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Green preparation of PtRu and PtCu/SBA-15 catalysts using supercritical CO_2

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ABSTRACT

Sustainability is emerging as design criteria in catalysts production. Hence, the preparation of Pt bimetallic catalysts using supercritical CO_2 ($scCO_2$) as a green solvent is proposed. PtRu and PtCu nanoparticles (NPs) were deposited on mesoporous SiO_2 SBA-15 by the reduction of Pt, Ru and Cu metalorganic precursor in $scCO_2$. The simultaneous and sequential deposition of both metals was attempted using different reduction methodologies. The materials were characterized by X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Energy-Dispersive X-ray analysis (EDX). XRD patterns matched closely that of cubic Pt. TEM images showed small NPs homogeneously distributed throughout the SBA-15 mesopores. Smaller particles were obtained when the reduction was performed in H_2/N_2 at low pressure. Sequential deposition of Cu or Ru in the first place followed by Pt yielded equimolar metal ratios. Samples prepared by sequential deposition were studied by Scanning Transmission Electron Microscopy (STEM). Composition profiles of the PtRu samples suggested an alloy structure. These catalysts were used in the hydrogenation of the renewable furfural in $scCO_2$ at 80 °C. PtRu materials presented a high activity and selectivity to furfuryl alcohol.

1. Introduction

Catalysts are essential in green chemistry research to reduce toxicity and increase chemical reactions efficiency aiming for a sustainable development [1]. In particular, the catalytic hydrogenation of organic molecules is of great importance in the pharmaceutical, petrochemical and food industries. From a green chemistry viewpoint, using molecular hydrogen increases the atom economy and at the same time it is considered a renewable feedstock. Common hydrogenation catalysts are formed by Ni, Pd or Pt supported nanoparticles (NPs). These materials generally lead to very high activities. Other metals such as Ru or Cu are used when a high selectivity to intermediate forms or other interesting products is sought. Bimetallic catalysts can show improved properties in comparison to monometallic catalysts. The presence of two metals changes the electronic structure of the system and may alter the activity and selectivity of the catalysts [2]. In the case of expensive noble metals, the addition of a cheaper metal also offers economic advantages. Finally, controlling the metal distribution on the NP (alloy structure, raspberry, core-shell,…), the catalytic activity can be also changed.

Supported bimetallic NPs can be produced following conventional techniques such as wet impregnation of the metal precursors followed by thermal or chemical reduction[3–5], electroless deposition [6] and Chemical Vapour Deposition (CVD) [4]. Colloidal [7] and reverse micelle [8] synthesis in which preformed nanoparticles are introduced into the support are also currently used. Some of these methods offer the possibility to perform a sequential or simultaneous deposition of the metals [3,5]. Furthermore, for the simultaneous preparation, a mixture of metal precursors or a bimetallic precursor can be used [9]. When the deposition of each metal is performed sequentially, several techniques can be combined [10].

If the process is carried out in a liquid solvent, the large viscosity and surface tension of most liquid solvents may cause the slow diffusion of the metal precursor or metal nanoparticles within the support pores leading to poorly dispersed and non-homogeneous materials. The drying process may also cause structural changes into the catalyst with a significant reduction of the support surface area and catalytic activity. On the other hand, gas phase processes such as CVD are generally limited by the low vapour pressure of the metal precursors and may not be suitable for preparation of homogeneous bimetallic materials with high metal loadings. Therefore conventional methods may lead to inhomogeneous materials of not well defined composition and structure and a broad particle size distribution. Moreover, some of these methods require the use of toxic solvents and or reagents and are multistep processes.

Supercritical CO_2 ($scCO_2$) has been proposed as a green solvent in the catalysts preparation following the Supercritical Fluid Deposition

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(SCFD) technique [11]. CO_2 used is obtained as a sub-product of many industrial processes, and there is large interest in its utilization. The CO_2 moderate critical temperature and pressure (T_c = 31.0 °C, P_c = 7.38 MPa) [12], its non-toxicity and non-flammability turn it into an excellent candidate to replace toxic organic solvents. Furthermore it is a gas at atmospheric pressure and does not leave any residue. The low viscosity, high diffusivity and very low surface tension of supercritical CO_2 and its high solvating power favour the penetration of metal precursors dissolved in $scCO_2$ within the catalyst support and at the same time avoid damage in the pore structure. The impregnated support is then reduced leading to metal NPs dispersed on the support. Different metals or metal oxides nanoparticles have been deposited on organic and inorganic substrates using $scCO_2$ [12–14]. Nanoparticle size distribution depends on concentration, reduction methodology and substrate [15]. Controlling the size, composition and morphology of the nanoparticles, their catalytic activity and selectivity can be tuned [16].

The deposition of bimetallic NPs onto different supports has been also addressed and reviewed by Bozbag and Erkey [14]. Supported metal NPs of PtRu, PtPd, PtCu, PtNi and PtAu, have been previously prepared using $scCO_2$. Apart from a very recent report by Qiao et al. on the deposition of PtPd NPs on mesoporous SiO_2 supports [17], bimetallic Pt NPs were deposited on carbon based supports such as carbon nanotubes (CNTs) [14,18,19], carbon black [14] and, recently, on functionalized graphene sheets [20] for catalytic applications. Lang et al. have also reported the preparation of $PtCuO/CeO_2/\alpha$-Al_2O_3 catalysts [21]. Pt/SnO_2 catalysts were also supported on Al_2O_3 foams [22]. With respect to the methodology, in most cases the simultaneous reduction of the metal precursors was carried out in H_2/CO_2 mixtures. Müller and Türk have successfully deposited AuAg core-shell structures following this methodology [23]. Prof. Erkey and coworkers have also studied the impregnation of both metal precursors on the support followed by thermal decomposition at ambient pressure and proposed the sequential deposition of both metals [14].

In this work, the preparation of PtRu and PtCu bimetallic NPs supported on mesoporous SiO_2 SBA-15 (SBA-15) using $scCO_2$ is studied. The utilization of CO_2 as solvent and reaction medium in the catalysts preparation may lead to very homogeneous materials. The effect that the reduction methodology has on the chemical composition, structure of the bimetallic material and their catalytic properties is addressed in this paper for the first time.

SBA-15 shows high thermal and chemical stability along a high surface area and an uniform pore size distributions. The support helps to stabilize the nanoparticles, preventing their sintering and aggregation and, at the same time, facilitates handling of the catalyst. The addition of Ru or Cu to Pt, reduces the cost of the catalyst and may allow a higher selectivity in hydrogenation reactions in comparison to Pt.

As a model reaction to test the materials prepared in $scCO_2$, the hydrogenation of furfural is proposed. Furfural is an important renewable, non-petroleum based, chemical feedstock, which is produced from lignocellulosic residues (agricultural by-products like sugarcane, bagasse and corn cobs). It is considered a potential platform chemical [24] because it can be readily hydrogenated to other value added chemicals such as furfuryl alcohol, 2-methylfuran and the corresponding tetrahydrofuran derivatives, among others.

Different Pd, Pt, Ru, Cu and Pt bimetallic supported based catalysts have been proposed in the hydrogenation of furfural [25,26]. Furthermore, the hydrogenation of furfural has been performed in $scCO_2$ [26,27]. The tuneable solvent properties and green nature of $scCO_2$ provide a very interesting medium for chemical reactions. Furfural and the possible products are highly soluble in CO_2 and H_2/CO_2 mixtures at supercritical conditions and the reaction can be performed in the one-phase region. Stevens et al. have shown that by a right combination of catalyst and temperature, a fine control of the product distribution can be achieved [27].

In this work we study the preparation of Pt bimetallic catalysts in $scCO_2$ and its use in the hydrogenation of furfural as a model reaction. The effect that the presence of the two metals and the preparation method has on the catalytic properties of these materials is studied. Both the catalyst preparation and the catalytic reaction are carried out in $scCO_2$, using a renewable feedstock making the whole process sustainable.

2. Materials and methods

2.1. Materials

The precursors dimethyl(1,5-cyclooctadiene)platinum(II) [$Pt(CH_3)_2$(cod)] (97%) and bis(2,2,6,6-tetramethyl-3,5-heptanodionato) (1,5-cyclooctadiene) ruthenium(II), [$Ru(tmhd)_2$(cod)] (99%) and bis (2,2,6,6-tetramethyl-3,5-heptanodionate) copper (II) ($Cu(tmhd)_2$) (99%) were provided by Strem Chemicals. Tetraethylorthosilicate (TEOS, > 99 + % pure), poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (M_w = 5800) (PEO-PPO-PEO), furfural (99%), 1,5-pentanediol (+97%, GC) and dichloromethane (99.9%, GC) were purchased from Sigma Aldrich. Furfuryl alcohol (98%), tetrahydrofurfuryl alcohol (+97%), 2-methyltetrahydrofurane (+99%) and 2-methylfuran (99%) were supplied by Acros Organics. All chemicals were used as received. CO_2 (purity > 99.99%) and H_2 (purity > 99.999%) were supplied by Air Liquide. H_2(5%)/N_2 was supplied by Contse. Mesoporous silica SBA-15 was synthesized following a procedure similar to that described by Zhao et al. [28,29] using PEO-PPO-PEO as structure-directing agent and TEOS as precursor.

The physical properties of the metal precursors are given in Table 1.

2.2. Materials preparation

Catalysts were prepared using a 100 mL stirred high-pressure Bolted Closure reactor (Autoclave Eng.) or a 60 mL custom made high-pressure stainless steel reactor heated with a small furnace provided with magnetic stirring. CO_2 was introduced into the reactor using a high pressure syringe pump (ISCO 260D), thermostated at 60–80 °C, depending on the experiments. When necessary, H_2 was introduced into the reactor using a 30 mL high-pressure auxiliary cell.

The SCFD comprises three different steps: (i) dissolution of the metal precursors in $scCO_2$ at a given conditions, (ii) adsorption of the precursor on the support from the fluid phase and (iii) precursor decomposition to the metal form.

A metal precursor or a mixture of the two metal precursors at the same molar concentration (1:1 molar ratio) and a given amount of support were placed into the reactor. Maximum metal loading for each metal relative to the support was 2% mol, which represents metal mass percentages of 6.2, 3.3 and 2.1% wt for Pt, Ru and Cu, respectively. The reactor was then heated to the selected temperature and was filled with CO_2 from the thermostated syringe pump at the given pressure. The precursor dissolved in $scCO_2$ and adsorbed onto the support. The adsorption equilibrium is governed by the relative affinity among precursors-CO_2 (solubility of each precursor), precursor-support (precursor adsorption) and CO_2-support (CO_2 adsorption) and can be tuned with the precursor concentration, pressure and temperature. In this work, the impregnation step for Pt and Cu precursors (either separated or

Table 1
Physical properties of the metal precursors: molar mass (M), % metal wt and melting temperature (T_m).

Metal Precursor	M (g/mol)	% metal wt	T_m (°C)	Ref.
$Pt(CH_3)_2$(cod)	333.3	58.5	105	[30]
$Ru(tmhd)_2$(cod)	575.8	17.5	187–190	http://www.strem.com
$Cu(tmhd)_2$	430.8	14.8	198	http://www.strem.com