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

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We report an operando XRD/MS experiment on nanocrystalline Pt supported on silica, monitoring quick growth of Pt in an NO atmosphere. XRD data following NO flow show structural changes typical of surface reconstruction. Although a small pressure of NO lifts surface reconstruction of a clean surface, a higher pressure of NO causes the 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 that we always see accompanying quick growth, we postulate a mechanism of selflifting cyclic reconstruction that drives the transport of whole clusters and their fusion.

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1 Introduction

Due to use of Pt in automotive catalysts for the abatement of NO_x from engine vehicle exhausts, the interaction of NO with Pt surfaces is of great technological importance. Furthermore, high losses of Pt during commercial plant nitric acid production still have a high cost problem and the reaction runs at a substantial NO concentration. In all these processes Pt surface reconstruction phenomena play a significant but not fully understood role. In explaining the atomistic mechanisms of these processes a crucial contribution was achieved by surface science vacuum techniques. There is, however, growing awareness that to fully understand practical reactions, normal to high pressure experimental techniques are needed and that high pressure conditions make a difference for the atomistic picture of the adsorbate layer.¹ A range of helpful techniques have been developed in recent years (e.g. frequency sum generation,^{2,3} high pressure STM^{4,5}) but the versatile and direct technique of powder diffraction seems to be undervalued and neglected in surface studies. However, XRD, when applied in situ to nanocrystalline materials, can provide sensitive data that to a large extent relates to the crystalline surface and can be well understood and interpreted with little help by atomistic simulations.^{6,7} Using this technique, for example, we have shown the time evolution of the surface reconstruction of Pt during desorption of H₂ and the magnitude of the measured response could be scaled to the particle size.8

We present here an operando XRD/MS study of the sintering of Pt nanocrystals supported on silica in an NO atmosphere and at moderate temperatures. Surprisingly we observe quick,

stepwise growth of Pt nanocrystals at temperatures of 353 K and above, controlled at a given temperature by the time of exposition to NO. During this process, transmission electron microscopy shows clearly separated Pt crystallites forming clusters on the way to growing to a larger size.

A rapid sintering in NO has been already observed for Pt supported on γ -Al₂O₃ at 473 K,⁹ which may suggest that for the effect, if support related, the difference between the oxide supports is irrelevant. For Pt/Al2O3 ° the authors suggest a Pt atom transport mechanism through emission (vaporization) from small Pt clusters - a mechanism resembling Ostwald ripening. The suggested migrating species are volatile NOcontaining Pt complexes. This may add to the understanding of the experimental observation of weight loss of a platinum gauze during ammonia oxidation approaching a constant value at temperatures falling from 1170 K to 1000 K.10 During ammonia oxidation, NO is an intermediate product interacting with O_2 and the catalyst. The loss occurs in an oxidizing environment and may resemble the weight loss of Pt foil heated in air,11 attributed to volatile PtO2. Oxygen, however, at 473 K affects Pt crystal growth with a much lower rate of the process than NO.9 It is expected that the Pt emission at a given temperature should be more likely for Pt nanoclusters than for larger crystals. The literature offers not much data on possible complexes of Pt containing NO although some unstable nitrosyl complexes are likely to exist. Our experiments show rapid sintering at temperatures as low as 353 K (80 °C) and the rate rather weakly depends on temperature up to 473 K. Above this temperature no further sintering was observed. We observe a rapid sintering of metal nanocrystals supported on silica in NO atmosphere for Pt but never for Pd metal. It also has not been observed in a CO atmosphere. During Pt/SiO₂ exposure to NO at 80 °C dissociation of NO leads to a noticeable evolution of N2O and O2.

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Our results suggest the sintering mechanism of Pt on silica slowly changing with temperature, at the lowest temperatures (353 K), is a whole cluster transport followed by cluster coalescence, which is the rate determining process. This observation contradicts the general opinion that coalescence can be a rate determining process only at high temperature, with lower temperature growth controlled by diffusion.¹² Since a moderate increase of temperature triggers further particle growth, the pore structure of the support here is not an important limiting factor and crystallites are allowed to migrate to grow by coalescence upon collision. This unexpected mobility and sintering may be ascribed to a specific character of NO chemisorption.

NO has a similar electronic structure to CO but with an extra unpaired electron in its $2\pi^*$ orbital. The interaction with a transition metal surface is *via* hybridization of molecular 5σ levels with unoccupied d states (sigma donation) and hybridization of molecular $2\pi^*$ levels with occupied d states (pi backbonding). The latter effect dominates for Pd and Pt.

NO may dissociate at the Pt crystallite surface even at room temperature¹³ but this ability strongly depends on the crystal face exposed. The dissociated species may associate into desorbing N₂O with low activation barrier and much less likely to gaseous N₂.¹⁴ Although there is no evidence of non-dissociative sorption of NO on silica, small amounts of O₂ released together with N₂O from the metal may cause formation of an NO₂ layer strongly sorbed on the support,¹⁵ weakening adhesion forces between Pt clusters and the support and reducing the activation energy for surface migration. On the other hand the chemisorption of NO on Pd at RT is mostly associative and only a small fraction of molecules may dissociate on defects of the metal structure.¹⁶

Pd, as well as other 4d metals, differs from 5d metals in that the latter have the ability of the crystal surface being easily reconstructed.^{17,18} It is, for example, known that the clean (110) face of Pt undergoes so called missing-raw reconstruction,19 whereas chemisorption of gases lifts this reconstruction with the surface atoms returning to their nearly perfect fcc node positions. Similarly, (001) facets are known to reconstruct quasihexagonally, forming hexagonal patches on top of the square structure of the bulk.18 Under chemisorption, for example, of CO the surface returns to its square form. At low coverage, NO adsorbs on Pt atoms with the NO bond perpendicular to the surface in bridge positions, whereas on-top positions are the most stable at high coverage. With increasing coverage, surface sites are populated nonsequentially, moving to more weakly adsorbing sites.^{20,21} Due to mutual NO interactions the adsorbate reorganizes at higher coverage with NO molecules tilting from the vertical position, minimizing their intermolecular repulsion.22 Interacting NO molecules adsorbed at higher pressures and low temperatures form multilayer Pt coverage with a dense chemisorbed adlayer fed by a more weakly bonded (NO)₂ species that slowly desorbs but multi-layer adsorption may remain up to 385 K.20 The mechanism for the incorporation of NO to the chemisorbed layer is unknown although the phenomenon was observed also for CO on Cu (100).23 Heating the adsorbate layer above 200 K causes lifting of the initial surface reconstruction, which causes a two-fold increase in the

number of top layer Pt atoms. The NO atoms from the depleted chemisorbed layer can thus move to more energetically favourable bridge bonded sites. With further temperature rise the layer is ordered and finally NO desorbs.²⁰

The above experiments concern, however, in vacuo evolution. One can expect that at high NO pressure maintained during the heating the scenario can differ as the adsorbate evolution depends on the starting pressure during initial sorption.20 With high pressure and high frequency collisions of NO with the surface, frequent adsorption-desorption phenomena may significantly modify the above picture. Using arguments from XRD analysis of a Pt surface we postulate here that the surface reconstruction occurs for Pt nanocrystals at temperatures of 353-423 K under close to atmospheric pressure of NO. On missing-raw reconstruction the number of Pt atoms exposed to chemisorption per surface unit increases but the number of top layer Pt atoms decreases. This may weaken the adsorption, leading to partial desorption of NO. An increased strength of the remaining NO bonds may be, however, sufficient to lift the reconstruction. Such a feedback phenomenon may lead to a semi-oscillatory behaviour driving high surface mobility and enable quick coalescence of the collided nanocrystals even at relatively low temperatures. This possibility, to our knowledge, has never been exploited in the literature and no experimental proof seems to exist.

The interaction of supported Pt clusters cannot be explained by magnetic forces although NO carries some magnetic moment. Bridge site adsorption of NO on (100) facets may effectively quench the magnetic moment of an NO molecule whereas a top-site adsorption may leave residual NO magnetic moment on Pd(100) and may induce ferromagnetism on Pt and Pd, which are paramagnetic in the bulk form.²⁴ The Curie temperature for this induced magnetism is, however, predicted to be rather low (≤ 40 K).²⁵ This and the occurrence of sintering at higher temperatures suggests its magnetic origin to be rather unlikely.

2 Experimental

In the present study we have used samples of 10% (wt) Pt on amorphous silica (Davison 62, 100–120 mesh, 300 m² g⁻¹). The material was obtained by impregnation of silica with a required amount of chloroplatinic acid using an incipient wetness method. It was then mixed and dried. Samples of about 60 mg used for measurements were spread over a thin porous sintered glass disc and mounted vertically on the stainless steel heating block of our vacuum-proof XRD camera. The environmental camera of 150 ml volume was similar to that described before,8 with a removable cap with an X-ray window secured by a 12.5 µm self adhesive Kapton foil. It was connected to the gas line via Swagelok vacuum fittings and stainless steel flexible tubing, enabling XRD measurements in Bragg-Brentano geometry. The outlet gas was collected from the back side of the porous glass through the heating block, assuring close contact with the sample load. Between camera and the flexible tubing a union tee fitting (Swagelok) provided splitting the stream between the output and the probing capillary of a mass

spectrometer (Hiden Analytical). The gas feeding system consisted of pressured gas bottles and a gas line containing two stainless steel manifolds (A and B in Fig. 1) separated from the bottles' entries and from a vacuum rotary pump by normally closed on/off solenoid valves (1-12 in Fig. 1). The manifold outlets were fitted with two mass-flow controllers (MKS1259C, 13 and 14 in Fig. 1) and their outlets linked into one steel line feeding the camera. The system enabled a clean switch of a supplied gas by pumping off the manifolds as well as a quick exchange of gases in the camera by evacuating and flushing twice with the selected gas. The gases used were helium of 99.999% purity, hydrogen (99.9995%) and NO (99.5% purity with N_2 , N_2O and CO_2 as a principal contaminants). The gas composition was recorded every 1-2 min during repeating powder pattern collection in the angular range 20-140° lasting 45 min per pattern. The mass spectrometer (MS) sample consisted of m/z scan from 1 to 50 using a Faraday cup detector and a second scan with an SEM detector over m/z ranges having detected partial pressure lower than 10^{-7} atm. The time of one MS sample depended thus on the gas composition.

The temperature was controlled *via* two RE-15 controllers (Lumel) and K-type thermocouples fitted to the heating camera block and to the front side of the porous glass disc.

The powder diffraction patterns were collected on a D5000 powder diffractometer (Bruker AXS) equipped with LynxEye strip detector, providing good resolution and quick data collection. The Cu K_{α} radiation was employed with the X-ray tube operating at 40 kV and 40 mA.

The whole setup was controlled by an integrated Linux client-server network architecture and the measurements could be repeatedly performed under the control of measurement scripts.

The control of gas purity after clean exchange of gases to He routinely shows a decaying low level of H_2 escaping from the stainless steel walls of the camera and low background of water. The oxygen content remained at the level of several ppm. This level of contamination in the case of nanocrystals has much less effect than for single-crystals, where 1 ppm of a contaminant may fully cover its surface. In the nanocrystalline case, the same level of impurities may affect only small percent of metal nanoparticles. The as prepared sample loaded into the camera



Fig. 1 The XRD camera gas feeding system used in the experiments.

was dried in He at 50 °C for one day and then reduced in H₂ at the same temperature. The reduction progress was controlled via XRD showing a slow transition of PtCl₂ phase (JCPDS card 85-0840) into Pt metal fcc phase. The appearance of the PtCl₂ phase is in agreement with the suggested path of chloroplatinic acid hydrolysis to PtCl₄(H₂O)₂ proceeding slowly at RT during the material's shelf life.²⁶ Upon drying, the dehydrated PtCl₄, having measurable vapor pressure, dissociates when heated, evolving chlorine²⁷ and depositing PtCl₂. In our procedure the reduction to metallic Pt was nearly complete after a few hours but the sample was left in H₂ for one day. After the procedure few very weak maxima that could not be attributed to known crystallographic phase remained in the diffraction pattern. A conventional catalysis procedure to stabilize the sample by calcination at higher temperatures was applied to another sample and the results compared. At this stage, as well as at the end of further 80 °C treatment, part of the sample was been investigated by TEM (FEI Titan CUBED 80-300) in SEM mode as well as in high resolution.

3 Results and discussion

Williamson–Hall (W–H) analysis²⁸ of the XRD pattern of the reduced sample (Fig. 2) results in an average Pt crystallite size of 5.45 nm and a relatively small strain parameter of 0.002. For the size calculation we have used a Scherrer constant equal to 1.03 resulting from direct comparison of several peak widths of a diffraction pattern calculated for model fcc metal cubo-octa-hedra with atomistic model size.⁶ This size can be compared to the one from TEM analysis (Fig. 3E). The images reveal quite uniform and narrow distribution of well separated Pt nanocrystals with average diameter of 3.56 nm. As XRD peak broadening analysis refers to the volume weighted average of the size distribution, the corresponding average is equal to:

$$D_{\rm V} = \frac{\sum_{i=1}^{\infty} n_i d_i^2}{\sum_{i=1}^{\infty} n_i d_i^2}$$



Fig. 2 Evolution of the 111, 200 and 220 diffraction peaks during Pt/ SiO_2 sample treatment. Legend refers to the pattern number of Fig. 4.



Fig. 3 TEM (A and B) and STEM (C and D) images with histograms of size (E and F) for the reduced sample (left) and the exposed to NO at 80 °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).

where n_i is a fraction of crystallites of size d_i in the whole population of crystallites. For the presented distribution the $D_V = 4.24$ nm.

It may seem a meaningful misfit, but to put this comparison on a realistic ground one has to notice that the volume average $D_{\rm V}$ quite strongly depends on very small changes of the distribution for higher sizes (*e.g.* $d_i > 10$ nm). On the other hand the histogram data for this region is either missing or prone to substantial error as within the observed field there are only a few (if any) larger crystallites and their statistics are poor. It can be a question of the choice of the area looked at as well as a simple economy limiting the number of TEM photographs to tens and not to hundreds. To illustrate this point Fig. 3E together with the measured size histogram of 608 particles shows two log-normal distributions. Both fit well to the central part of the histogram and differ for larger sizes (D > 5 nm)involving only 3% of counted particles. For example, between 5 and 6 nm falls only 12 particles and the observed difference between the distributions equal to 40% corresponds to only 5 counted particles. If standard deviation (σ) of the counting statistics is proportional to the square root of the count number then the observed difference between the distributions

corresponds to less than 2σ , which is common in counting phenomena. However the D_V values calculated for the presented log-normal distributions are 4.31 nm (2.78 nm the number average size – red curve) and 5.45 nm (2.88 nm the number average size – blue curve) respectively, the second one being in perfect fit with the XRD data.

The above discussion points to different information that can be obtained from XRD and TEM, where the former shifts its focus toward larger crystallite sizes if they exist in the studied sample. Different average particle sizes from both methods are thus quite common.

The reduced sample was subjected to the following treatment at 80 °C: (a) exposed to He stream (40 ml min⁻¹, 3 h); (b) 16 cycles of: exposure to mixture of NO (20 ml min⁻¹) and He (20 ml min^{-1}) lasting 1 hour followed by flushing with He (40 ml \min^{-1}) for 3 hours; (c) flushing with He (40 ml min⁻¹, 10 h); (d) exposure to NO (40 ml min⁻¹, 33 h). The temperature was then increased to 100 °C and (e) kept for the next 26 h in NO (20 ml min^{-1}) and He (20 ml min^{-1}) till no noticeable sintering was seen. Subsequently the sample was flushed with He (40 ml min⁻¹) and temperature was further increased to 120 °C then the sample was (f) kept in He for a further 13.5 h and (g) exposed to NO (20 ml min⁻¹) and He (20 ml min⁻¹) for 25.5 h. It was followed by a He flush (40 ml min^{-1}) and further temperature rise to 150 °C with the sample (h) kept for 22.5 h till no sintering was noticed and (i) exposed to NO (20 ml min⁻¹) and He (20 ml min^{-1}) for 12.5 h till no further sintering observed.

The whole process lasting nearly 9 days was monitored by powder diffraction and MS with every pattern analyzed similarly as described before.⁸ For each Pt fcc diffraction peak its position, intensity (peak amplitude and integral) and width (full width at half maximum – FWHM) was determined. All the analyzed parameters resulted from a procedure fitting the diffraction peaks to an analytical profile.⁸ As the data evolution for all reflections agree qualitatively, to minimize statistical scatter of the parameters, the peak positions for 111, 200 and 220 reflections were recalculated to a corresponding value of lattice constant and averaged. Fig. 4 collects the time evolution of these parameters, together with marked composition of the gas and temperatures. Fragments of the 111 peak width evolution (Fig. 4C) at constant temperature have been fitted to the rate–power law curves that are further discussed.

Several phases of the above described gas and temperature treatment have been repeated on fresh samples of the catalyst to check repeatability. For the MS gas analysis the same treatment has been applied to the clean porous glass disc mounted in the camera for a blind test.

During NO cycles at the beginning of the experiment at 80 °C only a small amount of NO dissociates with evolution of N₂O (m/z = 44, Fig. 5). After the 3rd cycle O₂ (m/z = 32) appears in growing quantities, quickly arriving at the level of approximately half of the N₂O emission in agreement with a global stoichiometry of N : O = 1 : 1. The lacking amount of oxygen agrees roughly with the sorption capacity of silica. The intensity of the m/z = 32 MS signal has been corrected for a 0.002 fraction of the m/z = 30 signal due to the MS fragmentation pattern of NO, also involving the m/z = 32 signal. The minimum level of



Fig. 4 Evolution of Pt fcc phase control parameters of powder diffraction pattern. ALP is an apparent lattice parameter as obtained from the peak position (A), peak height is Pt 111 peak amplitude (B) and average crystal size is the measured FWHM of Pt 111 recalculated to size *via* the Scherrer formula. Red lines are the results of the rate–power law fit.



Fig. 5 MS sampling of the gases outgoing from the camera. Only residual gases shown with partial pressure of NO being about 6.1 \times 10^{-7} atm.

m/z = 44 (dashed line) agrees well with the blind test m/z = 44 content in the pressured bottle. A growth of a small quantity of NO₂ (m/z = 46) to the level of 0.05% of that of NO is also noticeable from Fig. 5. Fig. 5 covers the gas composition

evolution from the beginning up to the pattern number 130 in Fig. 4. Note the nonlinearity of the MS sampling rate with time, the latter being dependent on the gas composition.

Analyzing Fig. 4A one can notice a slight shift of the lattice parameter (LP) by 0.003 Å (on average) upward on cyclic exposition to NO at 80 °C (phase b). Switching the gas composition from NO to He should not cause quick desorption of strongly bonded NO at this temperature. For example, TPD experiments suggest NO desorption occurring above 150 °C.29 This is why we do not interpret the upward shift as a manifestation of the adsorption phenomenon. The visible sign of the adsorption is an upward shift of the measured LP, in agreement with a simple model where adsorption saturates the surface bonds and causes expansion of the contracted surface layer, increasing the average LP - the model has been positively tested in our laboratory on many examples. The downward shift is, however, visible at the beginning of phase h at 150 °C, which is interpreted as slow (3 h) desorption of NO ending with by reconstruction of the surface with the LP shifted up. It is accompanied by rise of the peak height, in agreement with the analogous observation of the process of Pt surface reconstruction on desorption of hydrogen.8 Here the NO desorption is slow, running slightly below the thermodynamic temperature of desorption. Then, it is natural to interpret the cyclic LP shift upwards as a reconstruction of the Pt crystallite surfaces.

The observed phenomenon evidently concerns only the surface of the monitored Pt fcc phase. The upward shift of LP signifies the expansion of the Pt nanocrystal surface. It does not affect the scattering intensity (Fig. 4B) changing only due to gas X-ray absorption, so the observed structural transformation is not due to a deepening disorder of the surface. The measured effect is of just the same magnitude as observed by us before for surface reconstruction during H_2 desorption.

It is known, as stated in the introduction, that a multilayer adsorption of NO at high pressure causes shift of NO molecules from strongly to more weakly bonding sites while increasing the number of bonded molecules,²⁰ which may weaken the interaction with the surface to the point when it starts to behave like a clean surface and reconstruct or may interact specifically, promoting reconstruction. Exposition to He would cause weakly bonded NO to desorb with the remaining molecules moving back to the strongly bonding sites – the process lifting the reconstruction and moving the surface Pt atoms back to their lattice nodes.

In our study of Pt nanocrystal reconstruction during desorption of H₂⁸ its effect on diffraction peak position has been measured. For ~4.5 nm Pt crystallites and a temperature of 100 °C, we recorded the shift of the 111 reflection on reconstruction to be about 0.1° corresponding to a 0.01 Å shift in LP. The analogous shift of LP for Pt 3.1 nm crystallites was 0.02 Å (Fig. 7 of ref. 8). As the square of size ratio is 1 : 2, its decrease with the nanocrystal size is expected to be inversely proportional to the average nanocrystal surface. From Fig. 4A we can estimate LP shift for the beginning of phase (b) (estimated size 5.65 nm), transition from the phase (c) to (d) (size 6.95 nm), at 120 °C (size 9.45 nm), and at 150 °C (size

11.05 nm). These values, 0.003(4) Å, 0.0018(8) Å, 0.0024(3) Å and 0.0018(4) Å, correspond to those expected from the growing surface: 0.0064 Å, 0.0042 Å, 0.0023 Å and 0.0017 Å, respectively. The figures in parentheses give the standard deviation of the last figure estimated from averaging LP values over 10 points before and after the shift edge. The observed LP shift is about half of that expected for small nanocrystals and agree with the expected for larger sizes. As the expected values correspond to a full surface reconstruction it suggests that we do not observe full reconstruction of the whole Pt surface, with various fragments dynamically changing their state. The observation that the LP shift approaches its expected value for larger crystallites may be due to its growing surface with a decreasing fraction being in contact with other coalescing particles. Thus an increasing with size fraction of the surface undergoes reconstruction.

The LP (Fig. 4A) in phase (e) shows a marked increase during quick crystallite growth. This effect has been discussed before.⁶ The further evolution of the LP agrees well with the temperature lattice expansion of Pt assumed to be $8.8 \ 10^{-6} \ \text{K}^{-1}$.

Fig. 4B shows evolution of the 111 peak amplitude. The rate of growth is highly correlated with the estimated crystallite size *i.e.* inversely proportional to FWHM. The curve was not corrected for the X-ray absorption by gas in the camera but the visible oscillations as well as shifts on gas exchange are well described by this varying absorption of gas and are not interpreted structurally.

Fig. 4C presents evolution of the average crystallite size estimated directly from the FWHM using the Scherrer formula. The routine did not account for the material strain. To check its effect for several patterns the full range W–H analysis has been done, showing approximately constant strain parameters. This analysis also provides a slight correction to the values presented in Fig. 4C. No instrumental broadening was considered as for the studied particle sizes it provides negligible correction.

As the W–H correction is nearly constant, the values from Fig. 4C were used to fit the phases of quick growth (b–c–d, e, g, i) to the rate-power law of the form:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = -K_{\mathrm{S}}S^{n}$$

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

$$\frac{\mathrm{d}D}{\mathrm{d}t} = K_{\mathrm{D}}D^{2-n}$$

where *D* is the mean particle diameter D = 6V/S, $K_D = K_S(6V)^{n-1}$. This can be easily solved to the form:

$$D(t) = ((n-1)K_{\rm D}t + C)^{\frac{1}{n-1}}$$

The mean *D* in the formula above is a surface weighted average that differs from both the number weighted value (directly from TEM) and volume weighted average, from the Scherrer formula and XRD data. Assuming a log-normal distribution of crystallite size that widens during the process, we have tested several approximations to follow evolution of the surface weighted size average. However the best fit powers do not depend strongly on

these approximations as their evolution remains very similar, and the same set of values could be kept.

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 for coalescence at 700 °C ³⁰ but for the following growth are significantly higher than those reported in the literature (typically 4–5),³⁰ suggesting that the particle growth is very quick and its mechanism differs from the normally observed diffusion driven growth. They also suggest that the mechanism of growth changes after phase (e), when possibly a diffusion mechanism starts to dominate. The value of rate power does not necessarily characterize a simple process. In practice, a quite complex sequence of processes affecting sintering may change its value.²⁶

At the end of phase (d), part of the sample was analyzed by TEM and Fig. 3 shows representative pictures (B, D, F) compared with the initial sample after reduction (phase (a) – A, C, E). The tendency for Pt nanocrystals to group in clusters is striking. Linking this with the mean crystallite growth observed by XRD brings a natural conclusion that the coalescence is the growth rate determining phenomenon up to phase (d). Considering the evolving powers of the rate-power law, it probably dominates also during phase (e).

Quick growth of Pt nanocrystals supported on silica has been observed in our laboratory many times in various experimental setups. Fig. 6 shows an example of a quick sintering in NO



Fig. 6 An example of quick sintering for calcined 10% Pt/SiO_2 kept in NO at 200 $^\circ\text{C}.$

atmosphere at 200 °C measured using position sensitive detector INEL CPS120. The fresh sample was calcined in O₂ at 400 °C and reduced in H₂ at 500 °C for 6 h with Pt crystallites size of ~8 nm. Then the sample was briefly flushed with helium at 200 °C and exposed to NO (20 ml min⁻¹). The presented diagrams are rather noisy but the effect of surface reconstruction is clearly visible, accompanied by quick crystal growth with fitted rate power n = 6. It suggests that the actual mechanism of growth can be modified but the process is always observed together with reconstruction phenomena. Interestingly Fig. 6 suggests also a slight shape anisotropy of the Pt nanocrystals with maximum size in the 111 direction. This was also the direction of the quickest growth.

The experimental data presented above do not fully explain the precise atomistic mechanism of the observed coalescence. An answer to the question of why it occurs for Pt but was never observed for Pd may lay in a mechanism of nanocrystal transport specific to Pt as well as in a mechanism of growth of the collided nanocrystals specific to Pt. Upon collision, the collided surfaces should easily link as the chemisorption energies of NO reported in the literature^{31,32} are by far lower than the Pt cohesion energy. The cohesive energy of Pd is lower (3.94 eV versus 5.86 eV for Pt) but still larger than the chemisorption energy of NO (in the range 1-2 eV). The further build-up of larger nanocrystals requires, however, substantial mass transport and this may be provided by the reconstructing surfaces. The number of atoms exposed on reconstructed and unreconstructed surfaces is different and the phenomenon should involve mass transfer. It can be speculated that the reconstruction may cause desorption of a part of the sorbed NO, which can move to stronger bonding sites. It could then trigger lifting of the reconstruction, initiating cyclic surface rearrangement. This should provide an efficient mechanism for the motion of the whole clusters over the support. A traditionally considered mechanism is the nucleation of new monoatomic layers of the crystal facets, with its rate estimated from nucleation theory.9 But the surface reconstruction provides the necessary movement of surface atoms. The traditionally considered coalescence could provide sufficient mobility to 6 nm Pt nanocrystals on supports at temperatures above 600 °C.26,30 This is why it was rejected in literature as a possible factor affecting Pt sintering at low temperatures.9 However, the reconstruction phenomena can provide both a mechanism of cluster transport and a mechanism of growth.

Some light on the atomistic mechanism of sintering can be shed by TEM observations of Pd nanocrystals after heating in NO. If the mechanism is limited only to 5d transition metals, the experiments on Ir supported on silica can also add to an understanding of the phenomenon. Such experiments are in preparation. The shifts of the measured peak position observed by XRD agree very well with the reconstruction of the Pt nanocrystal surface studied by us and we know of no other phenomenon that could explain such behavior. A shift in the diffraction peak position is always connected to changing the distribution of atoms in the observed crystallographic phase. We observed cyclic shifts on exposition to NO conserving the fcc ordering. It is natural to ascribe them to surface phenomena. Crucial for the interpretation is the assumption that NO does not quickly desorb at 80 °C. TPD studies, *e.g.* ref. 29 with the heating rate 7 K s⁻¹, report desorption of NO at above 150 °C and possibly higher for very small nanoparticles. The desorption peak has, however, significant width and the desorption with low rate can be observed even below the desorption temperature. In our case, the process was already sufficiently slow at 150 °C to be observed over several hours with characteristic signs of surface reconstruction at the final stage.

The observed low temperature growth is specific to Pt. It was never observed below 80 °C and it is postulated here that the reconstruction provides a crucial mechanism driving quick coalescence at low temperature.

4 Conclusions

The presented results from TEM as well as from an operando XRD/MS study provide strong evidence that the low temperature, quick growth of Pt nanoparticles supported on silica, exposed to NO, results from coalescence. As coalescence in catalysis is known as a high temperature phenomenon, this opens up a question about a possible mechanism of low temperature coalescence. Our former experience in observation of reconstruction of Pt nanoparticles surface on desorption of H2 8 by XRD allows us to understand the peak position evolution in NO. It implies reconstruction of Pt surfaces occurring at high pressure coverage of NO. Such reconstruction at high pressure of NO at temperatures above 80 °C is as yet an unknown phenomenon. Known phenomena of surface reconstruction of Pt involve significant movement of atoms. If the reconstructed surface, changing number and energetics of chemisorption sites, desorbs part of weakly bonded NO, that may lift the reconstruction providing necessary feedback for the surface mobility. This may pose 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 crystallites. The proposed mechanism needs further confirmation both experimentally and theoretically. This low temperature coalescence could be used for a controlled Pt growth with a predictable size distribution or in selective growth of Pt nanocrystals in mixtures. The phenomenon and its mechanism is new and has never been reported previously in the literature.

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References

- 1 A. G. Somorjai and J. Y. Park, Phys. Today, 2007, 48-53.
- 2 H. J. Freund, H. Kuhlenbeck, J. Libuda, G. Rupprechter, M. Baumer and H. Hamann, *Top. Catal.*, 2001, **15**, 201–209.
- 3 X. C. Su, P. S. Cremer, Y. R. Shen and G. A. Somorjai, *J. Am. Chem. Soc.*, 1997, **119**, 3994–4000.

- 4 P. Thostrup, E. K. Vestergaard, T. An, E. Lgsgaard and F. Besenbacher, *J. Chem. Phys.*, 2003, **118**, 3724–3730.
- 5 R. T. Vang, E. Lgsgaard and F. Besenbacher, *Phys. Chem. Chem. Phys.*, 2007, **9**, 3460–3469.
- 6 Z. Kaszkur, J. Appl. Crystallogr., 2000, 33, 87–94.
- 7 Z. Kaszkur, J. Appl. Crystallogr., 2000, 33, 1262–1270.
- 8 P. Rzeszotarski and Z. Kaszkur, *Phys. Chem. Chem. Phys.*, 2009, **11**, 5416–5421.
- 9 P. Lööf, B. Stenbom, H. Norden and B. Kasemo, *J. Catal.*, 1993, 144, 60–76.
- 10 S. L. Handforth and J. N. Tilley, *Ind. Eng. Chem.*, 1934, 26, 1287–1292.
- 11 H. S. Taylor, J. Phys. Chem., 1926, 30, 145-171.
- 12 E. Ruckenstein and B. Pulvermacher, *J. Catal.*, 1973, **29**, 224–245.
- 13 W. F. Banholzer, Y. O. Park, K. M. Mak and R. I. Masel, *Surf. Sci.*, 1983, **128**, 176–190.
- 14 W. Hong, R. G. Tobin, C. L. DiMaggio, G. B. Fisher and D. K. Lambert, *J. Chem. Phys.*, 1997, **107**, 9569–9576.
- 15 N. D. Parkyns, Catal., Proc. Int. Congr., 5th, 1972, 12, 255–264.
- 16 D. Loffreda, D. Simon and P. Sautet, J. Chem. Phys., 1998, 108, 6447–6457.
- 17 K.-M. Ho and K. P. Bohnen, *Phys. Rev. Lett.*, 1987, **59**, 1833–1836.
- 18 S. Titmuss, A. Wander and D. A. King, *Chem. Rev.*, 1996, 96, 1291–1305.

- 19 C.-M. Chan, M. A. van Hove, W. H. Weinberg and E. D. Williams, *Solid State Commun.*, 1979, **30**, 47–49.
- 20 W. A. Brown, R. K. Sharma, Q. Ge and D. A. King, *Phys. Chem. Chem. Phys.*, 1999, **1**, 1995–2000.
- 21 E. H. Backus, A. Eichler, M. L. Grecea, A. W. Kleyn and M. Bonn, J. Chem. Phys., 2004, 121, 7946–7954.
- 22 B. Hammer and J. K. Norskov, Phys. Rev. Lett., 1997, 79, 4441-4444.
- 23 J. C. Cook and E. M. McCash, Surf. Sci., 1996, 356, L445.
- 24 K. C. Hass, M.-H. Tsai and R. V. Kasowski, *Phys. Rev. B:* Condens. Matter Mater. Phys., 1996, 53, 44-47.
- 25 G. A. Mulhollan, R. L. Fink and J. L. Erskine, *Phys. Rev. B:* Condens. Matter Mater. Phys., 1991, 44, 2393–2395.
- 26 J. R. Anderson, *Structure of Metallic Catalysts*, Academic Press, 1975, p. 182.
- 27 T. A. Dorling, B. W. J. Lynch and R. L. Moss, *J. Catal.*, 1971, **20**, 190–201.
- 28 G. K. Williamson and W. H. Hall, *Acta Metall.*, 1953, 1, 22–31;
 V. D. Mote, Y. Purushotham and B. N. Dole, *J. Theor. Appl. Phys.*, 2012, (6), 6.
- 29 E. I. Altman and R. J. Gorte, *J. Phys. Chem.*, 1989, **93**, 1993–1997.
- 30 P. J. F. Harris, Int. Mater. Rev., 1995, 40, 97-115.
- 31 W. A. Brown and D. A. King, J. Phys. Chem. B, 2000, 104, 2578–2596.
- 32 H. Tang and B. L. Trout, J. Phys. Chem. B, 2005, 109, 17630-17634.