

ADSORPTION OF Pd(hfac)₂ ON MESOPOROUS SILICA SBA-15 USING SUPERCRITICAL CO₂ AND ITS ROLE IN CATALYST PREPARATION

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INTRODUCTION

Supported Pd catalysts are used in reduction and oxidation reactions, hydrogenation, dehydrogenation, debenzylation, hydrocracking, carbonylation and other carbon – carbon coupling reactions [1]. In a fine heterogeneous catalyst the metal nanoparticles are evenly distributed throughout a large surface area support. The support helps to stabilize the nanoparticles, prevents them from sintering and aggregation and facilitates handling of the catalyst. Inorganic supports show high thermal and chemical stability and, among them, ordered mesoporous materials such as silica SBA-15 have been extensively investigated due to their larger surface area, pore size and ordered mesoporous structure [2].

The support is impregnated with a metal precursor, which usually decomposes upon thermal treatment to yield the catalyst. However, the large viscosity and surface tension of most liquid solvents cause the slow diffusion of the metal within the support pores and, oftentimes, yield poorly dispersed and non homogeneous materials. Furthermore, the drying process may cause structural changes into the catalyst with a significant reduction of the support surface area and catalytic activity.

On the contrary, supercritical fluids have been successfully used as reaction and/or impregnation medium to introduce metal precursors within porous supports [3]. Most experiments have been performed using supercritical CO₂ (scCO₂) because it is cheap, non-toxic and non-flammable and has relatively low critical temperature and pressure ($T_c = 31^\circ\text{C}$, $P_c = 73.8$ bar) [4]. The large solubility of many organometallic precursors in scCO₂ at moderate pressure and temperature and the exceptional transport properties of this fluid (low viscosity, high diffusivity relative to liquids and very low surface tension) have prompted its use as impregnation and/or reaction medium in materials synthesis [5]. Furthermore, CO₂ is a gas at ambient pressure and is eliminated completely upon depressurization.

At our laboratory we have recently deposited Pd into mesoporous silica SBA-15 using scCO₂ at 40 °C and 85 bar [6]. As precursor, we have used Palladium(II) hexafluoroacetylacetonate (Pd(hfac)₂) which dissolves at these conditions above 3.60 wt. % in scCO₂ [7]. The organometallic precursor is adsorbed onto the support and is reduced either introducing H₂ in the CO₂ mixture or, after depressurization, in pure H₂ at high pressure. Best results are obtained when the reduction is performed in pure H₂. The catalytic activity of these materials has been shown.

In order to control the amount of Pd deposited on the support, the knowledge of the adsorption equilibrium for the Pd(hfac)₂ – SBA-15 – scCO₂ system is required. These types of studies are scarce in the literature [8] and there is a lack of fundamental understanding of the adsorption

process at supercritical conditions. In this communication we report adsorption isotherms for Pd(hfac)₂ on SiO₂ – SBA-15. The influence of temperature, pressure and density of CO₂ on the adsorption equilibrium has been also examined.

MATERIALS AND METHODS

Materials

Tetraethylorthosilicate (TEOS, 99 +% pure), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Mw=5800) (PEO-PPO-PEO) and Palladium(II) hexafluoroacetylacetonate (Pd(hfac)₂) were obtained from Aldrich. Chemicals were used as received. CO₂ purity >99.99% and H₂ purity >99.999% were supplied by Air Liquide.

Support preparation

Mesoporous silica SBA-15 was prepared following the procedure described by Zhao et al. [9]. In a typical experiment 4.0 grams of PEO-PPO-PEO was dissolved in 30 g of water and 120 g of 2M HCl solution with stirring at 40 °C. Then 8.5 g of TEOS was added into the solution with stirring at 40 °C for 20 hours. The mixture was aged at 100 °C without stirring for a further 24 hours. Solid residue was filtered, washed with ethanol several times and calcined in air at 550 °C for 6 hours. Heating rate from room temperature was 1°C/min.

Impregnation experiments

The impregnation experiments were conducted in a *ca.* 100 mL stirred high-pressure reactor (Autoclave Eng. Inc.) in the batch mode. SBA-15 (*ca.* 100 mg) and different amounts of Pd(hfac)₂ (from 18 to 230 mg) were loaded into the reactor. The reactor was then heated by a heating jacket connected to a PDI controller to the impregnation temperature and was filled with CO₂ using a high-pressure syringe pump at the same temperature (Isco, Inc. Model 260D) up to the desired pressure. Temperature was measured using a K-type thermocouple. The pressure was measured using a pressure gauge. Impregnation of the mesoporous support with Pd(hfac)₂ was carried out in scCO₂ at 40 - 80 °C and 85 - 140 bar for 8 hours. Then the reactor was depressurized through a needle valve in 1 hour. The amount of precursor adsorbed on the support was determined from TGA analysis in O₂ flow.

Catalyst preparation

The catalysts were prepared by reduction of the impregnated supports in pure H₂. After impregnation, the reactor was loaded with pure H₂ at 60 bar and reduction was carried out at 40 °C for 3 hours. After depressurization the reactor was further extracted continuously with CO₂ at 60 °C and 200 bar to remove the reaction by-products.

RESULTS AND CONCLUSIONS

In the first place, the precursor adsorption on the support was studied at 40 °C and 85 bar at 3, 8 and 16 hours. The amount impregnated increases from 3 to 8 hours, but decreases slightly when impregnation time is 16 hours due to the partial decomposition of the precursor [6]. Therefore, in the following experiments the impregnation time was fixed to 8 hours, to assure thermodynamic equilibrium without precursor decomposition.

The metal precursor adsorption on the support was then studied at 40 °C and 85 bar at varying concentrations of Pd(hfac)₂ in scCO₂. Figure 1 shows how saturation of the support is reached at *ca.* 0.5 mol Pd(hfac)₂/kg SBA-15 when concentration of Pd(hfac)₂ in CO₂ is *ca.* 2.5 (mol/m³). A modified Langmuir model, for these conditions, was shown to describe this process.

$$q = \frac{K_1 Q_0 C}{1 + K_1 C} + kC \quad (1)$$

Assuming that saturation is reached at a similar concentration of Pd(hfac)₂ in CO₂ at every condition, the adsorption equilibrium of the metal precursor on the support at this concentration was studied at 40, 60 and 80 °C in the 85 – 140 bar interval.

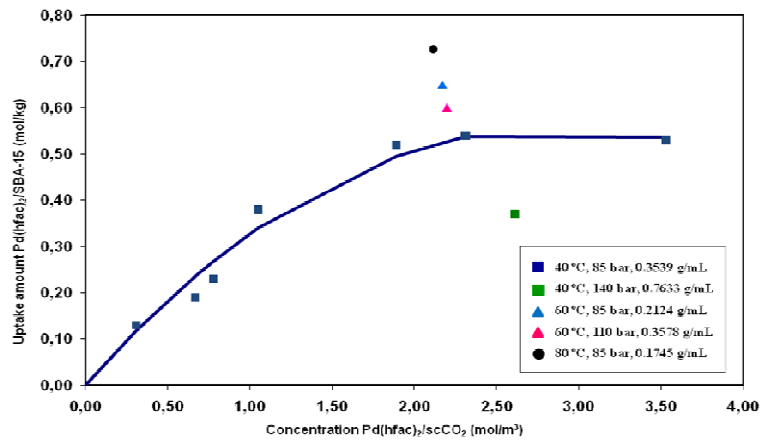


Figure 1. Adsorption isotherms for Pd(hfac)₂ on SiO₂ – SBA-15 at different temperature and pressure conditions (symbols) and fit of the adsorption isotherm at 40 °C and 85 bar to a modified Langmuir model (continuous line).

At constant temperature, 40 and 60 °C, the amount adsorbed on the support decreases as pressure increases. At 85 bar, the amount adsorbed increases as the temperature increases from 40 to 80 °C. At CO₂ constant density (0.35 g/mL) the adsorbed amount slightly increases with increasing temperature.

To understand the adsorption process, the relative affinity of the precursor between the support and the supercritical fluid must be considered. For this particular system the data measured seem to indicate that the high solubility of the precursor in the supercritical fluid is controlling the adsorption process. The solubility of the precursor in the fluid phase can be described using the Chrastil equation [10].

$$\ln C = k \ln \rho + \frac{a}{T} + b \quad (2)$$

At constant precursor concentration on the fluid phase, adsorption of Pd(hfac)₂ on the support decreases as solubility in the fluid increases. Knowledge of the adsorption process is essential to control the amount of Pd deposited on the support, which will determine the catalytic activity of the material produced.

TEM images of the composite material obtained after reduction in pure H₂ of a sample impregnated at 40 °C and 85 bar for different impregnation times are shown in figure 2. EDX analysis were performed on the TEM images and proved the presence of Pd in the sample. Pd appears evenly distributed through the cylindrical SBA-15 mesopores. Cluster size is limited by the pore size of the support. EDX analysis show a Pd content between 1.4 to 4.5 mol %.

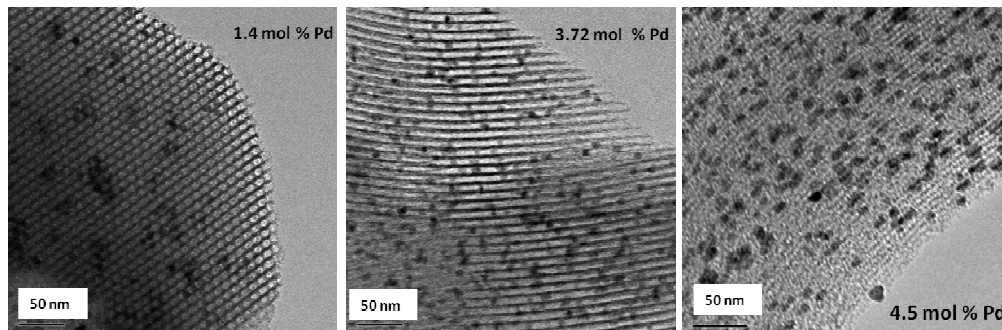


Figure 2. TEM images of Pd/SBA-15 composite materials obtained by impregnation of Pd(hfac)₂ on silica SBA-15 at 40 °C and 85 bar for 3, 8 and 16 hours.

The amount of Pd incorporated into the mesoporous material depends on the impregnation conditions. By changing the impregnation time, pressure and temperature, the amount of Pd in the material can be controlled. The catalytic activity of these materials has been demonstrated for the reduction of 4-nitrophenol in water [6]. Further catalytic tests in supercritical fluid mixtures are being conducted.

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REFERENCES

- [1] BLASER, H. U., INDOLESE, A., SCHNYDER, A., STEINER, H. and STUDER, M., *Journal of Molecular Catalysis a-Chemical*, **2001**, Vol. 173, p. 3.
- [2] WAN, Y. and ZHAO, D. Y. *Chemical Reviews*, **2007**, Vol. 107, p. 2821.
- [3] ZHANG, Y. and ERKEY, C., *Journal of Supercritical Fluids*, **2006**, Vol. 38, p. 252.
- [4] MCHUGH, M. A. and KRUKONIS, V. J., *Supercritical Fluid Extraction: Principles and Practice*, Butterworths, Boston, **1986**.
- [5] TENORIO, M. J., TORRALVO, M. J., ENCISO, E., PANDO, C., RENUNCIO, J. A. R. and CABAÑAS, A., *Journal of Supercritical Fluids*, **2009**, Vol. 49, p. 369.
- [6] MORÈRE, J., TENORIO, M. J., TORRALVO, M. J., PANDO, C., RENUNCIO, J. A. R. and CABAÑAS, A., *Journal of Supercritical Fluids*, **2011**, Vol. 56, p. 213.
- [7] TENORIO, M. J., PANDO, C., RENUNCIO, J. A. R. and CABAÑAS, A. 8th Green Chemistry Conference (Zaragoza - Spain) **2009**.
- [8] ZHANG, Y., CANGUL, B. GARRABOS, Y. and ERKEY, C., *Journal of Supercritical Fluids* **2008**, Vol. 44, p. 71.
- [9] ZHAO, D. Y., HUO, Q. S., FENG, J. L., CHMELKA, B. F. and STUCKY, G. D., *Journal American Chemical Society*. **1998**, Vol. 120, p. 6024.
- [10] CHRASTIL, J., *Journal of Physical Chemistry*. **1982**, Vol. 86, p. 3016.