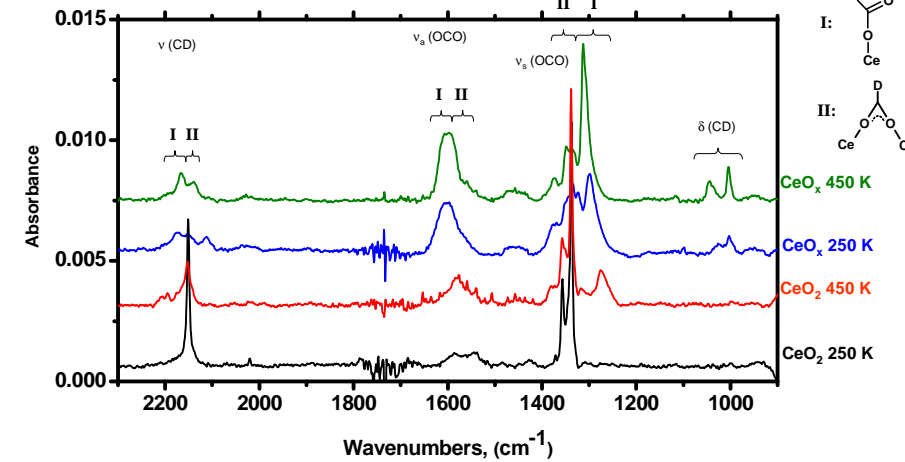
Surface selection rules for a given symmetry	
Mode	Allowed
$\nu_s(\text{OCO})$	A_1, A_2, A_1'
$\nu_a(\text{OCO})$	A_1, A_2, A_1'
$\delta(\text{CH})$	B_2, A_1'
$\pi(\text{CH})$	A_1'

Forbidden Allowed
Surf. Sci. 1979, 88, 319-330

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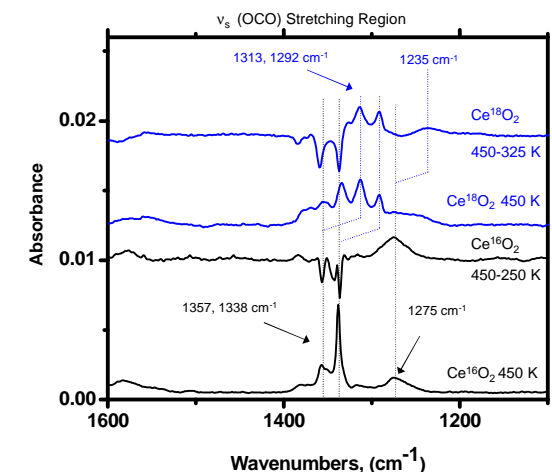
DCOOH exposure to CeO_2 and CeO_x at 160 K

Ø On ceria, the use of DCOOH prevents the overlap of $\delta(\text{CH})$ and $\nu_s(\text{OCO})$ modes



RAIR Data Results
 Ø CeO_2 :
 Ø C-H bond is nearly normal to the surface
 Ø C_{1v} or $\text{C}_s(1)$ bridging bidentate species
 Ø Two adsorption states observed at 250 K
 Ø Hydroxyls desorb as water @ 300 K, leaving O-vacancies
 Ø Monodentate or O-vacancy species grows in with increasing temperature
 Ø CeO_x :
 Ø Multiple heterogeneous sites with lower symmetry than on CeO_2 per selection rules
 Ø Mostly monodentate or O-vacancy species with C_s symmetry
 Ø Bridging species convert to monodentate or O-vacancy species
 Ø Hydroxyls remain on surface until formate decomposition

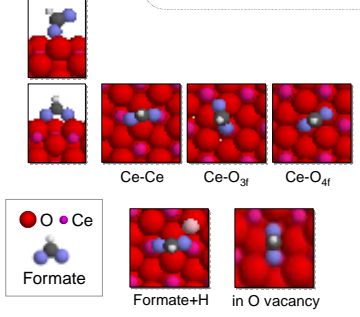
DCOOH exposure to ^{18}O -labelled CeO_2 at 160 K



Oxygen Labeling
 Ø Difference spectra confirm O scrambling occurs between oxide and formate on CeO_2 at 325 K
 Ø Red-shifted ($\Delta \sim 40\text{ cm}^{-1}$) $\nu_s(\text{OCO})$ modes indicate that both formate oxygens scramble with the oxide
 Ø Scrambling likely occurs on CeO_x above 400 K, but data is ambiguous

DFT Calculations Provide Additional Clues

To help interpret the vibrational spectra, several models of possible adsorbed formate species on $\text{CeO}_2(111)$ have been investigated using density functional theory calculations. Their geometries and adsorption energies are determined. The experimental and calculated vibrational frequencies are compared below.



States (1/9 ML)	Binding energy w.r.t. formate (g) (kJ/mol)	Notes
Bidentate	-94.7	Ø Monodentate formate not stable at low coverage
Ce-Ce	-90.0	Ø O vacancy binds formate much more strongly than stoichiometric surface
Ce-Ce (3/9ML)	-87.4	
Ce-O _{3f}	-87.4	
Ce-O _{4f}	-65.5	Ø Co-adsorbed formate and H mutually stabilize each other by 125 kJ/mol through charge transfer from H to formate
Monodentate	unstable	
In O _{vac}	-372	

Vibrational Frequencies of Formate Species on $\text{CeO}_2(111)$

Modes / Freq. (in cm^{-1})	Formic acid (g)		Formate (g)		Formate on $\text{CeO}_2(111)$		Formate* (Ce-Ce)		Formate* (Ce-Ce) +H*		D-Formate on $\text{CeO}_2(111)$	
	Expt'l (NIST)	Calc'd	Calc'd	Expt'l (250 K)	Expt'l (400 K)	Calc'd	Calc'd	Calc'd	Calc'd	Expt'l (400 K)	Calc'd	
$\pi(\text{OH})$	3570	3605		3575				3565				
$\pi(\text{CH})$	2943	2995	2953	2845	2848	2860	2914	2959	2196wk, 2156	2100	2100	
$\nu_{as}(\text{OCO})$	1229	1272	1585	1560	1592	1554	1533	1588	1585	1549	1549	
$\delta(\text{CH})$	1387	1364	1360				1291	1360	1355	1009	944	
$\nu_s(\text{OCO})$			1276	1375, 1360, 1330	1380, 1330, 1317	1242	1326	1283	1360-1275	1233	1233	

Ø 250 K data appear to match a combination of lone formate and formate+H
 Ø 400 K data appear to match a combination of lone formate and formate in O_{vac}
 Ø Experimental spectra for H-formate can only unambiguously identify bidentate states
 Ø Isotopically labeled D-formate may help identify monodentate states
 Ø Possibility of unidentified species exists

Conclusions

Ø On CeO_2 , formic acid dissociates to form C_{2v} or $\text{C}_s(1)$ bridging bidentate formate species
 Ø At 400 K, some bridging formates convert to monodentate or O-vacancy-bonded species
 Ø Formates are mobile on the surface above 325 K
 Ø On CeO_x , formates are more heterogeneous, displaying lower symmetry and favoring the monodentate or O-vacancy form
 Ø Water does not desorb until formate decomposition occurs, perhaps signaling a mutually stabilizing hydroxyl-formate interaction.
 Ø DFT calculations show that the $\text{C}_s(1)$ tilted bridging bidentate formate is favorable on CeO_2
 Ø New types of molecular states have been observed on reducible oxides due to ubiquitous surface vacancies. These O-vacancies may alter the interaction between oxide surfaces and organic oxygenates.

General Reaction Pathway

