Investigation of Model Heterogeneous Catalysts via Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRAS)

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Introduction

The key goal of heterogeneous catalysis is to get a molecular-level understanding of a heterogeneous catalytic reaction. Many previous surface science researches, usually under ultrahigh vacuum (UHV) condition with single crystal surfaces, have been done to realize this goal. However, it has been debated that whether the results of traditional surface science studies can be truly transferred to industrial heterogeneous catalysis, which are typically carried out at atmospheric (or even higher) pressures with far more complex surfaces. The two main discrepancies between UHV studies and technical heterogeneous catalysis are referred frequently to the “pressure gap” and “material gap” [1]. To bridge these gaps, experimental systems are required to be able to run reactions from UHV to elevated pressure (~10^3 Torr) conditions, and advanced in situ characterization techniques that can handle high-pressure detection are needed, since most conventional surface science techniques (e.g. AES or LEED) cannot be used at reaction conditions due to the short mean free path of electrons.

In this work, a custom designed UHV-compatible high pressure cell equipped with PM-IRAS is used to carry out in situ investigations of different heterogeneous catalytic reactions on model catalysts, ranging from single crystals, e.g. Pt(100), to model supported catalysts, e.g. Ru/Al2O3. At elevated pressures, higher surface coverage is observed on the catalyst surface and the adsorption of CO on Pt (100) surface at elevated pressures is discussed as an example.

Materials and Methods

The basic operational principle of PM-IRAS technique is the modulation of a linearly polarized IR beam between s- (parallel to the surface of the sample) and p- (perpendicular to the sample surface) polarized light. According to the surface selection rules [2], species on a metal surface can only absorb p-polarized IR light, whereas any molecule in the gaseous or liquid (isotropic) environment can absorb both p- and s-polarized IR radiation. Once the differential signal (p-s) signal is normalized to the average signal (p+s), the characteristic vibrational fingerprints of the surface species, (p-s)/(p+s), can be obtained without gas phase interferences. In this work, experiments are carried out in a UHV-compatible high pressure cell, which is equipped with an Argon ion gun, a quadrupole mass spectrometer (QMS) and PM-IRAS. The ion gun is used to clean the single crystal surface, and the QMS can be used to run temperature programmed desorption (TPD) studies, as well as gas analysis during experiments. The pressure changes during reactions are recorded, and the vibrational spectra of surface species are detected via PM-IRAS.

Results and Discussion

The temperature effect of CO adsorption on Pt (100) is investigated with PM-IRAS at 2 Torr. As shown in Figure 1, when temperature increases, the stretching band of CO adsorbed on Pt (100) shifts from 2096 cm⁻¹ at 325K to 2067 cm⁻¹ at 825K while the peak intensity decreases, which is in agreement with the decreased CO molecules on the surface with less coupling effects [3]. At 875K, CO desorbs from the surface completely, which is consistent with the Langmuirian adsorption model [4].

In addition, based on the peak positions, the surface coverage can be calculated using the dipole-coupling model [3]. As shown in Figure 2, at 325 K the surface is saturated with CO, and the surface coverage decreases as temperature increases. In comparison to the saturated surface coverage (0.6 at 10^3 Torr) of CO on Pt (100) from previous surface science experiments [5], a higher surface coverage at elevated pressure can be detected with PM-IRAS.

Figures

- Figure 1. The adsorption of CO on Pt (100) at 2 Torr
- Figure 2. Calculated surface coverage vs. temperature

Significance

PM-IRAS can remove the gas phase contributions successfully at elevated pressures and can be applied to carry out in situ investigations of surface reactions to bridge the pressure gap between surface science and realistic industrial catalysis.

References