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Rhodium colloidal suspension deposition on porous silica particles by dry impregnation: Study of the influence of the reaction conditions on nanoparticles location and dispersion and catalytic reactivity

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ABSTRACT

Rhodium composite nanomaterials were synthesized by an innovating process called dry impregnation in a fluidized bed. It consists in spraying an aqueous colloidal suspension of rhodium on silica porous particles. The use of this precursor solution containing preformed nanoparticles avoids calcination/activation step.

Different composite nanomaterials were prepared displaying various metal loadings. The operating conditions were tuned to modify τ_s, the solvent vapour saturation rate value, in order to influence the deposit location: either uniform on the whole silica particles or at the particles surface like a coating. τ_s is defined as the ratio between solvent content in the bed atmosphere and the maximum solvent content.

The obtained samples were investigated in catalytic hydrogenation of aromatic compounds under very mild conditions. Their catalytic performances were compared to those of the original colloidal suspension in one hand and of a similar catalyst prepared through wet impregnation in another hand. Interesting activity and selectivity were observed.

This illustrates the interest of the dry impregnation method: this way allows an easy control of the metal loading as well as of the metal loading location in the support particles. Moreover, the support particle size and morphology are preserved.

1. Introduction

The interest in metal nanoparticles for applications in catalysis is now well-known [1–4] and mainly results from their high specific surface area due to their small size giving rise to high active sites numbers. Metal nanoparticles are generally considered as species at the frontier between homogeneous and heterogeneous catalysts. From this particular matter state, catalytic specificities, which are not offered by classical catalysts, could be expected and several systems are now available in the literature illustrating their particular behaviour [5–7].

The preparation of metallic nanospecies in liquid-phase is possible through various chemical syntheses and the reduction of metal salts in aqueous media is one of the most known methods [8]. For example, colloidal suspensions of rhodium can be prepared by chemical reduction of $RhCl_3$ and stabilized by highly hydrosoluble quaternary ammonium salts and they have proved to be active catalysts for hydrogenation of various aromatic compounds [9]. Nevertheless, colloidal suspensions display some disadvantages as their lack of stability at elevated temperatures (agglomeration is often observed at temperature higher than 100 °C) or their recycling with soluble products. It appears then clearly that the deposition of metal nanoparticles onto a support would circumvent these drawbacks and afford the advantages of traditional supported catalysts. The way followed to prepare supported nanocatalysts is generally the wet impregnation method [10]. It consists in the immersion of the chosen support in a colloidal suspension under stirring to favour the diffusion of the nanoparticles inside the support grains. This technique is easy to carry out but can present some weak points such as: loss of precursor, reduction of the support particle size (most of the porous supports, prepared by sol–gel process, disaggregate in solution under stirring) and dependence of the deposit location on the physico-chemical properties of the solution-support couple.

Taking into account these different points, the preparation of supported catalysts following a dry impregnation method appears as an interesting alternative technique. The preparation of

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composite nanomaterials by dry impregnation in a fluidized bed has been developed by [11]. Its principle consists in spraying a solution containing a metal source into a hot fluidized bed of porous fine particles. After the impregnation step, metallic precursor decomposition and/or activation can be performed in the same apparatus. Up to now, this technique has been successfully applied using solutions of metal salts (iron, manganese and copper nitrate) or organometallic complexes (bis(dibenzylidene)palladium, $[Pd(dba)_2]$ or palladium allyl chloride $[PdCl(allyl)]_2$) as metal sources. Most particularly, the deposition of metal salts gave rise to interesting composite nanomaterials displaying catalytic properties [12].

This dry impregnation technique offers several advantages. For example, the whole sprayed metal precursor is deposited and the metal loading is thus controlled by the impregnation time. Moreover the initial size of support grains is conserved. But, its major advantage concerns the deposit location that can be oriented depending on the targeted composite nanomaterials [12,13]. Indeed, previous works with metal complexes showed that a competition between two phenomena, the drying and the capillarity, controls the deposit location. An adequate choice of operating conditions (bed temperature, liquid and fluidization gas flow rate), otherwise the appropriated values of τ_s, the solvent vapour saturation rate, and IM, the impregnation module, permit to predict the deposit location. τ_s is defined as the ration the ratio between solvent content in the bed atmosphere and the maximum solvent content. IM is defined as the ratio between a drying characteristic time, t_{dry}, and a capillary penetration time, t_{cap}.

t_{cap}, the time necessary for liquid penetration in the pores, can be estimated from the following equation taken from the model of the parallel capillary beam [14]:

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

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}, 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 wetted particle considering that the mass transfer is controlled by external resistance (gas phase). The model's equations described in previous works [13,15] lead to this last equation:

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

where d_p is the particle diameter, χ the internal support porosity, ρ_s the solvent density, k_y the overall mass transfer coefficient, $\bar{Y}$ 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 [13]).

According to these two parameters, homogeneous deposit of nanoparticles is located inside or at external surface of the support. For example, in the case of dry impregnation of fine silica particles by an iron nitrate aqueous solution, our experimental results show that soft drying conditions ($\tau_s \geq 0.2$ and IM ≥ 30) lead to a homogeneous deposit while under fast drying conditions ($\tau_s < 0.2$ and IM < 30), the deposit is located at the particle external surface.

After these findings, a new challenge for us consisted in the use of aqueous colloidal solutions containing preformed metal nanoparticles to check the applicability of our process to another metal source. This approach using metallic nanospecies could be promising since it avoids thus the necessary step of decomposition/activation of metal complexes. Nevertheless, this project was ambitious because no deposition of colloidal solution was known in the literature and this could present some technical difficulties.

This paper describes the dry impregnation of fine porous silica particles by a rhodium colloidal suspension. The so-prepared samples were characterised to follow the impregnation kinetics and check the metal deposit location. Finally, the activity of these composite nanomaterials was compared to that of colloidal suspension on one hand and to that of similar catalysts prepared with the same materials (colloidal suspension and support) by classical wet impregnation on the other hand.

2. Methods and materials

2.1. Starting materials

2.1.1. Metal source

Rhodium chloride hydrate was obtained from Strem Chemicals. Sodium borohydride and all aromatic substrates were purchased from Aldrich or Fluka and were used without further purification. Water was distilled twice before use by conventional method. The surfactant HEA-16Cl was prepared as previously described in the literature [16].

2.1.2. Solid supports

Fine porous silica particles of two different sizes but with similar physical properties were used as catalysts support (silica gel Merck 60). Their average pore diameter was 5.5 nm. Their other physical and hydrodynamic characteristics are listed in Table 1.

2.2. Experimental procedures

2.2.1. Preparation of rhodium colloidal suspensions

The rhodium colloidal aqueous suspensions containing rhodium (0) nanoparticles were prepared as previously described (Fig. 1a) [17]. More precisely, sodium borohydride (36 mg, 9.5×10^{-4} mol) was added to an aqueous solution of N,N-dimethyl-N-cetyl-N-(2-HydroxyEthyl)Ammonium chloride salts, namely HEA16Cl (95 mL, 7.6×10^{-3} mol L^{-1}). This solution was quickly added under vigorous stirring to an aqueous solution of the precursor $RhCl_3.3H_2O$ (100 mg, 3.8×10^{-4} mol). The initial red solution darkened immediately, proving the formation of the aqueous Rh(0) colloidal suspension. Transmission Electron Microscopy (TEM) images revealed well-dispersed rhodium nanoparticles (Fig. 1b) with a mean size of 2.4 nm (Fig. 1c). It was verified that such colloidal solutions are stable for several months at room temperature.

2.2.2. Preparation of supported nanoparticles by dry impregnation in fluidized bed (Dry Imp catalysts)

The experiments were carried out in a batch fluidized bed, allowing syntheses under controlled atmosphere (inert or reductive) depending on the metal precursor nature. The reactor is a stainless steel conical column with a 30 mm base diameter, a 112 mm top diameter and 300 mm in height (Fig. 2). Its dimensions make it possible to reduce the metal precursor consumption and the impregnation time since it operates at laboratory scale (production

Table 1
Physical and hydrodynamic characteristics of the silica particles used as supports.

Characteristics	Si 120	Si 80
Mean diameter d_p (μm)	120	80
Pore diameter d_{pore} (nm)	5.5	5.4
Specific surfaces S_{bet} (m^2/g)	530	490
Pore volume V_p (cm^3/g)	0.81	0.77
Internal porosity χ (%)	60	58
U_{mf} at 25 °C (minimum fluidization velocity) (m/s)	0.0035	0.0022
U_t at 25 °C (terminal velocity) (m/s)	0.23	0.15