

Chapter 2

Experimental Section

The work is mainly carried out in ultrahigh vacuum (UHV) systems and fixed-bed microreactor. The UHV systems include an Omicron Multi-NanoProbe System, a DUV-PEEM/LEEM System, and a Leybold XPS System. The fixed-bed microreactor for reactivity test of supported nanoparticles was designed and installed in laboratory.

2.1 Model Samples and Precursors of Supported Nanoparticles

Pt(111), φ (Diameter) = 10 mm, thickness = 2 mm

Fe wire, φ = 0.1 mm, Johnson Matthey, 99.998%

Ni wire, φ = 0.1 mm, Alfa Aesar, 99.994%

W wire, φ = 0.15 mm, Johnson Matthey, 99.95%

Highly orientated pyrolytic graphite (HOPG), size = $10 \times 10 \times 2 \text{ mm}^3$.

Hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and 3d transition metal nitrate salts ($\text{Fe}(\text{NO}_3)_3$, $\text{Co}(\text{NO}_3)_3$, $\text{Ni}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$) are analytical grade.

2.2 UHV Systems

2.2.1 Omicron Multi-nanoProbe System

Figure 2.1 shows the photograph of the Omicron Multi-NanoProbe System. The base pressure of this system is below 1.0×10^{-10} mbar during STM and XPS

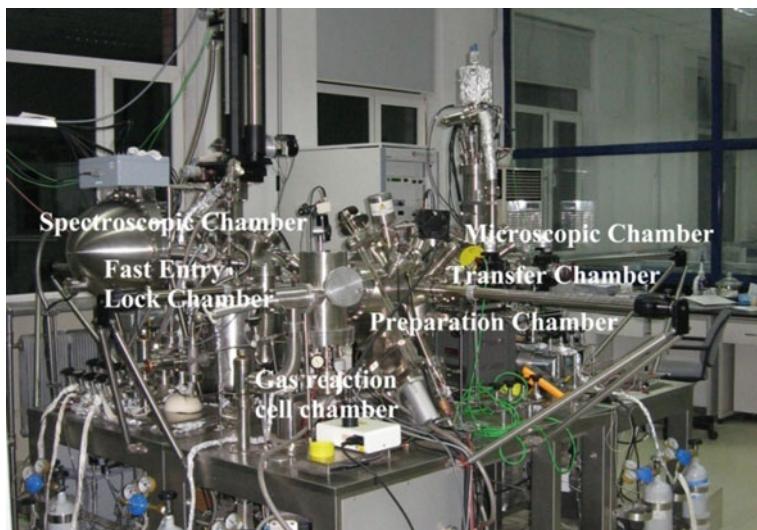


Fig. 2.1 Photograph of Omicron Multi-NanoProbe System

measurement. This Multi-NanoProbe UHV system consists of a preparation chamber, a spectroscopy chamber, a microscopy chamber, and a load lock for sample entering. Preparation chamber includes Ar^+ ion gun and various evaporation sources (Fe, Ni, and Pt) for sample cleaning and preparation. The sample temperature can be controlled between 150 and 1100 K in preparation chamber. Spectroscopy chamber equips with hemispheric energy analyzer (Omicron EA 125 5-channeltron), X-ray source (Omicron DAR400), UV light source (VUV source HIS13), ion gun (ISE100), and high-resolution electron energy loss spectroscopy (HREELS, LK ELS5000). Microscopy chamber contains variable temperature (VT) STM/AFM and PEEM (Focus IS-PEEM).

In Omicron Multi-NanoProbe System, the spectroscopy and microscopy data were recorded by Omicron EIS and Scala Pro5.0 software, respectively. HREELS data was acquired by LK firm software.

2.2.2 Deep Ultraviolet Photoemission Electron Microscopy System

As shown in Fig. 2.2, the DUV-PEEM system contains DUV laser source and ELMITEC PEEM/LEEM system. In DUV laser source, the wavelength of laser was converted from 355 nm (1 mw, 80 Hz) to 177.5 nm by a KBBF crystal (from Technical Institute of Physics and Chemistry, CAS). The DUV laser light was focused and introduced into the PEEM/LEEM system via a home-designed vacuum

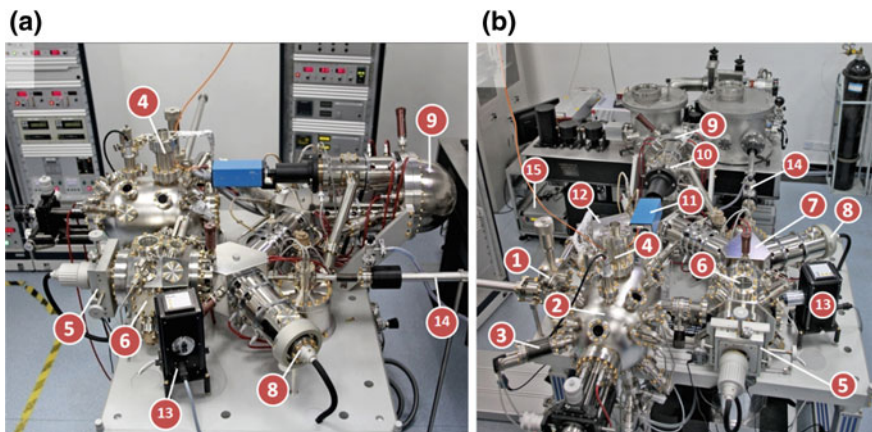


Fig. 2.2 Photographs of PEEM (LEEM-III) system. 1 load lock; 2 preparation chamber; 3 quartz oscillator; 4 mass spectroscopy; 5 Elmitec sample stage; 6 imaging chamber; 7 deflection lens; 8 electron gun; 9 energy analyzer; 10 MCP; 11 CCD; 12 aberration corrector; 13 Hg light source; 14 laser connector; 15 355 nm laser source

laser connector. The incident angle of DUV laser to the sample surface is 90° . The PEEM/LEEM system consists of a preparation chamber and an imaging system. The imaging system includes a hemispheric energy analyzer, an aberration corrector, a field emission electron gun, and other electron lens. The base pressure of PEEM/LEEM system can be maintained below 1.0×10^{-10} mbar after sufficient baking out.

Utilizing DUV light as the incident source, the resolution of PEEM image can reach 3.9 nm by testing graphene/Ru(0001) sample. In addition, we also use Hg or deuterium lamp as the incident source for PEEM studies. For LEEM and LEED measurements, we employ a LaB₆ filament as electron source. The resolution of LEEM image can reach 1.9 nm using standard Si(100) sample.

In this DUV-PEEM/LEEM system, the PEEM, LEEM and LEED measurements can be recorded at the temperatures between 150 and 2000 K, and at a partial pressure up to 1.0×10^{-5} mbar. The parameters of various electron lens were aligned through ELMITEC LEEM2000 software. Data was acquired by U-view2000 software.

2.2.3 Leybold XPS System

As shown in Fig. 2.3, the Leybold XPS system consists of a high pressure reaction cell and a XPS chamber. Various samples can be pretreated in the high pressure reaction cell at a temperature between room temperature and 900 K. After reaction,

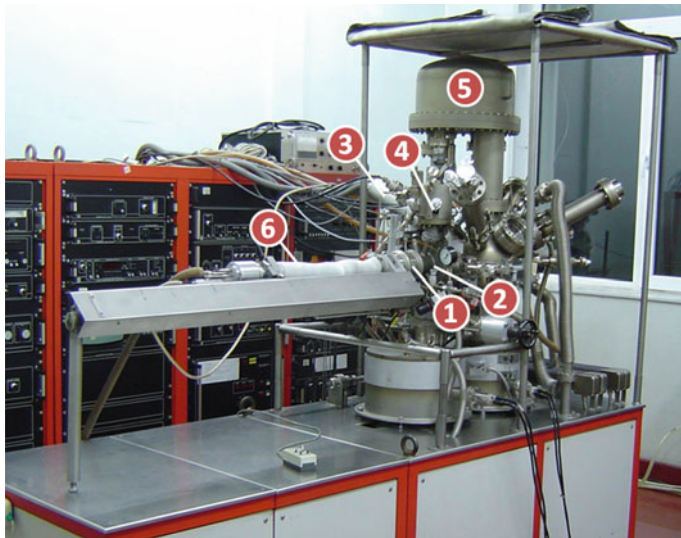


Fig. 2.3 Photograph of Leybold XPS system attached with a high pressure cell. 1 high pressure cell, 2 middle chamber, 3 X-ray source, 4 Ar^+ sputter gun, 5 energy analyzer, 6 sample transfer rod

the sample was transferred to XPS chamber without exposing to air. The base pressure of this system can be kept below 5.0×10^{-10} mbar during XPS measurements.

2.3 Experimental Methods of Model Systems

Cleanness of Pt(111) surface: to obtain a clean Pt(111) surface, cycles of Ar^+ sputtering ($P_{\text{Ar}} = 7.5 \times 10^{-6}$ mbar, 1.5 kV, 10 min), oxidation ($P_{\text{O}_2} = 1.3 \times 10^{-6}$ mbar, 800 K, 5 min), and high temperature UHV annealing (1060 K, 3 min) were carried out. Finally, no contamination can be detected by XPS, STM, and LEEM.

Fabrication of Fe and Ni source: The Fe(Ni) source was made up of a W filament wrapped with metallic Fe(Ni) wire. Degassing and evaporation of Fe(Ni) source was carried out by passing constant current through W filament. The coverage of Fe (Ni) was controlled by evaporation time.

Preparation of model Fe–Pt(111) and Ni–Pt(111) model catalytic systems: Fe/Pt(111) and Ni/Pt(111) surfaces were prepared by direct evaporating Fe and Ni on Pt(111) surface at room temperature. FeO_{1-x} /Pt(111) and NiO_{1-x} /Pt(111) surfaces were constructed by depositing Fe and Ni in 1.3×10^{-6} mbar O_2 atmosphere. In order to prepare highly dispersed FeO_{1-x} islands on Pt(111) surface, the temperature of Pt(111) surface was decreased to 170 K by using liquid nitrogen. The preparation of NiO_{1-x} /Pt(111) surface was carried out at room temperature.

Gas adsorption on model catalytic systems: Reactant gas adsorption was carried out through leak valve backfilling. The adsorption amount of reactant gas was given in Langmuir (L, $1\text{L} = 1 \times 10^{-6} \text{ Torr} \cdot \text{s}$).

Data record in model catalytic systems: In Omicron system, XPS spectra were recorded using Mg K α (1253.6 eV) radiation. UPS signals were acquired in the normal emission direction using He I (21.2 eV) or He II (40.8 eV) as the excitation source. STM images were obtained in constant current mode using a W-tip. In DUV-PEEM/LEEM system, PEEM images were acquired using Hg lamp (4.9 eV) or DUV laser source (6.9 eV). LEEM images were recorded using electron gun radiation. Each PEEM/LEEM image can be acquired in millisecond at a temperature between 150 and 2000 K.

2.4 Experimental Methods of Supported Nanoparticles

Preparation of pure Pt, Pt-3d transition metal (3d-TM: Fe, Co, Ni and Cu) nanoparticles on HOPG: First, a clean HOPG surface was obtained by using adhesive tape to peel off the outer layers. Then the surface was transferred into UHV system and slightly sputtered ($P_{\text{Ar}} = 5 \times 10^{-6} \text{ mbar}$, 2 kV, 45 s) to produce high density surface defects. Subsequently, ethanol solution of hexachloroplatinic acid (H_2PtCl_6) was dropped onto the sputtered HOPG surface and then reduced at elevated temperature ($\sim 473 \text{ K}$) in H_2 atmosphere to prepare Pt/HOPG sample. For Pt-3d TM/HOPG sample, a mixed ethanol solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and 3d transition metal nitrate salt was dropped onto the sputtered HOPG surface and then dried in air for further studies.

Preparation of PtFe/CB and PtNi/CB catalysts: PtFe and PtNi nanoparticles supported on carbon black (CB) were prepared by co-impregnation method using H_2PtCl_6 and nitrate salt as the precursors. After aging and nucleation overnight at 60°C , fresh PtFe/CB and PtNi/CB catalysts were obtained, in which the loading of Pt and Fe(Ni) was controlled at 4 wt% and 0.3 wt%, respectively (the molar ratio of Pt:Fe(Ni) = 4:1).

Synchrotron-based X-ray diffraction (XRD) and X-ray absorption spectroscopy (XAS) measurements were conducted to determine the structure and chemical state of PtNi/CB and PtFe/CB in VT-redox treatments and CO oxidation conditions. These experiments were carried out at the BL14B1 and BL14W1 beamlines in Shanghai Synchrotron Radiation Facility.

The acid leaching treatments combined with the inductively coupled plasma atomic emission spectrometry (ICP-AES) (Thermo Intrepid II) measurements were employed to study the distribution of Ni at various PtNi/CB catalysts.

The size of PtNi/CB catalysts was characterized by transmission electron microscopy (TEM) (FEI Tecnai G2 Spirit, 120 kV). The size of Pt-3d TM/HOPG model surface was studied by scanning electron microscopy (SEM) (FEI Quanta 200F).

In situ XRD (Rigaku D/MAX-2500/PC, $\lambda = 1.5406 \text{ \AA}$) was employed to investigate the structure of PtNi/CB catalysts in VT-redox cycles.

CO oxidation reactivity of PtFe/CB and PtNi/CB catalysts was measured in a fixed-bed microreactor using multichannel mass spectrometer (Omnistar) or gas chromatographic (Agilent 6890) for tail gas analysis. The CO oxidation gas with excess O_2 consists of 1% CO, 20% O_2 , and 79% He. The CO oxidation gas with excess H_2 consists of 1% CO, 0.5% O_2 , and 98.5% H_2 . The gas hourly space velocity (GHSV) of both was set at $30,000 \text{ mL g}^{-1} \text{ h}^{-1}$.

Construction and Reactivity of Pt-Based Bi-component
Catalytic Systems

Mu, R.

2017, XII, 90 p. 64 illus., 60 illus. in color., Hardcover

ISBN: 978-3-662-55242-1