Powder Technology 257 (2014) 198–202

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Nanoparticles deposit location control on porous particles during dry impregnation in a fluidized bed

Laurie Barthe [a], Karine Philippot [b], Bruno Chaudret [b], Nadine Le Bolay [a], Mehrdji Hemati [a],*

[a] *Université de Toulouse, Laboratoire de Génie Chimique, UMR CNRS 5503, INP-ENSIACET, 4, allée Emile Monso BP 84324, Toulouse Cedex 04, France*
[b] *Laboratoire de Chimie de Coordination, UPR CNRS 8241, 205 route de Narbonne, 31077 Toulouse Cedex 04, France*

ARTICLE INFO

Available online 18 February 2014

Keywords:
Metallic nanoparticles
Fluidized bed
Dry impregnation
Deposit location
Drying

ABSTRACT

This work deals with the synthesis of composite materials, catalytic or not, by an innovating technique named dry impregnation in a fluidized bed. This process permits the obtainment, in only one apparatus, of composite materials which, by the traditional way, must successively undergo the stages of impregnation, filtration, drying and calcination/activation. Its principle consists in the spraying of a solution containing a metallic precursor into a hot fluidized bed of porous particles as a chosen support. After the impregnation step, the decomposition of metallic precursor and metal activation can be operated in the same reactor. It is found that the competition between two phenomena (drying and capillary) controls the deposit location.

This paper presents experimental results obtained during the dry impregnation of coarse and fine porous particles using different types of precursors: inorganic precursors (metallic salts), metal organic complexes and a colloidal suspension containing preformed metallic nanoparticles (rhodium). The effect of drying parameters (solvent content in gas phase and temperature) on deposit distribution within the support grains at the local scale is examined.

It appeared that a fast drying leads to a deposit located only at the external particle surface (similar to a surface coating), whereas a uniform deposit on the whole particle volume is obtained with slow drying conditions. It indicates that dry impregnation in fluidized beds is very flexible and, by a simple modification of the operating conditions, we can fix the deposit location.

1. Introduction

Usually, the preparation method of composite materials such as supported catalysts consists in the immersion of the chosen support in a precursor solution under stirring to favour the diffusion inside the support grains. After this impregnation, the composite material successively undergoes the stages of filtration, drying and calcination/activation. This technique is easy to carry out but presents a weakness: the dependence of the deposit location on the physico-chemical properties of the solution-support couple. Indeed, a control of the deposit location represents a real challenge, particularly in catalysis [1,2]. Moreover, to obtain a high metal loading, these four steps should be repeated several times.

Supported catalyst synthesis can also be achieved using an innovating technique, namely dry impregnation in a fluidized bed [3]. This technique is a “one pot process”. It consists in spraying a precursor solution into a hot fluidized bed of porous particles.

During operation, the pulverised solution penetrates inside the porous support by capillarity (liquid spreading/penetration), and at the same time the solvent is evaporated thanks to the energy brought by the fluidization gas (drying). These phenomena depend on:

- The process related variables (fluidization gas flow rate, bed temperature, atomizing gas and liquid flow rates, and atomizer location),
- The physicochemical properties (liquid interfacial tension, liquid viscosity, contact angle between solid and liquid, nature and texture of solid particles).

The interdependency between these two kinds of parameters determines the product quality and the metal repartition into the porous particles.

Few studies are reported on the dry impregnation technique. Previous works from our laboratory, concerning impregnation of porous particles with aqueous solutions of metallic salts, showed the feasibility of manufacturing catalysts by direct impregnation of porous support particles through the pulverization of metallic precursor solutions in a hot fluidized bed [4–7]. It was shown that, under the chosen operating conditions, the efficiency of the metal deposition is close to 100% and the metal loading is directly related to the operating time and the liquid flow rate and concentration. It was found that the competition between the drying rate, depending on the process-related variables, and the capillary penetration rate, depending on the physicochemical-related variables, controls the deposit location. A quasi uniform deposit inside the support particles is observed for soft drying. The metal nanoparticle size is controlled by the pore

---

* Corresponding author.
E-mail address: Mehrdji.Hemati@ensiacet.fr (M. Hemati).

http://dx.doi.org/10.1016/j.powtec.2014.02.040
0032-5910/

mean diameter of the support as well as the calcination operating protocol.

In order to determine the importance of the solvent evaporation process compared to the solution penetration by capillarity, an impregnation module, *IM*, was defined. It is the ratio between the drying characteristic time (t_{dry}) and a capillary penetration time (t_{cap}).

- t_{cap}, the necessary time for liquid penetration in the pores, can be estimated from the following equation taken from the model of the parallel capillary beam [8]:

$$t_{cap} = \frac{2\mu x^2}{\gamma_{LV}(\cos\theta) \cdot r_{pore}} \tag{1}$$

where μ is the liquid viscosity, x the pore length equivalent to the radius particle multiplied by the tortuosity factor, γ_{LV} the interfacial tension, θ the contact angle and r_{pore} the pore radius.

- t_{dry} is the time necessary for a particle saturated by pure solvent to be transformed into a dry particle under defined fluidized bed conditions (temperature and humidity). The calculation of this characteristic time is based on the mass and energy balances on a single wet particle considering that the mass transfer is controlled by external resistance (gas phase). The model's equations described in previous works [3,9] lead to the following equation:

$$t_{dry} = \frac{d_p \chi \rho_s}{6k_y(Y_i - \overline{Y})} \tag{2}$$

where d_p is the particle diameter, χ the internal support porosity, ρ_s the solvent density, k_y the overall mass transfer coefficient, $\overline{Y}$ the average solvent content in the bed atmosphere determined by overall mass balance on the reactor, and Y_i the absolute solvent content at the interface (depending on the particle temperature and humidity).

Moreover, another criterion depending on $\overline{Y}$ and bed temperature was considered: ζs, the solvent vapour saturation rate value. It is defined as the ratio between gas solvent content in the bed and its value at saturation (saturation solvent content).

Different feasibility tests carried out in our laboratory at soft, intermediate and fast drying conditions have shown that:

- For high ζs ($0.8 \leq \zeta s \leq 1$) and high *IM*, an undesirable phenomenon of partial or complete bed defluidization (wet quenching) is observed.
- For slow drying conditions ($0.2 \leq \zeta s \leq 0.8$ and *IM* greater than 10), the metallic precursor deposit is located inside the porous matrix.
- For fast drying conditions ($\zeta s < 0.2$ and *IM* less than 10), the deposit is located on the support particle surface.

This study concerns the effect of drying parameters (solvent content in gas phase and temperature) on deposit distribution within the composite materials. The experiments are carried out using various types of precursors (metallic salts, metal organic precursor solutions and colloidal suspensions containing preformed metal nanoparticles) and various particle sizes (from 100 μm to a few millimetres).

2. Methods and materials

2.1. Supports and metal sources

Two solids, different in their nature and grain size, were used as catalyst supports: fine porous silica particles and coarse activated γ alumina particles. Their principal physical properties are reported in Table 1.

Various types of precursors were sprayed on the supports.

Aqueous solutions of metallic salts were prepared by dissolution of inorganic salts in water. Two precursors were used: iron nitrate $Fe(NO_3)_3 \cdot 9H_2O$ and manganese nitrate $Mn(NO_3)_2 \cdot 4H_2O$. The concentrations are indicated in Table 2. These precursors are very water soluble. The saturation concentration at 20 °C is respectively 300 g of crystals/100 g of water and 322 g of crystals/100 g of water.

Table 1
Physical properties of the porous supports.

Properties	Silica gel	Alumina
Mean diameter d50 d_p (μm)	120	2 400
Specific surfaces S_{bet} (m^2/g)	530	330
Pore volume V_p (cm^3/g)	0.8	0.3
Particle density ρ (kg/m^3)	910	2 200
Internal porosity X (%)	60	43

Metal organic precursor solutions were prepared with an organometallic complex as precursor such as $PdCl(\eta^3\text{-}C_3H_5)]_2$ (palladium allyl chloride). The most suitable solvent permitting the obtainment of a solution from the complex is tetrahydrofuran (THF). This solvent must be distilled and degassed before use to remove traces of peroxides, oxygen, and water to ensure the stability of the solution during the impregnation step.

Colloidal aqueous suspensions containing rhodium (0) colloids were prepared as previously described [10]. More precisely, sodium borohydride was added to an aqueous solution containing the surfactant HEA16Cl (N,N-dimethyl-N-cetyl-N-(2-hydroxyethyl)ammonium salts). This solution was quickly added under vigorous stirring to an aqueous solution of the precursor $RhCl_3 \cdot 3H_2O$. The initial red solution darkened immediately attesting that an aqueous Rh0 colloidal suspension is obtained, which remains stable for a long time. The average rhodium particles size is around 2.4 nm.

2.2. Experimental set-up

Depending on the metal source nature, the experiments were carried out under air or controlled atmosphere (inert or reductive) in a batch fluidized bed (Fig. 1). This reactor is a stainless steel cylindrical column with 0.1 m inner diameter and 0.5 m height, described by Barthe [7].

The gas distributor is a stainless steel perforated plate with a porosity of 0.5%. The fluidizing gas flow rate is measured by means of a rotameter and preheated by an electrical heater before entering the bed. The elutriated particles and solvent vapours are collected at the column outlet respectively by a cyclone and a condenser.

The metallic precursor solution is drawn up by a volumetric pump from a reservoir to an internal mixing of two-fluid spray nozzle. The atomizing gas flow rate is controlled by a needle valve and measured by a rotameter. The bed temperature is controlled by means of a PID regulator. Monitoring of temperature and pressure drop takes place during operation.

The solid sampling system is achieved with a vacuum circuit. The sampling with a controlled atmosphere is done through a nitrogen circuit. In addition it enables working with oxygen and water sensitive products.

2.3. Characterization methods

The metal deposit location of the samples was studied using different techniques. The composite materials were analysed by an optical microscope and a Transmission Electron Microscope (TEM). In the case of TEM observations, the samples were cut by ultramicrotomy.

2.4. Operating conditions

The different operating conditions are listed in Table 2. The first six experiments were carried out with inorganic precursors. Organometallic complexes have been used in experiment S7 while a colloidal suspension was sprayed for experiments S8 and S9. For each precursor type various experiments were carried out with different values of *IM*