Can IR substitute X-rays? Quantitative analysis of vibrational spectra powered by machine learning

A. Bugaev[1], O. Usoltsev[2], A. Skorynina[2], D. Ferri[1], M. Nachtegaal[1]

[1]PSI, Villigen, [2]ALBA Synchrotron, Spain

Vibrational spectroscopies are widespread techniques for operando characterization of heterogeneous catalysts. Being sensitive to the vibrational structure of the adsorbed molecules, they are often used to identify chemisorption sites, reaction intermediates etc. At the other hand, evolution of the structural parameters of the catalyst itself, which often affects the catalyst's performance, often require bulk sensitive techniques, such as X-ray absorption spectroscopy (XAS), application of which is troublesome due to the demand for synchrotron radiation sources. In this work, we demonstrate how vibrational spectra can be used as a source of quantitative structural information by applying machine learning (ML) algorithms. Focusing on the palladium hydride phase formation in the supported palladium nanoparticles (Pd/Al_2O_3), which can occur during numerous industrially relevant hydrogenation reactions, we collected, under exactly identical conditions, XAS and diffusive reflectance infrared Fourier-transformed spectroscopy (DRIFTS) data in a wide range of temperatures and partial hydrogen pressures in presence of CO as a probe molecule. Then, ML algorithm was trained on the dataset made of experimental XAS and DRIFTS data, showing that it is possible to predict structural parameters of Pd nanoparticles from DRIFTS spectra of the adsorbed CO and revealing perspective descriptors of both structural parameters of palladium nanoparticles and DRIFTS data. The experimental results were supported by the density functional theory (DFT) calculations modelling the change in vibrational modes upon the formation of hydride phase.

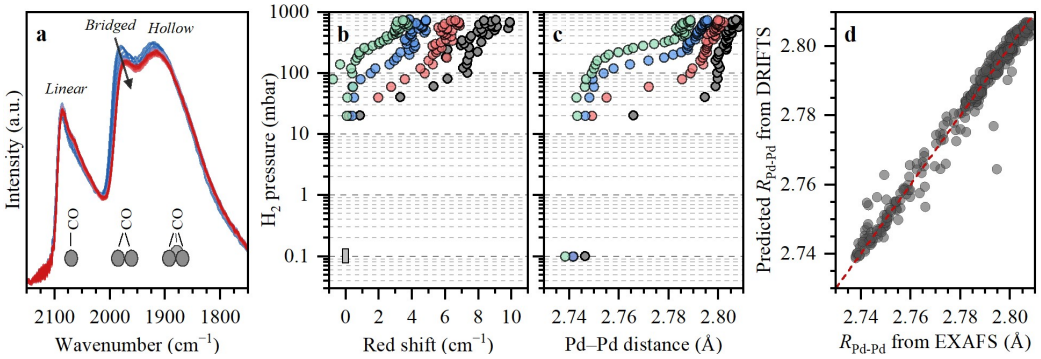


Figure 1. (a) Evolution of DRIFTS spectra in the region of CO vibration upon increase of the H_2 partial pressure (from blue to red) at 30 °C. (b) Red shift observed for bridge CO vibration upon increase of the H_2 partial pressure at 30 (black), 50 (red), 70 (blue) and 90 (green) °C. (c) Pd–Pd distance from EXAFS data measured under identical conditions. (d) Pd–Pd distance predicted from DRIFTS based on the absolute positions of three CO peaks versus true distance obtained from EXAFS.