Surface-Enhanced IR Absorption (SEIRA) of CO Adsorbed on Small Pt Particles Deposited on an Island Au Film

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CO adsorbed on Pt particles deposited on an island Au film exhibited strong IR adsorption. Since Au is not able to adsorb CO, this is attributable to surface-enhanced IR absorption (SEIRA) caused by the Au film. When Pt deposits were extremely small, C-O stretching band appeared at frequencies much lower than those observed for supported Pt catalysts, indicating that the Pt deposit was so small that adsorbed CO was isolated each other without a dipole-dipole interaction.

Drastic enhancement of IR absorption has been reported for molecules that exist in the close vicinity of a thin film of free electron metals such as Au, and is called surface-enhanced IR absorption (SEIRA).[1-3] A theory as well as an application of SEIRA has developed in these years.[3] Its enhancement is so high (10 – 1000 hold) that SEIRA is promising for IR detection of surface intermediates during catalytic reactions over metals. In addition, SEIRA spectroscopy (SEIRAS) is available even in the presence of gas or liquid which absorbs IR light intensively, when IR beam is injected from the backside of the SEIRA-active film coated on an IR transparent substrate and reflected IR beam is monitored (external back reflection method). Thus, SEIRAS enables us to monitor surface species during a surface reaction without removing reactants or solvents. For investigations of a catalytic reaction, however, the catalytic activity of SEIRA-active metals is so poor for most of reactions at room temperature that a measurable amount of reaction intermediates on the surface could not be expected. Catalytically active metals such as Pt, on the other hand, exhibit very weak SEIRA as far as it was reported so far.[4] We report in the present paper the SEIRA of CO adsorbed on Pt particles deposited on a SEIRA-active Au film. This result shows the possibility of applying SEIRAS to any kinds of catalytically active materials by keeping them in close proximity to a SEIRA-active film. A similar result has been reported for surface-enhanced Raman scattering (SERS); thin films of Pt and Pd electrodeposited on a roughened Au electrode yielded SERS effect for adsorbed CO.[5]

Au deposition on a CaF_2 disc (30 mm in diameter, 2 mm thick) was carried out in a high vacuum chamber by evaporating Au from an alumina-coated W basket, which was ca. 20 cm away from the substrate. The thickness of Au film was monitored with a quartz film-thickness meter (Inficon XTM/2) and the deposition rate was controlled at 0.27 nm/min. The thickness of the Au film was 6.0 nm. Since Pt may lose its catalytic activity when exposed to the air, its deposition onto the Au film was carried out in an IR cell, to which the Au film/CaF_2 sample was attached using a Viton O-ring. Pt was evaporated from a Pt wire (0.4 mm diameter) by electrically heating in a vacuum higher than 1×10^{-6} torr. The film thickness of Pt was not measured since the IR cell was too small to build in a sensor of the film-thickness meter. The current for heating Pt wire was, therefore, gradually increased until the spectrum of adsorbed CO was observed. An IR beam from FTIR (Perkin Elmer 1720X) was injected from the CaF_2 side at an incident angle of ca. 50° and reflected at the interface of Au film. The reflected IR beam was monitored with an MCT detector at a liquid-nitrogen temperature. IR spectra were recorded with the resolution of 4 cm^{-1} and with 200 scan.

When an Au film alone was present on the substrate, no IR bands due to adsorbed CO as well as gas-phase CO were observed in the presence of gas-phase CO, indicating that CO is not able to adsorb on the Au film and a gas phase molecule is not observed by SEIRAS. Therefore, the appearance of CO band after the deposition of Pt on the Au film conclusively indicates CO adsorption on Pt. The Au film transmittance was apparently unchanged when CO bands were observed at first, indicating a very small amount of Pt deposits. Figure 1 shows the SEIRA spectra of CO adsorbed on the Pt deposited on the Au film. Two strong C-O stretching bands, which are assigned to on-top CO,[6] appeared at 2014 and 2032 cm^{-1} at 1.0 torr of CO. The latter band increased in intensity with increasing CO pressure and virtually disappeared after evacuation of gas-phase CO. This band may be attributed to special CO species which exists only in the presence of gas-phase CO, but its details are not clear at

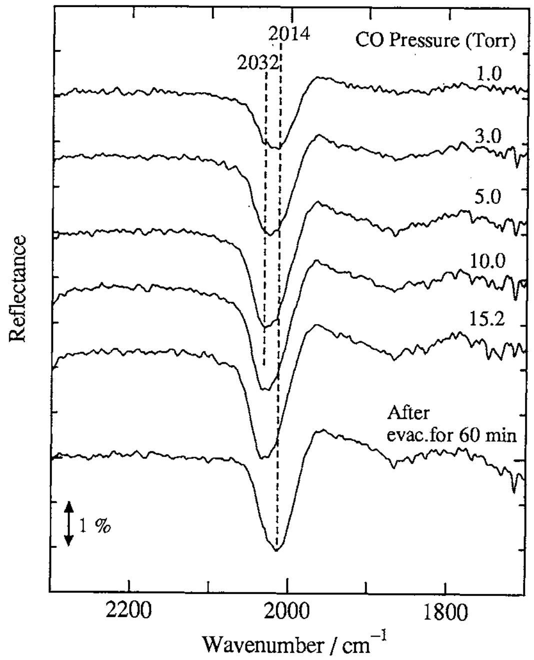

Figure 1. SEIRA spectra of CO adsorbed on Pt deposited on the Au island film. IR beam was introduced from the CaF_2 substrate side at ca. 50° of incident angle and reflected at the Au film.

the present. With increase in CO pressure, a broad and weak band became discernible at 1872 cm^{-1}, which may be assigned to bridge CO.[6] The Pt surface was probably saturated with CO at 10 torr, since the peak intensity leveled off with further increase in CO pressure. It is widely known that the C-O stretching band of on-top CO on noble metals such as Pt significantly shifts to higher frequencies with increasing coverage due to large dipole-dipole interactions.[7] For instance, on a 5 % Pt/SiO_2 catalyst, the band shifted from 2062 cm^{-1} at ca. 0.1 monolayer coverage to 2078 cm^{-1} at full coverage at room temperature.[8] For Pt(111) surface, the frequency shift from 2094 to 2109 cm^{-1} occurred with increasing coverage from 0.01 to 0.65 at 95 K.[9] The frequencies of on-top CO bands in Figure 1 are extremely lower than those reported for supported Pt catalysts[6,8] as well as for single crystal Pt surfaces[7,9] in literatures. This is probably because the Pt particles deposited on the Au film are as small as cluster and isolated each other so that a dipole-dipole interaction is virtually absent. In addition, an extremely small Pt particle may be different in chemical character from large Pt particles. Longoni and Chini[10] reported the IR spectra of $[Pt_3(CO)_6]_n^{2-}$ (n = 1 – 6) in THF solution, in which the terminal CO band shifts drastically from 2065 to 1945 cm^{-1} with decreasing n from 6 to 1. Their results definitely show that the C-O stretching frequency of ligand carbonyl decreases with decrease in the number of Pt atoms in the cluster. Since the negative charge of a metal carbonyl lowers the terminal CO frequency[6], their results are not directly applicable to the present system for estimation of the number of Pt atoms in the Pt island. It is however reasonably concluded that the Pt deposit on the Au film is so small as to match Pt carbonyl clusters. After adsorbed CO on the Pt deposit was removed by the reaction with O_2 at temperatures a little higher than room temperature, Pt was evaporated further to increase the amount of Pt deposit. As shown in Figure 2, on-top CO exhibits more intense band than in Figure 1. The band appeared at 2048 cm^{-1}, which is ca. 30 cm^{-1} higher than before the addition of Pt deposit, as expected from the results of the Pt carbonyl clusters. Bridge CO exhibited a broad but distinct band at 1874 cm^{-1}. The band position of bridge CO adsorbed on Pt was hardly affected by the coverage of CO.

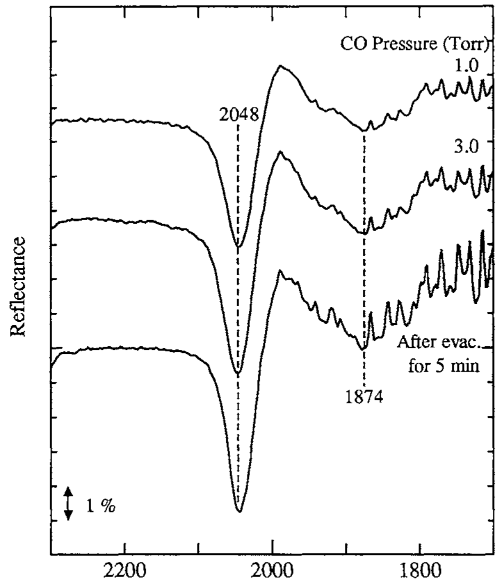

Figure 2. SEIRA spectra of CO adsorbed on Pt deposited further on the film used in the experiments of Figure 1.

The SEIRA spectrum of adsorbed CO showed the distortion of the band of on-top CO; the reflectance exceeded 100 % at the low frequency end of the band. A similar band distortion was observed for the transmission SEIRA spectrum of $Fe(CO)_5$ adsorbed on an Au island film at 115 K, but the transmittance exceeded 100 % at the high frequency end of the C-O stretching band in this case.[11] Such band distortion has been often observed in the IR reflection absorption spectrum of adsorbed molecule with a high extinction coefficient, and explained in terms of the anomalous dispersion of the refractive index in the region of the observed band.[12] However, it is uncertain at the present whether or not the band distortion in SEIRA is due to the anomalous dispersion of refractive index.

In summary, SEIRA was observed for CO adsorbed on small Pt particles deposited on an Au island film. Although the extent of SEIRA effect could not be estimated, the present method is sensitive enough to detect a submonolayer coverage of adsorbed species on the Pt deposit and would be useful to *in-situ* observation of a catalytic reaction over Pt particles even in the presence of gas-phase reactant species.

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