Applied Catalysis A: General 510 (2016) 49–56

Contents lists available at ScienceDirect

Applied Catalysis A: General

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

Influence of the pore generation method on the metal dispersion and oxidation activity of supported Pt in monolithic catalysts

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ARTICLE INFO

Article history:
Received 12 August 2015
Received in revised form 24 October 2015
Accepted 30 October 2015
Available online 7 November 2015

Keywords:
VOCs
Oxidation
Dispersion
Porosity
Monolith

ABSTRACT

The catalytic oxidation activity of structured macro/mesoporous Pt catalysts obtained by the one-step impregnated carbon procedure (ICP) with different binder/support combinations (sepiolite or mixtures with TiO_2 or Al_2O_3) is compared to that of catalysts with the same composition obtained by conventional impregnation of the previously shaped support, with and without activated carbon as pore-generating agent. The superior results of the former are explained in terms of porosity and metal dispersion, estimated by calculation of the platinum apparent molar surface coverage from electrophoretic migration measurements. The big macropores generated reduce the internal diffusion limitations, facilitating the accessibility of the gaseous compounds to the active phase. However, the main improvement for these sepiolite-based monoliths must be mainly attributed to the good Pt dispersion obtained by this method, with metal particles smaller than 10 nm, confirming the role of the activated carbon template not only as a macroporosity generating agent, but also as a dispersant and stabilizer of the metal particles – preventing agglomeration – and as source of CO for in situ reduction of the precursor. In addition, the ICP method minimizes the calcination steps needed for the preparation of the catalyst.

1. Introduction

Supported noble metals are widely used in the industry, and their activity as well as their economic viability depends on the metal dispersion on the surface of the support and the accessibility of the active phase. To optimize these parameters while minimizing the environmental impact and economical costs of the catalysts is a priority for the society and the industry. The conventional preparation methods for these types of catalysts are relatively complex and costly, since they involve several synthesis stages [1]:

a) preparation of a high surface area support,
b) incorporation of the active phase precursor, generally by wet impregnation or chemical vapor deposition, and
c) reduction of the metal precursor to obtain the active metallic phase.

Therefore, a series of heat treatments are usually needed to obtain the final catalyst:

a) calcination of the support in the adequate conditions (temperature and atmosphere) so as to obtain the desired phase transformations and eliminate any hard template used as pore generating agent (PGA) or other additives;
b) drying to remove the solvent of the precursors solution, during this process the dissolved salts may migrate from inside the pores to the entrance, resulting in poor dispersion of the active phase;
c) calcination at high temperatures (300–600 °C) in a reducing atmosphere to convert the precursors into active phases, a process usually accompanied by salt decomposition reactions with the consequent release of gases.

The drying stage and the final heat treatment are challenging. They can induce agglomeration or sintering of the active phases, resulting in low dispersion, with the subsequent decrease in the catalytic performance. In environmental and industrial applications catalytic supports are often shaped as monolithic structures with parallel channels because it gives the superior balance between low pressure drop in the reactor and high geometric surface area of the catalytic material [2]. Also the specific surface area, related to smaller pores, must be maximized in order to increase the number of available active sites, and the wall thickness must be minimized to reduce catalyst volume and internal diffu-

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http://dx.doi.org/10.1016/j.apcata.2015.10.050

sion limitations. Moreover, meso and macroporosity may facilitate the accessibility of active sites located within the walls with a less significant decrease of mechanical strength compared to a further reduction of wall thickness [3].

The literature reports on the generation of meso and/or macroporous materials during the synthesis process using surfactants as soft templates [4] or hard templates such as polymers [5] or carbonaceous materials [6]. In the last years the preparation of ceramic structured supports with high and hierarchical porosity has gathered the attention of the scientific community [3]. Highly porous magnesia, with macropores in the micron range and mesopores smaller than 100 nm, has been obtained by spray freeze drying of magnesium sulfate solutions, where fine salt particles with open pores were produced due to sublimation of ice crystal, after calcination at temperatures up to 1300–1500 °C [7]. Si–B–C–N monoliths with high, interconnected and hierarchical meso and macroporosity have been prepared by spark plasma sintering of ordered mesoporous powders at 800–1000 °C [8]. Oxidation-bonding of graphite incorporated into SiC powders yields high porosity ceramics with tunable pore diameter [9]. Moreover, hierarchical macro-mesoporous monoliths can be also prepared combining sol–gel routes with phase separation to obtain TiO_2[10], mullite [11] or cordierite [12].

Earlier some of us prepared sepiolite and titania–sepiolite honeycomb monoliths from commercial powders by extrusion using activated carbon as template for macroporosity generation [13]. The addition of activated carbon resulted in the enlargement of the inter-particular distances, without chemical interaction with the other components of the support. More recently we proposed the so-called “impregnated carbon procedure” (ICP) [14], which gives very active functionalized structured materials minimizing energy and reagents consumption by in situ reduction and dispersion of the metal precursor together with the generation of porosity in one single calcination step [15]. The method consists in the kneading of an aqueous paste composed by a binder and activated carbon (AC) particles, where the active phase precursor has been pre-impregnated. Additionally, a metal oxide can be included as support. After extrusion of the paste, the green body presents the desired final form of the catalyst: honeycomb, pellet, etc. This material is then transformed in one step into an activated dispersed catalyst by heat treatment in a lean oxygen atmosphere. The calcination conditions facilitate the burnout of the carbon particles, whereby macroporosity is generated simultaneously with an intra-pore gas-phase transfer of the metal to the final support in a similar way to chemical vapor deposition. The activated carbon dispersed throughout the material serves as a reducing element of metallic cations either directly or by the action of carbon monoxide formed at the sites of combustion with low oxygen supply. Thus, shaped catalysts can be directly prepared in their final monolithic form in one step, adding a green chemistry value [16] to the synthesis process.

The ICP method has been optimized regarding activated carbon particle size and amount, heat treatment temperature, and particle size and loading of platinum [17]. However, the higher performance of catalysts prepared with impregnated carbon with respect to those obtained by conventional impregnation can be related to several factors and their role has not been assessed yet. In order to get a deeper understanding, here the ICP method is employed to synthesize structured macro/mesoporous Pt catalysts

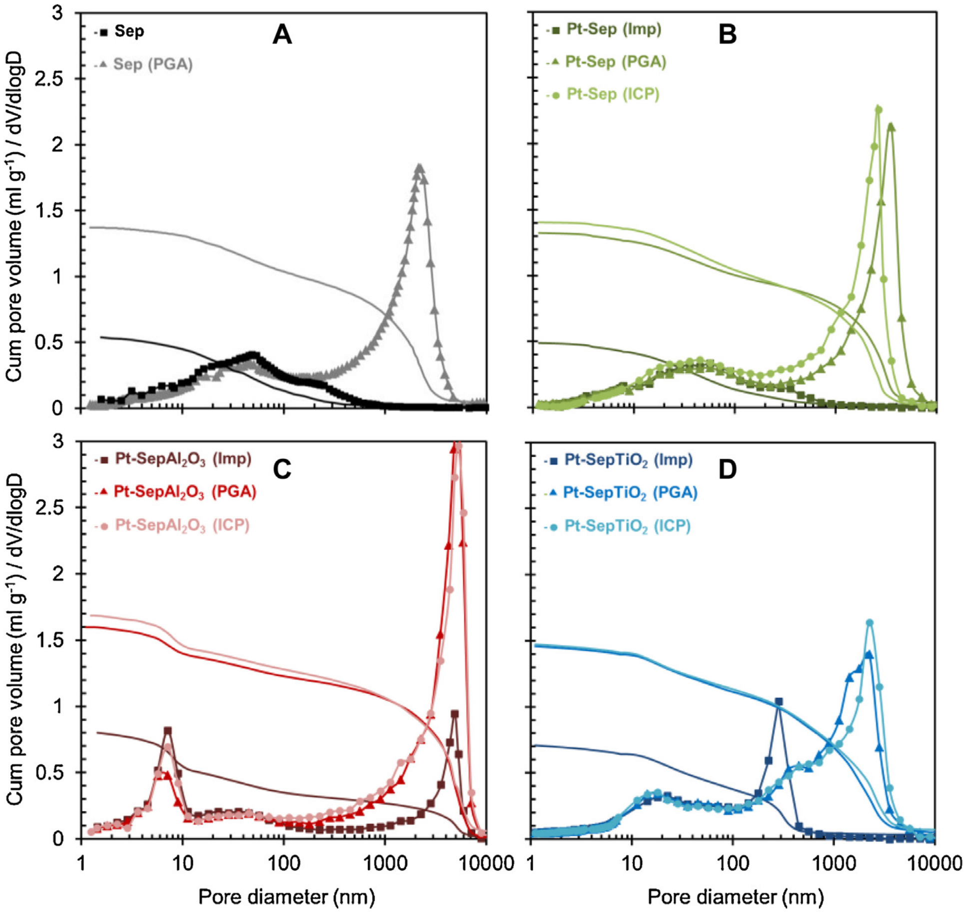

Fig. 1. Pore size distribution (lines + symbols) and cumulated pore volume (lines) of sepiolite-based structured monoliths: (A) Sepiolite supports, (B) Pt-Sep catalysts, (C) Pt-SepAl$_2$O$_3$ catalysts, and (D) Pt-SepTiO$_2$ catalysts.