

Particular IR Optical Properties of Pd Nanoparticles Confined in Supercage of Y-Zeolite for CO Adsorption at Electrochemical Solid/Liquid Interface

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Zeolite or molecular sieve materials, with regular cages or ordered channels of molecular size, are widely used in the fields such as adsorption, heterogeneous catalysis and ion-exchanging. Less work has been done so far in employing this material in electrochemical studies. The regular cages and channels of zeolite can be regarded as “nanometer-size micro-reactors”, which offer templates for the synthesis of nanoparticles and nanowires^[1]. The unique structure of zeolite cannot only confine metal clusters of dimensions within nanometer order, but also block their aggregation and improve their stability. We have synthesized recently Pd nanoparticles in supercages of Y-zeolite, and investigated the adsorption of CO on Pd nanoparticles at electrochemical solid / liquid interfaces using *in situ* FTIR reflection spectroscopy. Particular IR optical properties were observed for the first time upon adsorption of CO on Pd nanoparticles confined in supercages of Y-zeolite.

The *in situ* electrochemical FTIR spectroscopic studies were carried out on a Nexus 870 FTIR spectrometer (Nicolet) equipped with a Gopher IR source and a liquid nitrogen-cooled MCT-A detector. A CaF₂ disk was used as the IR window. The resulting spectrum is defined as potential different spectrum, i.e., $\Delta R/R = [R(E_S) - R(E_R)]/R(E_R)$.

The Pd²⁺ ions were introduced into the zeolite by ion-exchanging between PdCl₂ and Na⁺Y, and they were then reduced electrochemically by applying potential cycling at negative electrode potentials. The material so formed is denoted as Pd⁰Y(e). In a second way the [Pd(NH₃)₄]²⁺Y precursors prepared by ion-exchanging were calcined and reduced chemically in a hydrogen flow at high temperature^[2], which is indicated Pd⁰Y(c). It is known that Pd nanoparticles of size 8.2 Å can be formed in supercages of Y-zeolite by introducing and releasing pure CO gas into the supercages at electrochemical solid-liquid interfaces^[2].

Fig. 1a and 1b display respectively FTIR spectra of CO adsorbed on electrodes of Pd⁰Y(e) and Pd⁰Y(c) supported on glassy carbon (Pd⁰Y(e)/GC, Pd⁰Y(c)/GC). Three strong bands

can be observed, one positive-going band near 2345cm⁻¹ assigned to IR absorption of CO₂, and two negative-going bands around 2060 and 1940 cm⁻¹ which are ascribed to IR absorption of linear (CO_L) and bridge (CO_B) bonded CO species. The FTIR spectrum of CO_{ad} on a massive Pd electrode is shown by Fig. 1c. Only two bands, a strong CO₂ band and a weak CO_B band, are appeared. It is evident that the IR absorption of CO adsorbed on Pd nanoparticles confined in supercages of Y-zeolite has been significantly enhanced. The values of the enhancement factor of IR absorption Δ_{IR} , which is defined as the ratio of integrate intensity of the CO_{ad} bands on Pd⁰Y/GC to that of the same quantity of CO on a massive Pd electrode, have been determined at 36.4 or 39.8 respectively on Pd⁰Y(e)/GC and Pd⁰Y(c)/GC electrodes. In order to figure out the origin of the enhancement of IR absorption of CO_{ad} on Pd⁰Y/GC electrodes, other Pd support materials were prepared: (1) Pd⁰ supported on Al₂O₃ by impregnation, calcinations and reduction (Pd/Al₂O₃/GC); (2) Pd⁰ supported on aluminosilicate formed by immersing Y-zeolite in acid solution (Pd-aluminosilicate/GC); (3) Pd⁰ dispersed directly by electrochemical deposition onto a Na⁺Y zeolite supported on Pt substrate (Pd⁰-Na⁺Y/Pt). Fig. 1d, e and f are spectra of CO adsorbed on electrodes of the three materials. Only CO₂ band is appeared in these spectra, indicating that the CO_{ad} bands are too weak to be distinguished. The results indicate that these materials do not present enhancement of IR absorption.

The single beam spectra of CO adsorbed on Pd⁰Y(e)/GC electrode at different E_S are displayed in Fig.2. Due to the enhancement of IR absorption, we can observe directly CO_B band in these single-beam spectra in the range between 1900 and 1950 cm⁻¹. Following the increase of E_S , the center of CO_B band is varied in three ways: (1) it decreases quickly in the potential range between -0.7 and -0.64V, yielding a Stark shift rate of -195 cm⁻¹V⁻¹; (2) it keeps a constant value about 1907cm⁻¹ from -0.64 to -0.50V, manifesting a Stark shift rate of 0 cm⁻¹V⁻¹; (3) it increases fast at E_S above -0.50V, manifesting a Stark shift rate of 187 cm⁻¹V⁻¹. In the case of a massive Pd electrode the Stark shift rate of CO_B band is measured only at 41 cm⁻¹V⁻¹. Therefore, we may speculate that this special phenomenon is related to the negatively charged environment resulting from the framework of the Y zeolite, which may interfere with the electric field surrounding the Pd particles.

The particular IR optical properties of Pd nanoparticles in supercages of Y-zeolite, i.e., the significant enhancement of IR absorption and the unusual Stark effects in CO adsorption, may be attributed to the nanometer scale of Pd

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particles and the special environment of Y-zeolite. The findings of this paper are of great importance in understanding the origin of novel effects of nanostructured materials.

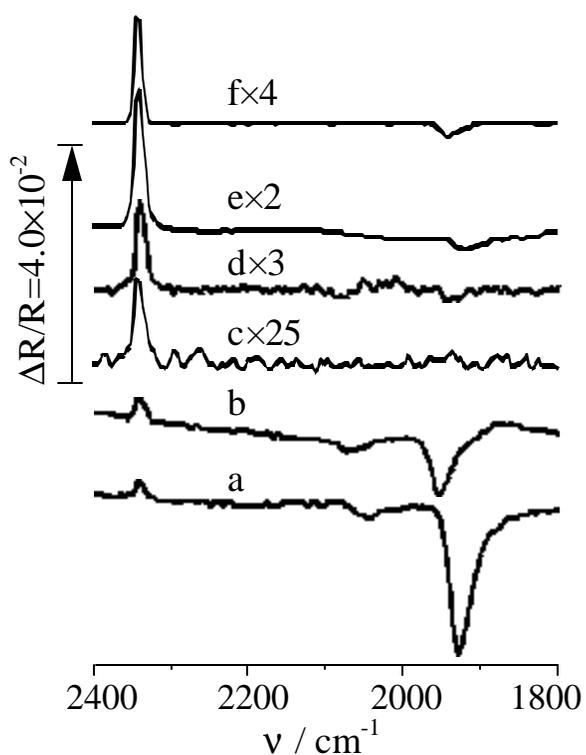


Fig.1 *In situ* spectra for CO adsorbed on: electrodes of (a) Pd⁰Y(e)/GC; (b) Pd⁰Y(c)/GC; (c) Pd⁰-Al₂O₃/GC; (d) Pd-aluminosilicate/GC; (e) Pd⁰-NaY/Pt; (f) massive Pd, 0.1M Na₂SO₄ (PH=3.3) solution, $E_s = -0.4V$ (vs. SCE), E_R is indicated for each spectrum.

References

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- [2] Z. Zhang, H. Chent, W. M. H. Sachtler, *J. Chem. Soc. Faraday Trans.*, 1991, **87(9)**: 1413.

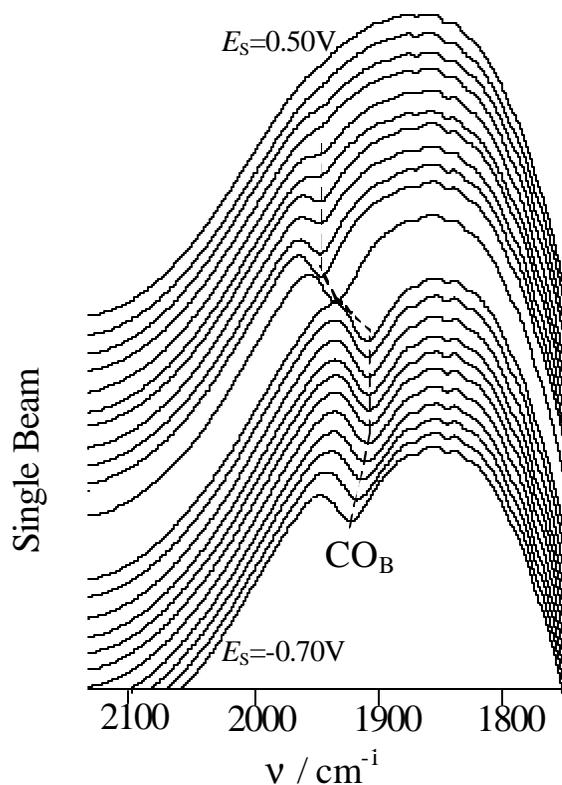


Fig.2 Single beam spectra of CO-Pd⁰Y(e)/GC in 0.1 M Na₂SO₄ solution (pH=3.3). E_s is increased gradually from -0.7 to 0.50 with interval of 0.02 V, the last four spectra are recorded at E_R (1.0V) at different oxidation time.