Modulation Excitation Hard X-ray Diffraction to Capture Red-ox Dynamics of Supported Pd Catalysts

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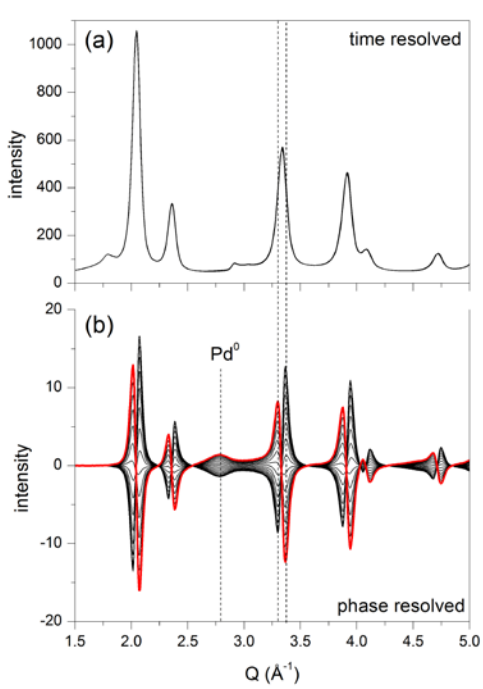
Introduction and Objectives

Bulk physical methods such as X-ray diffraction are considered silent with respect to surface dynamics. XRD is limited by crystallite size and therefore supported metal nano-particles of certain size limit are hardly accessible by XRD. However, synchrotron hard-XRD was used to unravel dynamics of metal nano-particles in Pd/Al_2O_3 [1]. Also, it is intrinsic to the bulk nature of XRD that a complete picture of the working catalyst can be obtained in one shot. Here we apply for the first time a concentration modulation excitation approach using phase sensitive detection [2] to observe reduction-oxidation of small Pd nano-particles supported on an otherwise 'difficult' oxide, ceria-zirconia (CZ).

Results and Discussion

A concentration modulation experiment consisted in the periodic switch between 1 vol% CO-He (25 sec) and 1 vol% O_2-He (25 sec) at 573 K on 2 wt% Pd/CZ in a homemade cell [3]. A modulation period is the time required to conclude a full CO vs. O_2 sequence. The sets of time-resolved XRD (100 patterns/period, 0.5 sec/pattern) were processed into sets of phase-resolved XRD by phase sensitive detection (PSD) [2,4]. PSD generates diffractograms free from contributions responding with a frequency different from that of the stimulation. Therefore, only the changes biased by the external stimulus, i.e. the concentration variation, are emphasized; all static signals are filtered out and do not appear in the phase-resolved data. The time-resolved hard-XRD data collected during a modulation experiment (100 XRD x 25 periods, Fig. 1) exhibit the reflections of cubic CZ but hardly display any tangible change. No information is available about the state of Pd. This is typically associated with the fine dispersion of PdO particles induced by CZ. The corresponding phase-resolved XRD data exhibit only the very subtle changes associated with the signals responding to the modulation experiment. All signals of the CZ support shift repeatedly to lower and back to higher Q values in response to the CO and the O_2 pulses, respectively. This behaviour qualitatively describes the reduction and the re-oxidation of CZ associated with its oxygen storage capacity. Importantly, the data also exhibit addi-



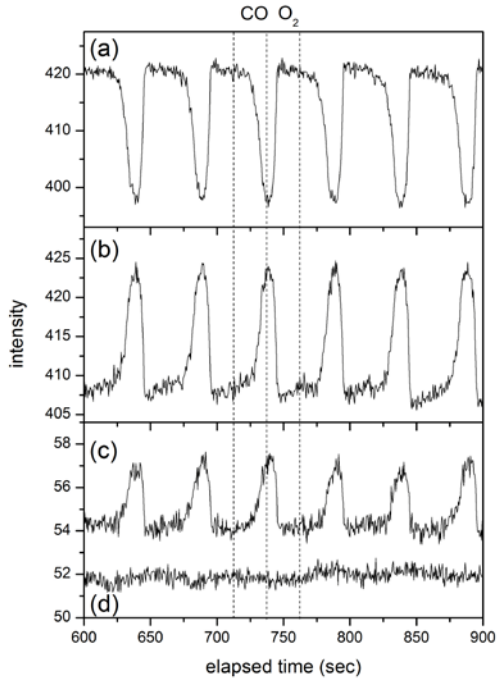


Fig. 1: (a) time resolved hard-XRD data during a CO vs. O_2 modulation experiment at 573 K on PdCZ; (b) corresponding phase-resolved data. Fig. 2: temporal evolution of signals marked in Fig. 1: (a) 3.4, (b) 3.3, (c) 2.8 $Å^{-1}$ and (d) 2.8 $Å^{-1}$ for CZ.

tional broad features (e.g. at ca 2.8 $Å^{-1}$) that correspond to metallic Pd reflections. The sole intensity change is associated with the relative increase of long range order attributed to PdO reduction. Therefore, the modulation data can capture the dynamic reduction and re-oxidation of PdO and CZ. From the PSD envelopes one can precisely assess the temporal behaviour of the structural changes using the time-resolved XRD patterns and access the detailed structural-dynamic behaviour of the system. Reduction of both PdO and CZ occurs much slower than re-oxidation (Fig. 2). Comparison with Pd/Al_2O_3 reveals that this is the effect of the OSC of CZ.

Conclusions

Modulation excitation spectroscopy and phase sensitive detection demonstrate powerful tools to increase the sensitivity of XRD to capture precious metal nanoparticles at work.

References

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