Quick low temperature coalescence of Pt nanocrystals on silica exposed to NO - the case of reconstruction driven growth.

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We report operando XRD/MS experiment on nanocrystalline Pt supported on silica monitoring quick growth of Pt in NO atmosphere. XRD data following NO flow show structural changes typical for surface reconstruction. This would mean that although small pressure of NO lifts surface reconstruction of clean surface, the high pressure of NO causes surface to reconstruct again. TEM photographs show formation of clusters of Pt nanoparticles pointing to growth controlled by coalescence. As surface reconstruction is the phenomenon we always see accompanying quick growth, we postulate mechanism of self-lifting cyclic reconstruction that drives transport of whole clusters and their fusion.

Below we show experimental results for 10% wt. Pt supported on SiO₂. Initial Pt crystal size 4 nm. A figure to the left shows evidence of NO disproportionation and NO₂ formation. The O₂ deficit at the beginning agrees with the sorption capacity of SiO₂.

The values from fig. C were used to fit the phases of quick growth (b-c-d, e, g, i) to the rate-power law of the form:

\[ \frac{dS}{dt} = -K_S S^n \]

where S is the exposed metal surface and Kₙ is constant. This can be rewritten in the form:

\[ \frac{dD}{dt} = K_D D^{2-n} \]

where D is the mean particle diameter D=6V/S, Kₙ=K₉(6V)⁻¹. This can be easily solved to the form:

\[ D(t) = (\frac{n-1}{n})^{1/(n-1)} K_D t + C \]

The best fit to the rate-power law results in the following powers: phase (b-c-d), n=14; phase (e), n=13; phase (g), n=20 and phase (i), n=40. These values for the initial process are similar to observed in literature for coalescence at 700 deg C but for the following growth are significantly higher than the reported in literature (typically 4-5) suggesting that the particle growth is very quick and its mechanism differs from normally observed diffusion driven growth. They also suggest that the mechanism of growth changes after phase (e), when possible diffusion mechanism starts to dominate.

The process of quick growth occurs only for NO and for Pt - not for Pd. The 4d metals differ from 5d metals in the latter having the ability of crystal surface to easily reconstruct. Due to mutual NO interactions the adsorbate reorganizes at higher coverages and surface sites are populated not sequentially with NO moving to more weakly adsorbing sites.

TEM (A, B) and STEM (C, D) images with histogram of size (E, F) for the reduced sample (left) and the exposed to NO at 80 deg C for two days (right). The particle size histograms include fit to a log-normal distribution (E, red curve, F - two fits: black and blue curve), to a log-normal distribution slightly modified to provide volume weighted average in agreement with XRD (E - blue curve) and to an exponential-power distribution (E - green curve, F - circles).

Coalescence in catalysis is known as a high temperature phenomenon - the observed process is the first example of a low temperature coalescence. It implies reconstruction of Pt surface occurring at high pressure coverage of NO. Such reconstruction at high pressure of NO at temperatures above 80 deg C is yet unknown phenomenon. Known phenomena of surface reconstruction of Pt involve significant movement of atoms. If the reconstructed surface changing number and energetic of chemisorption sites, desorbs part of a weakly bonded NO, that may lift the reconstruction providing necessary feed back for cycles of repeatable reconstruction and the surface mobility. This may pave sufficient drive to move whole Pt clusters over the support as well as means to build up a larger crystallite out of two smaller collided.

PXRD applied to nanocrystals is a unique tool detecting a high pressure surface reconstruction!