

# Catalyst nanoparticles stabilization and/or redispersion: A new anti-sintering strategy based on the effect of the $O^{\delta-}$ electric double layer account of metal-support interactions.

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## Introduction

Effective promotion of catalytic reactions performance is always a grand challenge for heterogeneous catalysis [1-5]. Nevertheless, catalyst nanoparticle stabilization (anti-sintering behaviour) at the typically elevated operation temperatures of catalysis is at least of equivalent, unless of much more importance. Sintering of catalyst nanoparticles is inevitably a leading cause of the degradation of industrial catalysts used for energy and environmental applications as well as for large-scale synthesis of commodity chemicals with obvious economic drawbacks; this justifies the intense research interest on the topic [6-7]. Nanoparticles sintering in supported catalysts implicates two main mechanisms [7, 8]: the so-called Particle Migration and Coalescence (PMC), which concerns the coordinated motion of multiple atoms clusters on the support surface with subsequent coalescence leading to particles growth, and Ostwald ripening (OR), which refers to atomic particles migration from smaller to larger nanoparticles, driven by differences in free energy and local adatom concentrations on the support surface. Since all heterogeneous catalysts are inevitably subjected to sintering during operation and/or catalyst regeneration procedures [6], regardless of what sintering mechanism dominates, the effect poses a grand challenge for the development of sinter-resistant catalysts [8-11].

We have found that the *effective-double-layer*,  $[O^{\delta-}, \delta^+]$  -spontaneously created on the catalyst nanoparticle surfaces via metal-support interactions due to thermally-driven lattice oxygen spillover from supports with substantial oxygen ion lability onto the nanoparticle surfaces [4,5]- can play a key role not only on the intrinsic catalytic activity of the particles [1-3], but also on their sintering behavior [9-11]. This oxygen ions  $O^{\delta-}$  electric layer on the surface of catalyst particles can effectively stabilize their nano-structure even at extreme (high temperature) oxidative sintering conditions, an effect of great importance in heterogeneous catalysis and especially in the cases of catalysts that are prone to sintering or used in high temperature processes. We have developed a mechanistic model which convincingly explains the anti-sintering (anti-PMC and anti-Ostwald ripening) induced by the  $O^{\delta-}$  layer and is schematically shown in Fig. 1.

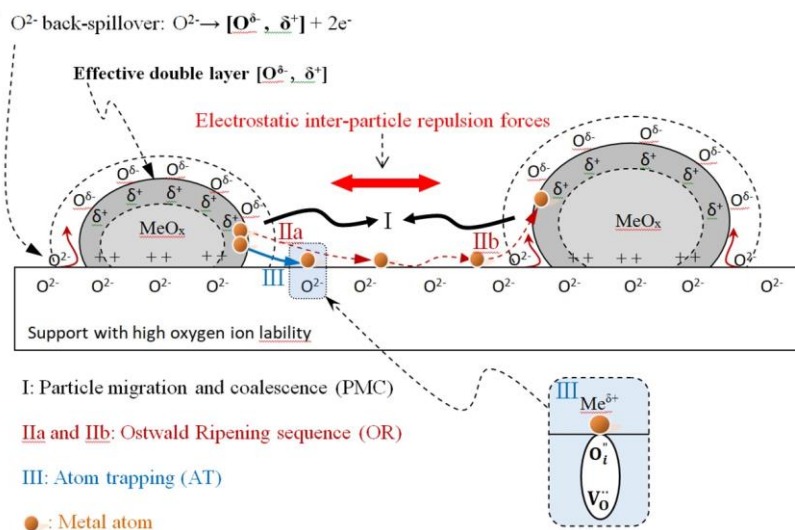


Figure 1. Model for anti-sintering behavior (anti-PMC and anti-OR) and redispersion induced by the simultaneous action of interparticle repulsion forces arising from the  $O^{\delta-}$  layer and atom trapping at oxygen ion vacancies.

In brief, the  $O^{\delta-}$  layer created on catalyst particles interfaced with supports with high oxygen ions lability endows the particle with a net negative charge at its gas-exposed surface, leading to inter-particle repulsion at short range, thus preventing particle-particle encounters followed by coalescence (anti-PMC). At the same time, the  $O^{\delta-}$  modifies surface barrier present on large catalyst particles increasing the activation energies for detachment and reattachment of metal entities whose transport would otherwise lead to continuous growth of large particles at the expense of smaller particles according to the OR model (anti-OR). In addition, atomic trapping by surface oxygen vacancies ( $V_o^{\bullet\bullet}$ ) [2] existing on supports with high oxygen ions lability acts as a contributing factor in the anti-OR mechanism or even better can lead to re-dispersion [9].

Here, we report results on the resistance, or lack of resistance, to sintering and even the in situ redispersion at high-temperature oxidative conditions of Ir and Rh nanoparticles dispersed on supports encompassing a wide range of lattice oxygen ion lability.

## Experimental

Commercial or laboratory made (via co-precipitation)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, ACZ (80wt%Al<sub>2</sub>O<sub>3</sub>–20wt% Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2- $\delta$</sub> ), CZ (Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2- $\delta$</sub> ), GDC (10mol%Gd<sub>2</sub>O<sub>3</sub>-CeO<sub>2</sub>) and YSZ (8mol%Y<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>) oxide supports were used for the deposition of Ir and Rh nanoparticles, via wet impregnation, at a nominal metal loading of ~1wt%. Textural, structural and morphological characterizations of the as-produced catalysts were performed by using BET, H<sub>2</sub>-chemisorption, H<sub>2</sub>-TPR, XRD and TEM techniques, among others.

## Results and Discussion

Figure 2 shows the sintering behavior of Ir (Fig. 2a) and Rh (Fig. 2b) nanoparticles under high temperature oxidative treatment (see figure caption for details) when dispersed on supports with different OSC. A strong correlation is evident in both cases. Independent of the nature of metal particles, supports with low or zero OSC (Al<sub>2</sub>O<sub>3</sub> or YSZ) do not prevent particle growth; the opposite is true for supports with high OSC. For Rh particles, in particular, dispersed on supports with high OSC the sintering treatment can cause even re-dispersion.

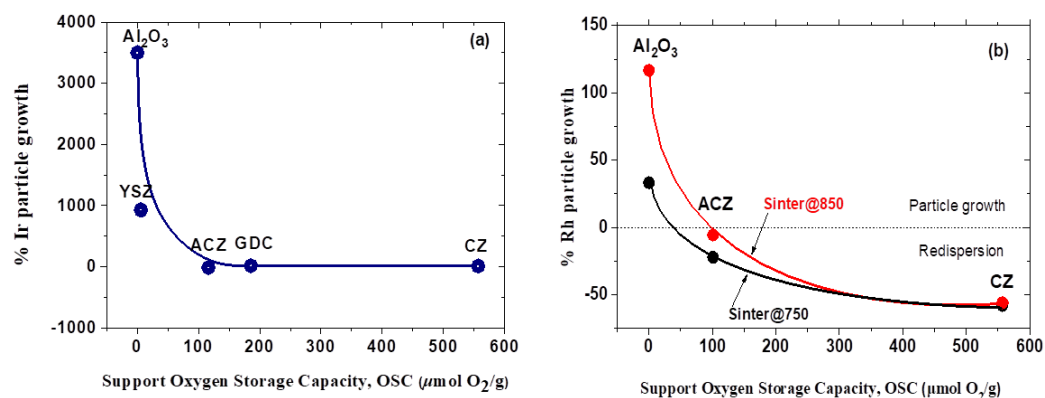


Figure 2. Percentage Iridium (a) and Rhodium (b) particle growth (positive values) or redispersion (negative values) as a function of the oxygen storage capacity (OSC) of the support for Ir catalysts sintered at 750°C for 2h and Rh catalysts sintered at 750°C for 2 h (sinter@750) or at 750°C for 2h + 850°C for 2h (sinter@850) at oxidative atmosphere (air).

## Conclusions

Supports with negligible OSC (e.g.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, YSZ) provided no or little resistance to sintering of catalyst nanoparticles. In striking contrast, high resistance to sintering and even redispersion of catalyst nanoparticles resulted on supports characterized by moderate and high OSC values (ACZ, GDC and CZ, respectively). These findings provide a new methodology for sintering prevention or even in situ controlled redispersion of metal catalyst particles. A model has been developed convincingly explains the obtained results. The new methodology of catalyst nanostructure stabilization and/or particle redispersion is of significant fundamental and practical importance for energy and environmental applications (such an implementation is included in the full paper).

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