

Supplementary Information for

Reversible structural transformation of FeO_x nanostructures on Pt under cycling redox conditions and its effect on oxidation catalysis[†]

Qiang Fu,^{*a} Yunxi Yao,^a Xiaoguang Guo,^a Mingming Wei,^a Yanxiao Ning,^a Hongyang Liu,^{ab} Fan Yang,^a Zhi Liu^c and Xinhe Bao^{*a}

^a State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, the Chinese Academy of Sciences, Dalian 116023, P.R. China. Email: qfu@dicp.ac.cn; xhbao@dicp.ac.cn

^b Shenyang national laboratory of materials science, institute of Metal Research, the Chinese Academy of Sciences, Shenyang 110016, P.R. China

^c Advanced Light Source, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, USA

Experimental details

Surface science studies were carried out in two ultrahigh vacuum (UHV) systems. An Omicron multi-probe system consists of three main chambers and is equipped with X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscope (UPS), high-resolution electron energy loss spectroscopy (HREELS), and variable-temperature scanning tunneling microscopy (STM). Submonolayer FeO nanostructures were deposited on the Pt(111) surface via evaporation of Fe onto the substrate surface with the surface temperature ranged from 150 to 300 K in the presence of O₂ followed by annealing in UHV. The obtained FeO/Pt(111) surfaces can be treated in the UHV chambers with O₂ partial pressure up to 10⁻⁶ mbar range. Additionally, a batch reactor is coupled to the main UHV system, in which samples can be treated with up to 10 bar gas and at elevated temperatures. After the treatments, the samples were transferred to the main chambers for XPS, UPS, HREELS, and STM measurements without exposing to air. A Createc low temperature STM (LT-STM) system has been installed with a cryostat for LT-STM and an energy analyzer for XPS and UPS measurements. The FeO nanoislands were prepared on Pt(111) surface by the same process. The high resolution STM images were recorded at liquid nitrogen temperature. Annealing treatments were carried out by heating the sample to the setting temperature followed by cooling. XPS spectra were acquired using Mg-Kα radiation (hν= 1253.6 eV) with the pass energy at 30 eV. All XPS spectra were calibrated using the binding energy (BE) of Fe 2p_{3/2} at 707.0 eV from the thick Fe films grown on the Pt(111) surface.

Ambient pressure XPS (AP-XPS) measurements were performed at beamline 9.3.2 at the Advanced Light Source, Berkeley with a specially designed photoemission spectrometer that can operate at

near-ambient pressures (up to 2 Torr). The XPS Fe 2p spectra were recorded at photon energies of 830 eV. The FeO nanostructures were prepared by the similar recipe as we did in the Omicron multi-probe system and the Createc LT-STM system. The FeO coverage was calibrated by titration of CO on the surfaces at RT, which is around 0.44 ML.

The Pt-Fe nanoparticles supported on carbon black (Pt-Fe/CB) were prepared by co-impregnation method, using H_2PtCl_6 and $\text{Fe}(\text{NO}_3)_3$ as the precursors. Through aging and drying overnight, fresh Pt-Fe/CB catalysts were produced, in which the loading of Pt and Fe was controlled at 4 wt. % and 0.3 wt. %. The reduction was carried out in flowing H_2 gas at 523 K for 2h before reactions. CO oxidation reactions were performed in a fixed-bed microreactor, and the tail gas was analyzed on-line with a gas chromatography (GC) (Agilent 6890N).

In-situ Fe K-edge X-ray absorption near edge spectroscopy (XANES) measurements were done in BL14W1 beamline in Shanghai Synchrotron Radiation Facility/SSRF. The treatments of the catalysts were done in an in-situ reaction cell (Anton Paar, XRK900). The Pt-Fe/CB catalysts were characterized by Fe K-edge XANES in a fluorescence mode.

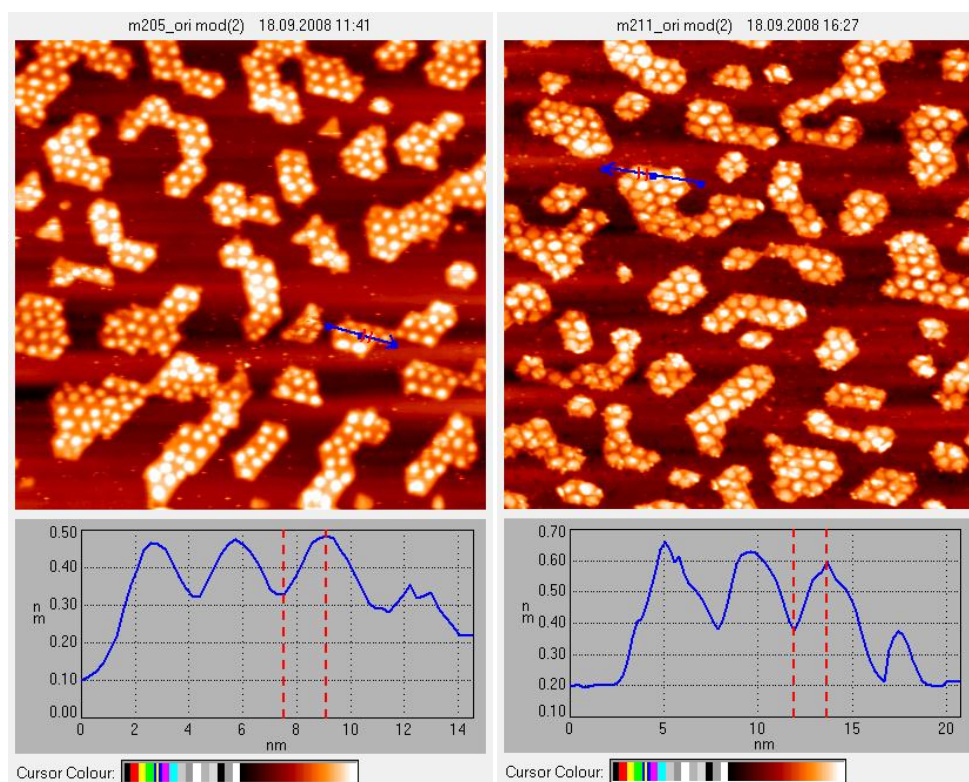


Figure S1. (left), the STM image shown in Figure 1A and a line profile in the bottom figure was taken along the line drawn in the image as marked in the image; (right), the STM image shown in Figure 1B and a line profile in the bottom figure was taken along the line drawn in the image as marked in the image.

The oxidized islands present higher corrugation by around 0.5 Å. Correspondingly, the oxidized islands have larger island height by the same amount compared to the pristine FeO nanoislands.

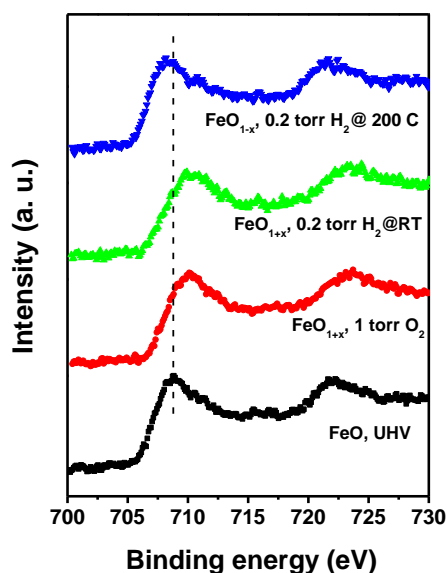


Figure S2. In-situ AP-XPS Fe 2p spectra of a 0.44 ML FeO/Pt(111) surface exposed to high pressure O₂ and H₂ atmospheres, respectively. Exposure of the FeO/Pt(111) to 1 torr O₂ at room temperature results in the Fe 2p BE shift of 1.0 eV, indicating the transformation of the O-Fe bilayer to the O-Fe-O trilayer structure. Exposure of the O-Fe-O trilayer structure to 0.2 torr H₂ at room temperature cannot reduce to the O-Fe structure. In 0.2 torr H₂ gas, increase of the surface temperature up to 353 K already transforms the O-Fe-O structure to the O-Fe structure. At much higher temperature, e.g. 473 K, the surface iron oxide can be reduced to metallic Fe state.

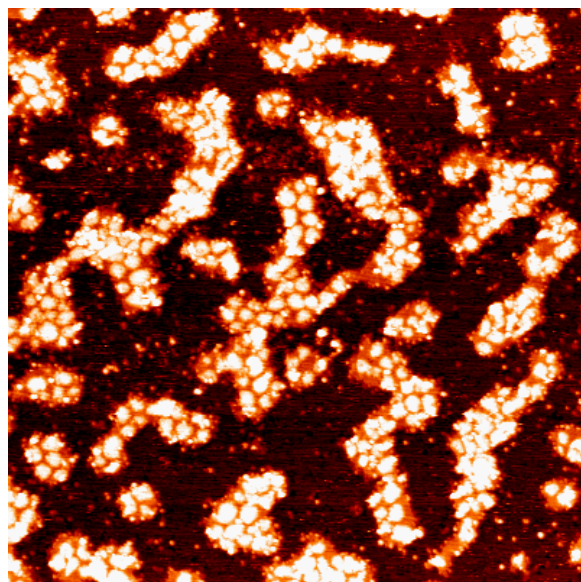


Figure S3. A 0.25 ML FeO/Pt(111) surface was exposed to 5 mbar O₂ at room temperature in the batch reactor for 0.5 h and then transferred to UHV chamber for STM imaging. The STM image (100 nm × 100 nm, -1.19 V/0.03 nA) of the surface shows the appearance of the characteristic FeO₂ domains. Due to the high pressure exposure, contaminations can be observed as well.