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DRIFTS Study of CO Adsorption on Pt Nanoparticles Supported by DFT Calculations

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Abstract

Extensive research has been devoted to the assignment of IR bands of CO adsorbed on Pt nanoparticles, which are widely used in heterogeneous and electro-catalysis (*e.g.* fuel cells). In contrast to single crystal studies, the assignment of CO adsorption to the nanoparticle structure is still controversial. Here we provide a case study where we assign CO adsorption bands to the structure of Platinum nanoparticles with a given size distribution. Using a special diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) cell allows to achieve high quality data under in-situ conditions. Temperature dependent CO adsorption spectra are resolved into three bands which depend on the applied flow and pretreatment conditions. Our calculations using Density Functional Theory (DFT) can mimic the experimental findings and link these bands to the particle structure. By explicitly calculating the IR spectra of CO/Pt nanoparticles of different sizes we show that the IR bands are due to a combined size and site effect. For fully-covered small nanoparticles the IR bands are attributed to all binding sites. For larger nanoparticles the dominant contribution is related to {111} facets but the other bands are still site independent. Here we provide a tool to assign CO adsorption bands on Platinum nanoparticles with a given size distribution. This can be related to the structure-acitvity relationship which is required for a tailored catalyst design.

Keywords: CO adsorption, DRIFTS, infrared spectroscopy, DFT, platinum nanoparticles, size distribution, size effect, EuroPt-1, adsorption sites.

Introduction

Carbon monoxide (CO) is a widely-used probe molecule for the characterization of catalysts [1, 2]. Infrared spectroscopy (IR) has been established since 1950's to monitor the CO vibrational stretching modes on metal nanoparticles [3]. The position of bands in the IR spectrum of adsorbed CO on the surface of a metal is very sensitive to adsorption sites, coverage of CO, and surface orientation, all of which cause changes in the dipole moment of CO upon adsorption. For nanoparticles, size distribution is an additional factor that determines the shape of the IR spectrum. The following range of wavenumbers has been observed for adsorption of CO with different coverages and different binding types on metal nanoparticles (*e.g.* Cu, Pt and Pd): atop bonded 2000 to 2100 cm^{-1}, bridge bonded 1800 to 1970 cm^{-1}, and three-fold hollow bonded 1700 to 1770 cm^{-1} [4–9]. In many cases, IR studies on Pt show that wavenumbers increase with the coverage of CO [8, 10, 11]. Brandt *et al.* [12] and Kappers *et al.* [13] found a linear relation of the wavenumber of atop bonded CO with the coordination number of the platinum atoms for both low and high CO coverage. Both studies show that independent of the coverage a similar wavenumber range of 2050 to 2100 cm^{-1} is observed for platinum with coordination numbers from 6 to 9. Friedrich *et al.* [10] have studied Pt nanoparticles of 2.2 nm and 8.5 nm under electrochemical conditions and found two bands at low CO coverages. A band at 2013 cm^{-1} was assigned to CO adsorption on small nanoparticles and a band at 2046 cm^{-1} to that on the larger ones, respectively [10]. Similar size effects have also been reported by other groups [14–17]. Maillard *et al.* have studied contributions from size and site dependency [11] using FTIR and electrochemical CO oxidation for Pt/C with

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