

# Study of the reaction mechanisms between Pt(acac)<sub>2</sub> and alumina surface sites

## Application to a new refilling technique for the controlled variation of the particle size of Pt/Al<sub>2</sub>O<sub>3</sub> catalysts

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### Abstract

A new preparation technique is presented allowing the controlled variation of the average size of platinum particles in small steps of 0.2–0.5 nm in the size range between 1 and 2 nm. The particle growth is achieved by refilling, i.e. by increasing the metal loading of a parent catalyst in a separate preparation step. The technique makes use of the selective decomposition of a platinum complex, platinum bis-acetylacetonate, Pt(acac)<sub>2</sub>, on reduced platinum particles. Anchoring of the complex on the surface of the support and thus appearance of new small particles is completely avoided by appropriate surface treatments developed on the basis of a study of the reaction mechanisms between Pt(acac)<sub>2</sub> and the support. Three types of surface sites could be identified in this study by their specific reactivity towards Pt(acac)<sub>2</sub>. A model is presented describing the nature of these sites, the occurrence of which is correlated with the degree of dehydroxylation of the alumina surface. The efficiency of the new technique in increasing the particle size while reducing to a minimum any broadening of the initial narrow size distribution is demonstrated. The results are discussed in terms of particle shapes and two- and three-dimensional growth mechanisms.

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### 1. Introduction

The catalytic properties of supported metals are determined by a number of parameters of which one of the most important is the size of the metal particles. Many

attempts have therefore been made to prepare series of catalysts with different particle sizes and size distributions as narrow as possible in order to establish meaningful relationships between size and properties. One of the methods commonly used to vary this parameter is sintering of the metallic phase at elevated temperatures under specific atmospheres [1–3]. Particle growth by sintering is, however, difficult to control since it involves a number of random processes, like migration, collision and coalescence of particles, or emission of surface atoms by one particle and their capture by others (see, e.g., the detailed studies of sintering processes in [4,5]). Both processes are size dependent. Small particles are more mobile than large ones and are progressively consumed by collisions with other particles. Interparticle mass transport by emission of surface

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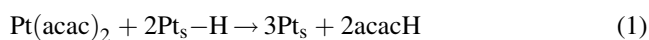
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atoms also occurs preferentially from smaller to larger particles. Sintering may cause a very rapid particle growth resulting in particle size distributions extending from a few to several tens of nanometers [4,5]. Moreover, redispersion, i.e. splitting of large particles into several smaller ones may occur simultaneously with sintering under certain conditions [6], leading to a bimodal size distribution with coexistence of small and large particles. It is obvious that conclusions on particle size effects drawn from samples with large or bimodal size distributions must remain ambiguous.

Alternative methods have therefore been developed with the aim to better control the particle growth process. One of these methods consists in increasing the metal loading of a parent catalyst by refilling, i.e. by the controlled anchoring of further metal on the particles of the parent catalyst in a separate preparation step. The technique makes use of the principle of Controlled Surface Reactions [7] now widely used for the preparation of monometallic [8] and bimetallic [9–11] catalysts. However, the high reactivity of certain alumina surface sites towards commonly used precursors, like platinum bis-acetylacetonate,  $\text{Pt}(\text{acac})_2$ , leads to anchoring not only on metal particles, but also on reactive surface sites. The consequence of such a nucleation of new particles is a bimodal size distribution with simultaneous presence of large and small agglomerates. Nucleation is thought to take place on surface ions, which are coordinatively unsaturated (c.u.s.) due to the treatments the support has been exposed to before. These can be any high temperature treatment having partially dehydroxylated the surface (e.g. calcinations) or any step during the production process having led to a defective surface structure. C.u.s. aluminium and oxygen ions act as strong Lewis acid and base sites, respectively. Nucleation sites must therefore be saturated prior to the refilling run to avoid undesired competing reactions. This problem has previously been overcome by saturating reactive sites by the precursor itself, which necessitated extremely high metal loadings of more than 10 wt.% and led to size distributions extending from 1 to more than 5 nm [12].

We therefore developed an improved refilling technique, allowing the controlled variation of the particle size in the range between 1 and 2 nm. This interval is of particular importance since it comprises the particle sizes of technically relevant catalysts and it is also the domain where the variations of catalytic properties with particle size are strongest [13–16]. The new technique is, like previous methods, based on the principle of Controlled Surface Reactions. It consists in the selective decomposition of  $\text{Pt}(\text{acac})_2$  on reduced platinum particles of a parent catalyst and can be described by the following equation:



where  $\text{Pt}_s$  denotes a surface platinum atom and  $\text{acacH}$  stands for acetylacetone.

The safest way to avoid nucleation of new particles during the refilling run is to completely inhibit any

adsorption of  $\text{Pt}(\text{acac})_2$  on the support which necessitated the development of an appropriate surface treatment. Previous work on  $\text{H}_2\text{PtCl}_6$  [17,18] has shown that the interaction between precursor and surface depends critically on the nature of the surface sites. In contrast to  $\text{H}_2\text{PtCl}_6$ , however, little is known about the way  $\text{Pt}(\text{acac})_2$  interacts with alumina surfaces. van Veen et al. [19] reported immediate complete decomposition of the complex on c.u.s. aluminium of dehydroxylated supports and additionally physisorption on hydroxylated surfaces. Other authors reported the loss of the two ligands of  $\text{Pd}(\text{acac})_2$  [20] and  $\text{Ni}(\text{acac})_2$  [21] in two separate steps and no adsorption of  $\text{Pt}(\text{acac})_2$  on hydroxyl groups [22]. A detailed study of alumina surface properties, the incidence of various surface treatments, the nature of the resulting surface sites, and their respective reactivity towards  $\text{Pt}(\text{acac})_2$  was therefore necessary.

Our work is divided into two parts: the first part is devoted to the study of alumina surface properties and reaction mechanisms of  $\text{Pt}(\text{acac})_2$  with alumina surfaces. In the second part, we present first results of controlled particle growth studied by transmission electron microscopy (TEM) and discuss these results in terms of particle shape and two- and three-dimensional growth mechanisms. We further discuss the incidence that sintering may have on the particle growth.

## 2. Experimental

### 2.1. Sample preparation

Samples were prepared on pellets of  $\gamma$ -alumina of a diameter of 2 mm and a specific surface area of 200 m<sup>2</sup>/g supplied by Axens.

#### 2.1.1. Preparation of highly dispersed first generation catalysts

Several methods of surface pre-treatments prior to impregnation with  $\text{Pt}(\text{acac})_2$  were tested in order to study the interaction mechanisms between  $\text{Pt}(\text{acac})_2$  and alumina surface sites:

- (i) Calcination of the support during 2 h at 350 °C in a dry air stream, followed by cooling down to room temperature overnight in the same air stream. In the following, a support treated in this way will be referred to as a reactive support (“R”).
- (ii) Hydroxylation by incipient wetness impregnation with an amount of water corresponding to the pore volume of the pellets. The support was then dried at 120 °C overnight. No calcination prior to the hydroxylation was carried out. These supports will be referred to as deactivated supports (“D”).
- (iii) Hydroxylation as under (ii). The support was then immersed in a solution of acetylacetone ( $\text{acacH}$ ) in

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