Observation of Gas Adsorbates with Time-Resolved Vibrational EELS

Yifan Wang[1*], Peter A. Crozier[1]

[1.] School for Engineering of Matter, Transport & Energy, Arizona State University, Tempe, AZ, United States.
[*] Corresponding author: ywan1240@asu.edu

Chemical reactions with gas phase reactant and catalysts, e.g., CO oxidation, involve chemisorption of reactant molecules onto the catalytic surfaces [1]. By binding with various active sites, e.g., different surface terminations, reacting pathways are enhanced or suppressed, thus regulating the kinetics of chemical reaction. To have a fundamental understanding of chemical reaction, it is important to study the properties of the adsorbates with both high spatial and energy resolution. Studies with photon spectroscopies, e.g., diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS), have provided detailed information on the adsorbate bonding on catalytic surfaces [2]. However, due to the low spatial resolution of photon spectroscopies compared with the typical size of a catalytic nanoparticle, there is lack of spatially resolved information on the local molecular bonding on nanosurfaces. The development of monochromated electron energy-loss spectroscopy coupled with scanning transmission electron microscopy (STEM-EELS) provide a potential approach to study adsorption processes within the infrared regime with atomic resolution. Moreover, the availability of direct electron detectors [3] for vibrational EELS should further enhance our ability to detect gas adsorbates on nanoparticle surfaces. By largely suppressing the readout noise, direct electron detectors make the detection of events with low signal-to-noise (SNR) more feasible. Also, time-resolved EELS becomes more accessible. CO on Pt, as a common reaction system, is widely studied and there are abundant measurements with photon spectroscopies. The binding energy of CO on Pt nanoparticles ranges from 1-2 eV depending upon the site [4]. Such high binding energy makes the adsorption robust against high energy electron beam irradiation, thus making CO adsorbate a good candidate to study. Here we demonstrate the possibility to detect CO adsorbates on Pt nanoparticles with vibrational EELS.

Commercially purchased yttria-stabilized zirconia (YSZ) was loaded with Pt nanoparticles via wet impregnation method. The sample was reduced in H_2 at 400 °C for 2 hours to remove any surface contaminations. CO was chemisorbed on Pt by flowing the gas through the Pt loaded YSZ powder in the reactor. Before loading the powder (dry-loading) onto a standard TEM copper grid with lacey carbon coating, the grid was baked at 120 °C for 2 hours to remove any contamination and cooled down to room temperature. Monochromated STEM-EELS was performed on a Nion UltraSTEM 100 operated at 60 kV. A small probe of 30 mrad convergence semi-angle was selected with a low probe current of 0.7 pA to achieve high spatial resolution and minimize the radiation damage respectively. The full width at half maximum (FWHM) of zero-loss peak (ZLP) was measured to be 15 meV. The measurement was performed in aloof geometry, where the beam was placed 5 nm away from the Pt nanoparticles. Energy-loss spectra were acquired from the location in a time series of 2000 frames with 10 ms dwell time, yielding adequate time resolution. To enhance the visualization of signal, the $I*E^2$ scale is used here, where E and I are the energy loss and corresponding intensity, respectively.

Figure 1a shows the high angle annular dark field (HAADF) image of the sample where the Pt and YSZ support are marked. **Figure 1b** shows the total integrated spectra of 20 s exposure time. A very small peak at around 260 meV is seen in the spectrum (as indicated by the arrow). After the $I*E^2$ scale is applied, as presented in **figure 1c**, the 260 meV peak becomes more clear, which corresponds to the vibration of CO molecule adsorbed on Pt as evidenced by FTIR [2]. Other peaks, e.g., carbonate species peaks and YSZ optical phonon, are also shown in the spectra. In order to confirm the observation, the summed spectrum was sliced into a series of 4 spectra: 0-5s, 5-10s, 10-15s, and 15-20s. As shown in **figure 2a** and **2b,** a peak at 260 meV in the 0-5s spectrum for both raw and $I*E^2$ spectrum is visible. For the spectrum from the time interval of 5-10 sec, the peak broadens and decrease in intensity, while for the 10-15s and 15-20s spectra, there are no sign of peak around 260 meV. The changes in the spectra possibly result from the desorption of CO molecule due to the beam irradiation.

As **figure 1b-c** shows, the dominant contribution to the spectrum comes from the YSZ support. This is because the signal we were collecting, i.e., dipole signal, is highly delocalized, and the information comes from a large sample volume. Since the dipole signal from the substrate is strong, it contributes to the background of the adsorbate peaks and decrease the signal-to-background ratio for adsorbate peaks. In order to suppress the dipole contribution from the substrate, we are currently exploring alternative approaches to sensing adsorbates using more localized impact scattering signals. Although such approaches will potentially be more damaging to the adsorbate layer, they may yield vibration spectra with enhanced signal-to-background ratios for the adsorbate peaks.

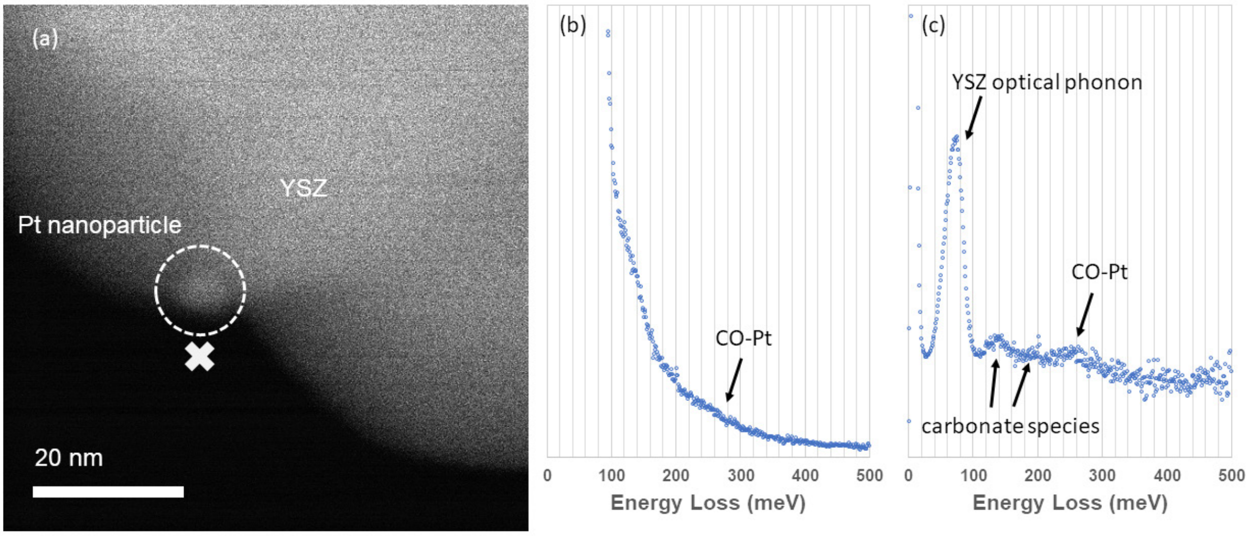

Figure 1 (a) HAADF image of the Pt loaded on YSZ. The position of Pt nanoparticle and the beam is marked with a dotted circle and ‘x’ mark respectively. (b) Raw energy-loss spectra of the 20s exposure time. The bump correspond to CO is denoted as CO-Pt. (c) Energy-loss spectra of the 20s exposure time with $I*E^2$ scale.

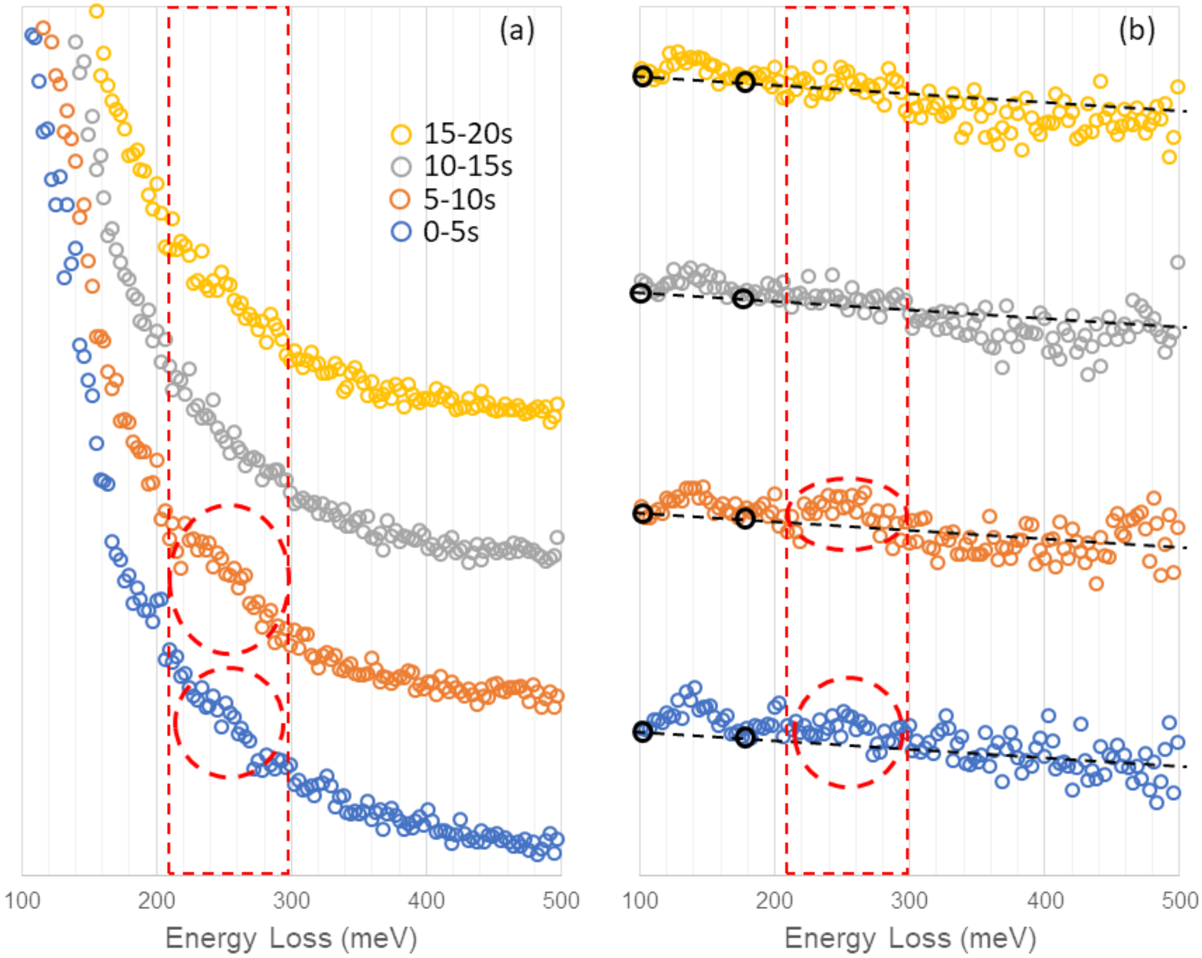

Figure 2 (a) Raw energy-loss spectra of different time series. (b) Corresponding energy-loss spectra with $I*E^2$ scale. The different time series are colored as blue(0-5s), orange(5-10s), gray (10-15s), and yellow (15-20s). A red dotted box is used to mark the energy region of interest. The red circles and ovals point out the CO peak on Pt at around 260 eV. The back dashed line is the linear extrapolation of the spectra at 100meV and 180 meV (denoted using the black circle), where there are no features.

References:

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