# HIGH RESOLUTION ELECTRON ENERGY LOSS SPECTROSCOPY FOR STUDYING PLANAR MODEL CATALYST: A TEST OF NO ON Rh(100)

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High resolution electron energy loss spectroscopy (HREELS) is an analytical technique used to describe the chemistry, bonding and electronic structure of thin samples of materials. It involves analyzing the energy distribution of initially monoenergetic electrons, after they have interacted with a sample. HREELS is a sensitive technique which is tested for NO on Rh(100) single surface catalyst. NO is one of the toxic gases released in the air during the combustion of gasoline in the cars. Rhodium has distinctively a high activity for the reduction of NO_x gases to N_2.
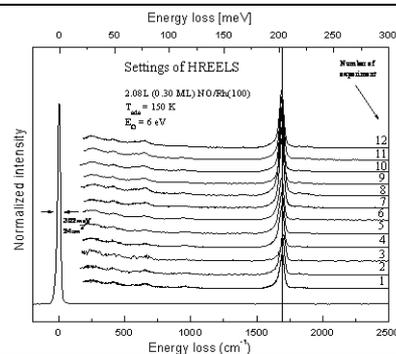
INTRODUCTION

In HREELS a beam of monochromatic, low energy electrons falls on the surface, where it excites lattice vibrations of the substrate, molecular vibrations of adsorbed species and even electronic transitions.[1] An energy spectrum of the scattered electrons reveals how much energy the electrons have lost to vibrations, according to the formula: $E_s = E_i - h\nu \rightarrow E_{loss}$, where, E_s is the energy of the scattered electron, E_i is the energy of the incident electron, h is Planck's constant, ν is the frequency of the excited vibration. The use of the electrons necessitates that experiments are performed in ultrahigh vacuum (UHV) and preferably on the flat surfaces of single crystals or foils.[1] This requirement assures that electrons are not deflected by gas molecules and the filament and sample are not contaminated. Focusing on the primary signals created by the interaction between electrons and the crystalline solid we may divide the scattered electrons in two groups: electrons which have undergone elastic collisions and lost no energy (elastic scattering) and electrons which have undergone inelastic collision with electrons in the solid and lost a small amount of their energy (inelastic scattering). HREELS is used for studying the chemistry of planar surfaces and of adsorbed atoms and molecules. It readily provides important information on adsorbate vibrational frequencies, molecular structure of adsorbates, bond strengths at surfaces, adsorption geometry-surface bonding sites, surface chemistry and adsorbate-adsorbate interactions. Two excitation mechanisms play role in HREELS: dipole and impact scattering. In dipole scattering we are dealing with the wave character of the electron. When an electron comes close to the surface, the electron sets up an electric field with its image charge in the metal.[1] The oscillating field is perpendicular to the surface and excites only those vibrations in which a dipole moment changes in a direction normal to the surface. This is a long range interaction and it

involves the electrostatic interaction of the incoming electron with dynamic electric dipole due to the molecular vibrations. As the interaction is of a long range the electron will "see" a composite of the true molecular dipole and its imagine in the conducting substrate. The electron momentum perpendicular to the surface is preserved and the energy loss results in small angle deflection around the specular direction-dipole scattering lobe. The situation appears differently if the molecule is lying down. The true dipole and its own imagine are cancelled out, therefore there is no net field, hence dipole scattering will not occur. In the upright adsorption position the true and the image dipoles will strengthen each other and there will be a net dynamic dipole moment and therefore scattering will happen (Fig. 1). So, in HREELS energy is lost only to those vibrations which have a component of their dynamic dipole moment oriented perpendicular to the surface known as surface selection rule.

From the most commonly used vibrational spectroscopies, infrared spectroscopy and high resolution electron energy loss spectroscopy (HREELS) are the most suited to study adsorbed molecules on the surface.[2] Infrared spectroscopy of species adsorbed on metal surfaces has to be performed in reflection since metals are opaque for infrared light. This technique is called reflection absorption infrared spectroscopy (RAIRS).[2] The advantage of HREELS is the detecting of vibrations as low as 100 cm^{-1}. RAIRS is limited between 800 and 4000 cm^{-1}. Aiming to use HREELS for fundamental studies, we have tested several settings for the present technique by recording HREELS spectra for a precovered NO, Rh(100) surface, optimizing in this manner the accuracy of the measurement.

RESULTS

Settings of HREELS: to test the settings twelve HREELS spectra were recorded for a precovered NO, Rh(100) surface. Before starting a measurement several settings are defined as input number passes (scans), step size per channel (meV) and input time per channel (sec). Based on these settings, time per each measurement can be estimated (Table 1). In order to include wavenumbers up to 2500 per each measurement, 1800 channels are needed for step size 0.203 meV, 800 channels for step size 0.457 meV, and 465 channels for step size 0.799 meV.

The above settings were applied for a precovered NO (2.08 L), Rh (100) surface and twelve spectra were recorded (Fig. 2).
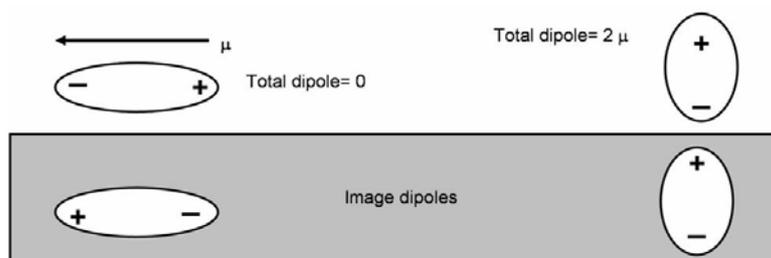

Fig. 1 – Molecule "lying down" true and image dipoles cancel, molecule "standing up" true and dipoles reinforce.

Table 1

Input for HREELS settings

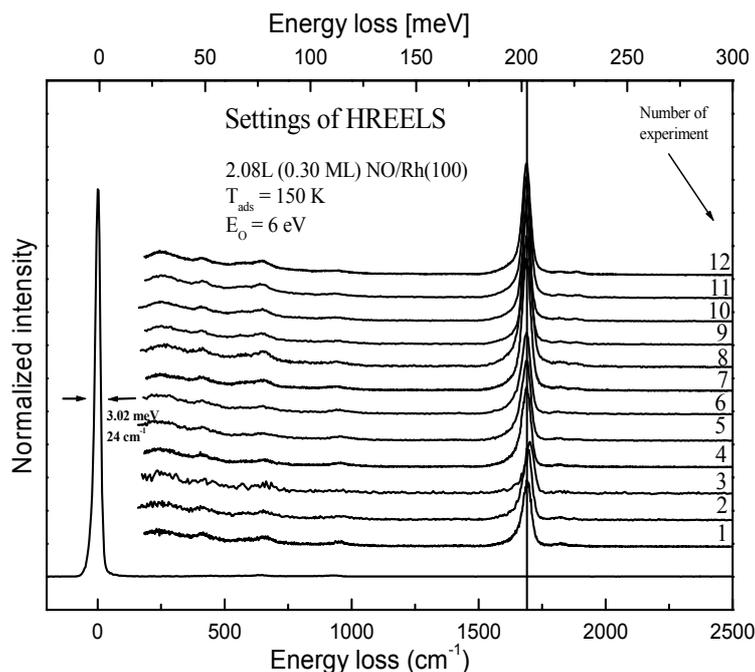| Number of experiments	Input number passes (scans)	Step size (per channel (meV)	Input time per channel (sec)	Time per each measurement (min)
1	5	0.203	0.1	15
2	5	0.457	0.1	6.7
3	5	0.799	0.1	3,9
4	10	0.203	0.1	30
5	10	0.457	0.1	13.3
6	10	0.799	0.1	7.7
7	5	0.203	0.5	75
8	5	0.457	0.5	33.3
9	5	0.799	0.5	19.4
10	10	0.457	0.5	66.6
11	10	0.799	0.5	38.7
12	10	0.203	0.5	150

Fig. 2 – HREELS spectra of NO/Rh (100) for different settings.

DISCUSSION

The NO frequencies displayed in Table 1 are plotted as energy losses versus the number of experiments (Fig. 3). The frequencies values fall in a close range by using different settings. All the spectra for testing the settings of HREELS are obtained with incident electron energy 6 eV, incident angle of 65° with respect to the surface. The wavenumbers ranges in the values 1685-1691 cm^{-1}. These values belong to NO adsorbed in the upright position (bridge position, adsorbed between to atoms of Rh catalyst).[3] HREELS study has indicated that NO is preferentially adsorbed in bridge sites in an upright position at all coverages.[3] HREELS has been used by applying settings: input number passes (scans) 5, step size per channel 0.457 meV (including 800 channels), input time per channel 0.1 sec. and time of measurement ~7 min for adsorption of NO/Rh(100), CO/Rh(100) and co-adsorption CO-NO on Rh(100) and proved to be successful.[3]
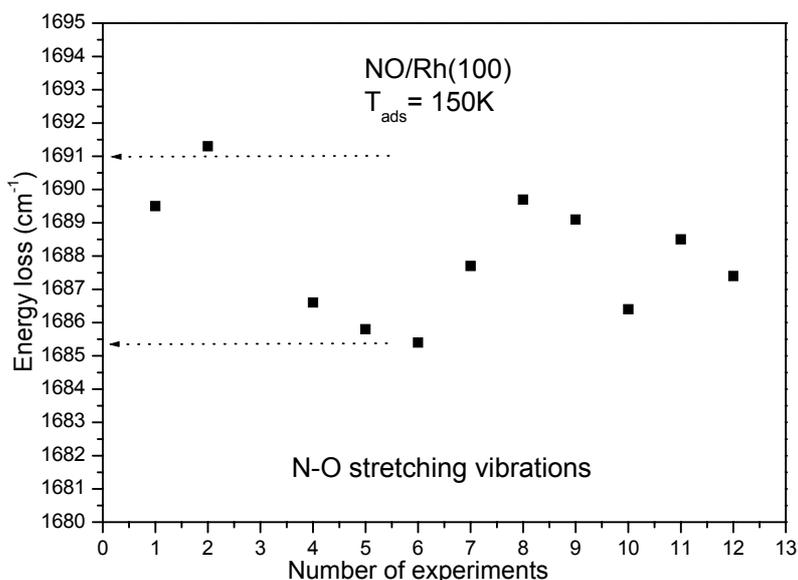

Fig. 3 – N-O stretching frequencies.

EXPERIMENTAL

To detect vibrational losses the incident electron beam must be highly monochromatic, having energy spread less than 10 meV. Modern HREELS spectrometers can achieve resolutions as low as 8 cm^{-1} (~1meV). In high resolution instruments two sectors are needed for the monochromator and two for the analyzer. The design of the HREELS chamber is mostly determined by the size of the spectrometer and the experimental requirements that come with the HREELS technique. The purpose is to use this vacuum chamber only to perform HREELS, in order to avoid disturbances by otherwise necessary equipment. Sample treatments are performed in the prechamber as adsorption of contaminants on the spectrometer can change its performance. Since low energy electrons are used in HREELS the magnetic field inside the chamber has to be lower than 10 mGauss (preferably <1 mGauss). Therefore, a double μ-metal shield is mounted in the chamber.[4]

HREELS spectrometer: A typical electron energy loss spectrometer (Fig. 4) consists of a cathode emission system, one or more energy dispersive elements for the monochromator.[5] A lens system between the monochromator and the sample, a second lens system between the sample and the analyzer, an energy dispersive element (the analyzer) and the electron detector.[5] The region around the sample is encapsulated within equipotential electrodes in order to create a field-free region around the sample and ensure well-defined scattering parameters in the experiments. The cathode (LaB$_6$) provides the electron source, while emission system (repeller plus A-lenses system, which are placed near the cathode) focuses the beam on the monochromator. The monochromator produces a beam with high energy resolution. B-lenses system (placed close to the sample) focuses the beam on sample and analyzer. The dual analyser analyses scattered beam with high energy resolution. The channeltron counts the number of electrons.[5]

Electron monochromator: The energy resolution of an energy analysis system is controlled by the energy in the electron beam incident on the crystal. If the electrons are produced by a thermal source operating at a temperature T$_s$ the energy of the electrons leaving the cathode will follow a Maxwellian distribution, whose full width at half maximum (FWHM) is ΔE_s = 2.45 (KT$_s$). For a lanthanum hexaboride (LaB$_6$) whose emission surface is at a temperature of 1700 K, ΔE_s=0.3 eV[5].

Magnetic Shielding: A considerable loss of energy resolution can occur if drift of magnetic fields penetrate into the spectrometer. Field penetration can be reduced by enclosing the magnet and more importantly the entrance and the exit drift spaces in a soft magnetic material such as μ–metal.[5]

Set up of HREELS: the experiments were performed in a two stainless-steel ultrahigh vacuum chambers with a base pressure of about $5 x 10^{-10}$ mbar. The first chamber (Fig. 5, preparation section) is equipped with a sputter gun and can be separated by a gate valve from the main chamber. The latter contains the spectroscopic equipment, set in three sections. The first section contains a quadrupole mass spectrometer (Prisma QME200, Balzers) for temperature programmed desorption (TPD) and residual gas analysis. The second section contains a four-grid, reverse-view low energy electron diffraction (LEED) system (RVL2000/8R, LK Technologies) which can be used as well for Auger electron spectroscopy (AES). The last section contains a high resolution electron energy loss spectrometer (ELS3000, LK Technologies) enclosed in a double μ-metal shielding (the magnetic field is about 0.5 milligauss (mG)).

A rhodium crystal is oriented in the (100) direction. The crystal has a thickness of about 1.2 mm and is mounted with 0.3 mm tantalum wires on a sample holder where it can be cooled to liquid nitrogen temperature (100 K) and heated by ohmic resistance over 1450 K. The temperature is measured with a Chromel-Alumel thermocouple spot-welded placed to the back of the crystal. Ultrahigh vacuum (10^{-10} mbar) is maintained by a combination of turbo pumps and titanium sublimation pump. The sample is cleaned by the standard procedure of extended argon ion sputtering at 925 K (1.5 KeV, 5 μA/cm^2), subsequent annealing at elevated oxygen pressure ($1x10^{-7}$ mbar) and temperatures between 925 K and 1100 K and flash annealing to 1400 K. Surface cleanliness is checked before every experiment by HREELS.
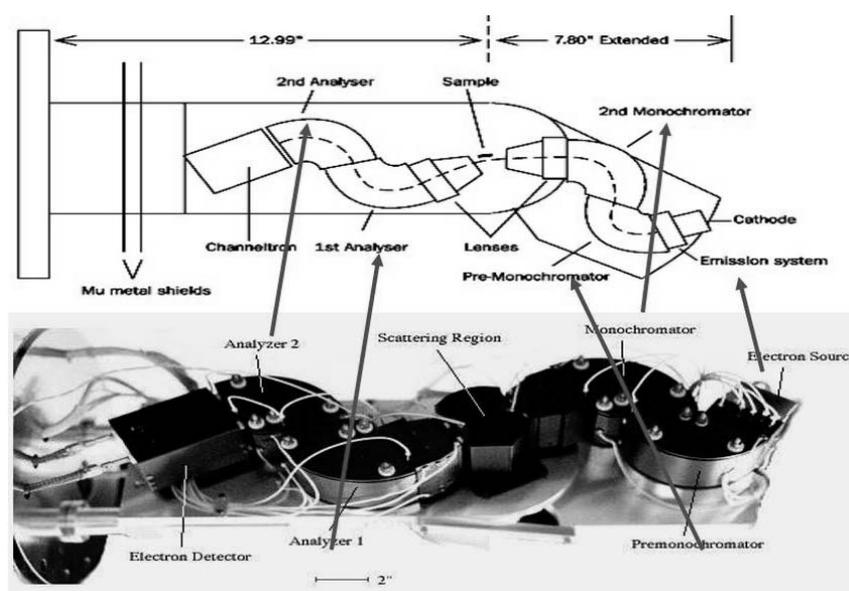

Fig. 4 – Internal part of spectrometer (from LK technologies[4] and Ibach[5]).
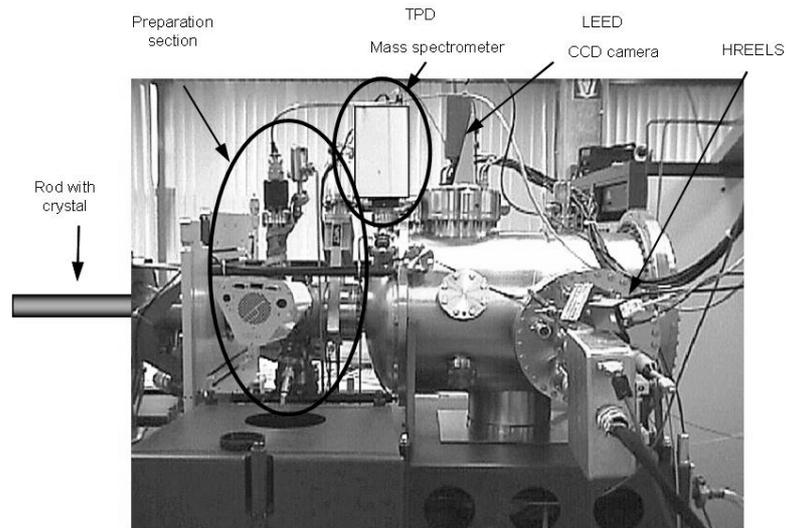
Fig. 5 – Experimental set up.

CONCLUSIONS

High Resolution Electron Energy Loss Spectroscopy (HREELS) was introduced as a spectroscopic technique for studying planar catalytic systems by application of different settings. HREELS was employed to study NO adsorption on Rh(100) at fixed coverage at adsorption temperature 150 K. The preferential adsorption site and bonding geometry of NO was identified.

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