

## Nanoscale Probing of Adsorbates on Pt/CeO<sub>2</sub> with Aloof-beam Vibrational Electron Energy-loss Spectroscopy

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The ability to perform high spatial resolution mapping of adsorbate molecules or layers and correlate this with atomic structure would provide a transformative new tool for investigating the surface chemistry taking place on nanoparticles. Such a tool can be used to detect “active” sites on catalyst surfaces and study bonding arrangements of adsorbates at different crystallographic facets. Electron energy-loss spectroscopy (EELS) in the scanning transmission electron microscope (STEM) has the potential to probe bonding with high spatial resolution using vibrational excitations [1]. Radiation damage may be substantial when a focused electron probe is placed directly on the adsorbate layer. We adopt the aloof beam EELS technique that makes use of the long-range Coulomb interaction to minimize damage when the probe is placed a few nanometers outside the adsorbate layer [2]. To develop this technique, experiments need to be performed on simple model systems and the spectra compared with results from conventional vibrational spectroscopies like Fourier-transform infrared (FTIR) spectroscopy. Here, we explore the adsorption of CO gas on the Pt/CeO<sub>2</sub> metal-support catalyst system, since it is suitable for a quantitative investigation of the sensitivity of aloof beam vibrational EELS.

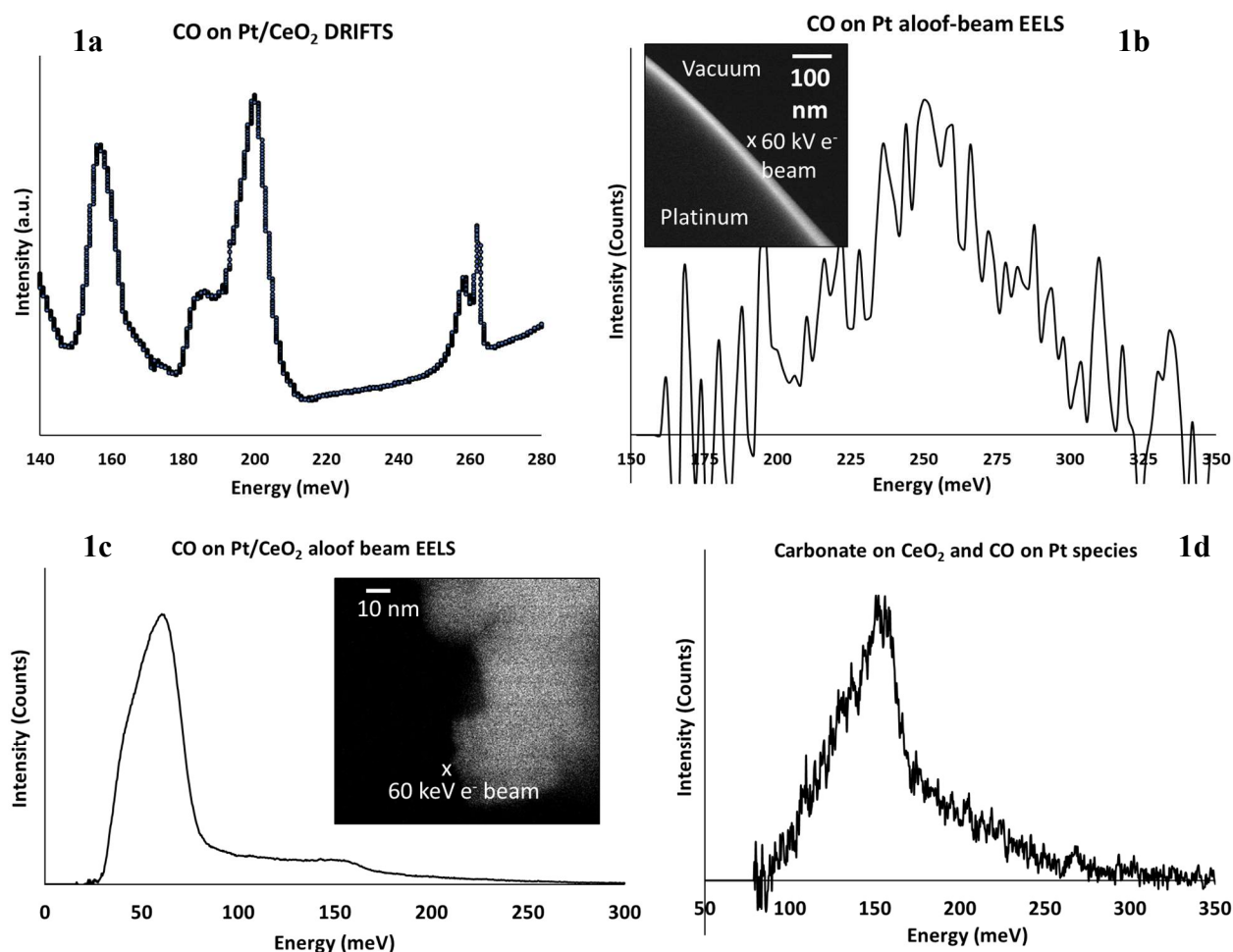
CeO<sub>2</sub> nanocubes were synthesized by hydrothermally reducing Ce(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O in an autoclave at 250°C for 24 hours. Pt nanoparticles were loaded onto the nanocubes by incipient wetness impregnation of PtCl<sub>4</sub>/ethanol solution (235 mg/ml) at room temperature followed by reduction under flowing H<sub>2</sub> at 250°C for 2 hours. Larger Pt particles were also employed to make preliminary detection of CO easier (10 μm average diameter, Sigma-Aldrich). Surface pre-treatment involved heating the Pt/CeO<sub>2</sub> nanoparticles or commercial Pt to 400°C in flowing H<sub>2</sub> for 3 hours. CO was chemisorbed on Pt by flowing the gas (40 cc/min) through a bed of adsorbent powder at room temperature for 1 hour in a RIG 150 micro-reactor. This also resulted in carbonates being adsorbed on the CeO<sub>2</sub> nanocubes. A NION UltraSTEM 100 aberration-corrected electron microscope equipped with a monochromator (8-16 meV energy resolution) was used to perform aloof-beam EELS. The microscope was operated at 60 kV, with probe convergence and collection semi-angles of 28-33 mrad and 40 mrad respectively. The background was subtracted using the Gatan Microscopy Suite.

Diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) was performed to confirm chemisorption of CO on Pt and carbonates on CeO<sub>2</sub>; the spectrum is shown in Fig. 1a. The 158 meV and 200 meV peaks are associated with carbonate species while the 187 meV shoulder is associated with the carboxylate species on CeO<sub>2</sub>. The peaks at 259 meV and 262 meV are associated with on-top bonding of the CO molecule to Pt [3]. Figure 1b shows the background subtracted energy-loss spectrum from CO adsorbed on a Pt micro-particle along with an annular dark-field (ADF) image of the Pt surface showing the relative electron beam position. A weak and broad signal peak at ~260 meV can be observed in the spectrum corresponding to the CO bonded to Pt. Figure 1c shows the energy-loss spectrum from CO

adsorbed on Pt/CeO<sub>2</sub> nanoparticles with an ADF image of the electron beam position relative to the nanoparticles. The stronger peak at 60 meV corresponds to the surface Ce-O vibrational stretch and the weaker peak at 158 meV corresponds to the carbonate species on CeO<sub>2</sub>. We will discuss more experiments to determine the limiting number of CO molecules on Pt nano-particles that can be detected with the current instrumentation [4].

#### References:

- [1] D Haiber et al., ACS Nano **12** (2018), p. 5463.  
 [2] PA Crozier, Ultramicroscopy **180** (2017), p. 104.  
 [3] T Jin et al., J. Phys. Chem. **91** (1987), p. 5931.  
 [4] The support from National Science Foundation CHE-1508667 and the use of (S)TEM at Eyring Materials Center at Arizona State University is gratefully acknowledged.



**Figure 1.** DRIFTS spectrum from CO on Pt/CeO<sub>2</sub> nanoparticles showing vibrational signals from the carbonates on CeO<sub>2</sub> at 158 and 200 meV and CO on Pt at 262 meV. b) ADF-beam vibrational energy-loss spectrum from CO on a Pt micro-particle showing the CO signal at ~260 meV. The electron beam position is shown as an insert. c) ADF-beam vibrational energy-loss spectrum from CO on a Pt/CeO<sub>2</sub> nano-particles showing the surface Ce-O vibrational stretch at 60 meV and the carbonate stretch on CeO<sub>2</sub> at 158 meV. The electron beam position is shown as an insert. d) The spectrum in c) magnified on the carbonate and CO vibrational stretches at 158 meV and 260 meV.