Local structure of PdO/Al_2O_3 catalysts during aqueous phase reduction

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Pd catalysts are widely used in catalysed hydrogenation reactions for the synthesis of fine and bulk chemicals, which are often conducted in liquid phase. Since the Pd active phase is commonly deposited in its oxidised form on the support, previous works sought to study how the catalyst activation procedure affects the reducibility of the PdO phase, as well as the properties of the supported Pd nanoparticles (dispersion, particle size, morphology, interaction with the support, structural order, and surface properties), and how these factors correlate with the catalyst behaviour during hydrogenation [1].

In this work, we investigated the isothermal reduction of PdO (5 wt%) supported on different polymorphs of Al_2O_3 and their combinations using aqueous solutions of common reducing agents ($NaBH_4$, HCOONa), thus mimicking the procedure adopted by the catalyst manufacturer. For comparison, water saturated by H_2 was also used. In order to follow reduction at 65°C and ambient pressure, we used high-energy X-ray diffraction (HE-XRD) and pair distribution function (PDF) analysis at beamline ID15A of the ESRF to identify and quantify Pd components in both average and local structure, and thus separate long-range from shortrange structural effects.

Analysis of HE-XRD data (Rietveld) suggested that most of the supports are made of a lowersymmetry, inter-grown composite phase and not a mixture of the ideal structures of the various polymorphs [2]. Both HE-XRD and PDF analysis were able to clearly follow the isothermal consumption of the PdO phase upon reduction, the subsequent formation of metallic Pd and the nucleation of the Pd hydride phase with a time resolution of 1-2 s. The results reveal that the rate of the reduction process is influenced by the nature of the Al_2O_3 polymorph at constant PdO particle size. For example, γ-Al_2O_3 delayed significantly the formation of Pd hydrides under these experimental conditions. Reduction by H_2 was also slow probably as a result of the low solubility of H_2 in water. Chemically different reducing agents proved to require different concentrations in order to provide comparable extents of hydride formation, suggesting a different extent of reducing ability.

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