

# Ionic Liquids Mediated Ionothermal Process for the One-Step Synthesis of High Surface Area Alumina Supported Noble Metals

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Received March 25, 2013; revised April 27, 2013; accepted May 23, 2013

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## ABSTRACT

Aluminas supported noble metal nanoparticles have been synthesized by a new ionothermal process. The method used is easy to implement and allows obtaining catalysts in one step with high specific surface area. In addition, the metallic phase in the composites is highly dispersed and exhibits homogeneous size.

**Keywords:** Mesostructuration; Alumina; Noble Metals; Ionothermal Process; EISA

## 1. Introduction

Since the discovery of the M41S family by Mobil, the interest in mesostructured materials becomes more and more important due to the possibility of controlling the pore structure of solids [1,2]. Indeed their tuneable properties allow emerging applications in different fields, amongst physics, medicine, catalysis, etc. Among all the materials studied, the synthesis of Al<sub>2</sub>O<sub>3</sub> with high specific surface area still represents a major challenge for chemical industries because of its extensive use as adsorbents and catalysts supports for numerous applications such as catalytic cracking, hydrocarbons reforming, environmental reactions, etc. Among the known structures of alumina, the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> transition form is the most used as catalyst support. Indeed, the morphology of the boehmite (hydrate precursor) confers to the  $\gamma$ - form adequate textural and surface chemical properties. Consequently, the synthesis of mesoporous aluminas is currently extensively studied in the literature [3-7]. In most cases, these syntheses are generally made by a solvothermal process, with processes very close to the classical ones with structuring agent added to the synthesis media [8].

To overcome the use of a hydrothermal synthesis, with the well-known limitation associated to the pressure increase with temperature, it is possible to use nonaqueous

solvents [9]. In this line, Room Temperature Ionic Liquids (RTILs) are considered as organic solvents with high polarity and preorganized solvent structures [10]. RTILs received more and more attention since the last decade. Indeed, they can be considered as liquids at room temperature, or temperature < 100°C, meaning the presence of ions only [11]. Moreover their physical and chemical properties are very interesting in the viewpoint of inorganic material synthesis. They exhibit low melting point (<100°C), negligible vapour pressure, thermal stability, high polarity and high ionic conductivity [12-14]. Facile route syntheses are described in literature using RTILs as solvents that catalyse some processes [15-23] but recent developments using RTILs as templating agents have also been described [25-33]. Indeed, one of the advantages of RTILs is that they can form extended hydrogen bond systems and are therefore highly structured which is adequate for the condensation of an inorganic matter to obtain structured pore systems [34].

In this work, we report a method allowing the direct (one-pot synthesis) functionalization of aluminas by noble metals using the Evaporation Induced Self Assembly (EISA) process. Noble metals are selected for their extensive use in heterogeneous catalysis, in environment and energy conversion applications.

## 2. Experimental Section

For the syntheses described here, the RTIL used is  $C_{10}$ mimCl. Pt, Pd and Rh functionalization of the aluminas will be done in one-pot synthesis.

In a typical synthesis 1-decyl, 3-methylimidazole chloride ( $C_{10}$ mimCl) is obtained by mixing 53.9 g (0.65 mol) of 1-methylimidazole (99%) and 117.2 g (0.65 mol) of decyl chloride (98%) is stirred during 72 h at 80°C in a 500 mL round bottom flask equipped with a condenser. The yellow oil obtained is washed three times with ethyl acetate then the solvent is evaporated at 60°C under vacuum during 24 h.

$\gamma$ - $Al_2O_3$  is synthesized according to an EISA procedure, as successfully used by Yuan *et al.* [4] for the synthesis of hexagonal-type pore structure aluminas.  $C_{10}$ mimCl, as template and co-solvent, is dissolved in anhydrous ethanol (solution pH closed to 7).  $HNO_3$  65 wt% is added to the solution in order to acidify the media (pH  $\sim$  1.4). Then a quantity of Al-sec-butoxide is added, the solution is stirred at room temperature for 5 h. The gel composition is: 1 Al: 0.65  $C_{10}$ mimCl: 3.8  $H_2O$ : 35 EtOH: 2.1  $HNO_3$ . The solvent is evaporated at 60°C in an oven until the solid is completely dry ( $\sim$ 10 days). The solid obtained is calcined for 4 h at 550°C in a muffle furnace, which is enough to ensure the complete removal of any carbonaceous matter for the solid (temperature increase ramp: 1°C·min<sup>-1</sup>). The obtained alumina is denoted: Al-EISA.

The synthesis of the functionalized alumina is performed as described for the alumina. Before adding the aluminium precursor, a known quantity of noble metal precursor ( $H_2PtCl_6$ ,  $Pd(NO_3)_2$  or  $RhCl_3$ ) diluted in a solvent, is added in order to obtain a 1 wt% loading of metal, dispersed in the  $Al_2O_3$  matrix. After calcination, the samples are reduced at 500°C under  $H_2$  flow for obtaining the supported metallic phase. The nomenclature used for the samples is as follows:

*NM*-Al-EISA

where *NM* designs the noble metal: Pt, Pd or Rh.

RTIL was analyzed by  $^1H$  and  $^{13}C$  NMR spectroscopy. The spectra were recorded on a BRUKER ADVANCE DPX 300 and 400.

Powder wide angle XRD patterns were obtained on a BRUKER AXS D5005 X-ray diffractometer, using a  $CuK\alpha$  radiation ( $\lambda = 1.54184 \text{ \AA}$ ) as X-ray source and equipped with a SolX detector. Signal was recorded for  $2\theta$  comprised between 10° and 80° with a step of 0.05° (step time of 2 s).

Specific surface area, pore size distribution and pore volume measurements were obtained from  $N_2$  adsorption-desorption experiments. A known mass of sample was first outgassed under vacuum at 250°C. Isotherms were obtained on a MICROMERITICS TRISTAR instrument. The specific surface area,  $S_{BET}$ , was calculated

from the linear part of the BET plot. The mesopore size distribution was determined from the desorption branch using the BJH model. Mesopore volume was determined on the isotherms at  $P/P_0 = 0.97$ .

Noble metal particle distribution within the alumina grains was evaluated by Transmission Electronic Microscopy (TEM). Micrographs were collected on a JEOL 2100 instrument (operated at 200 kV with a  $LaB_6$  source and equipped with a Gatan UltraScan camera).

## 3. Results and Discussion

The  $C_{10}$ mimCl structure (Figure 1) was confirmed by  $^1H$  and  $^{13}C$  NMR spectra (Figure 2).

The physical properties of the functionalized aluminas are gathered in Table 1.

All the *NM*-aluminas synthesized exhibit isotherms of

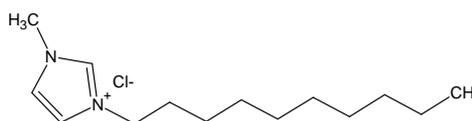
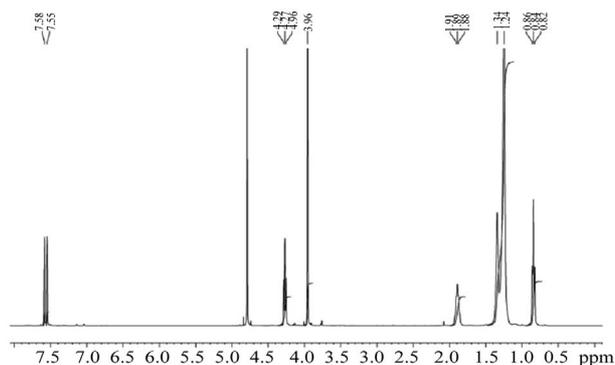


Figure 1.  $C_{10}$ mimCl structure.

$^1H$  NMR  $\delta$ : 0.84 (t,  $J = 8$  Hz, 3H), 1.20-1.40 (m, 14H), 1.89 (m, 2H), 3.96 (s, 3H), 4.27 (t,  $J = 8$  Hz, 2H), 7.55 (s, 1H), 7.58 (s, 1H).



$^{13}C$  NMR  $\delta$ : 13.78, 22.56, 26.09, 29.07, 29.38, 29.51, 29.70, 29.74, 29.84, 31.88, 35.87, 49.47, 122.06, 123.79

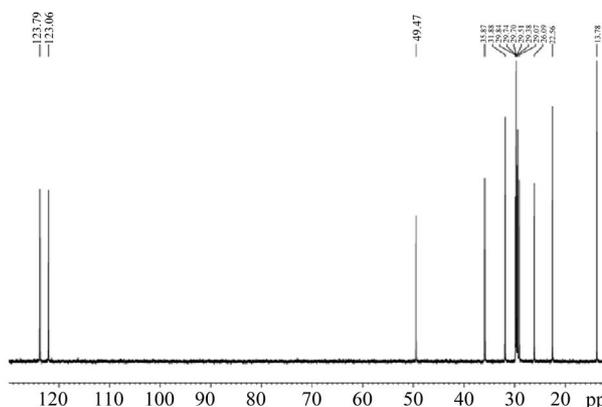
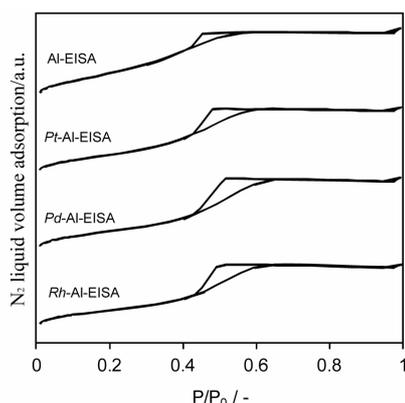


Figure 2.  $^1H$  NMR and  $^{13}C$  NMR of 1-decyl-3-methylimidazolium chloride.

type IV with a type 2 hysteresis, according to the IUPAC classification [35], see **Figure 3**.

The Specific Surface Area ( $S_{\text{BET}}$ ) of the functionalized supports are relatively low (297 to 328  $\text{m}^2\cdot\text{g}^{-1}$ ) compared to the  $S_{\text{BET}}$  of the alumina synthesized without any noble metal (380  $\text{m}^2\cdot\text{g}^{-1}$ ). However, the method proposed here allows simply obtaining alumina with high  $S_{\text{BET}}$ , since 300  $\text{m}^2\cdot\text{g}^{-1}$  remains a high value. In addition, the protocol described here is simple to proceed, does not use organic solvent or toxic templating agent, and allows to obtain aluminas with competitive physical properties that is comparable or sometimes higher than that can be classically obtained. Indeed, classical routes generally lead to the production of surface areas below 300  $\text{m}^2\cdot\text{g}^{-1}$ , when prepared by precipitation followed by thermal stabilization at similar temperature [6,36]. For obtaining mesostructured aluminas, precipitation route is often used since a uniform mesoporous distribution can be obtained by a precise control of the pH solution, the precipitation rate and the aging conditions [5,6,37-39]. Aluminas synthesized by this way often exhibit  $S_{\text{BET}}$  comprised between 250 and 370  $\text{m}^2\cdot\text{g}^{-1}$  [37-40]. However, a careful synthesis parameter control is needed to ensure a satisfying reproducibility of the synthesis. Another way of synthesis largely studied for mesostructured alumina is the sol-gel method. It has been studied since 1996 [7] and is still widely studied because the hydrolysis rate of the alumina precursor can be controlled, allowing a growth and agglomeration of crystallites adjustment [3,7,41]. By this



**Figure 3.**  $\text{N}_2$  adsorption-desorption isotherms obtained for the aluminas synthesized by EISA route.

**Table 1.** Physical properties of functionalized aluminas.

Sample	$S_{\text{BET}}$ ( $\text{m}^2\cdot\text{g}^{-1}$ )	$V_p$ ( $\text{cm}^3\cdot\text{g}^{-1}$ )	$D_p$ (nm)	Crystal structure	$d_{\text{metal}}$ (nm)
Al-EISA	380	0.32	3.2	$\text{Al}_2\text{O}_3 \gamma$	-
Pt-Al-EISA	328	0.32	3.8	$\text{Pt}^0, \text{Al}_2\text{O}_3 \gamma$	1.8
Pd-Al-EISA	323	0.33	3.9	$\text{Pd}^0, \text{Al}_2\text{O}_3 \gamma$	4.9
Rh-Al-EISA	297	0.30	3.9	$\text{Al}_2\text{O}_3 \gamma$	nd

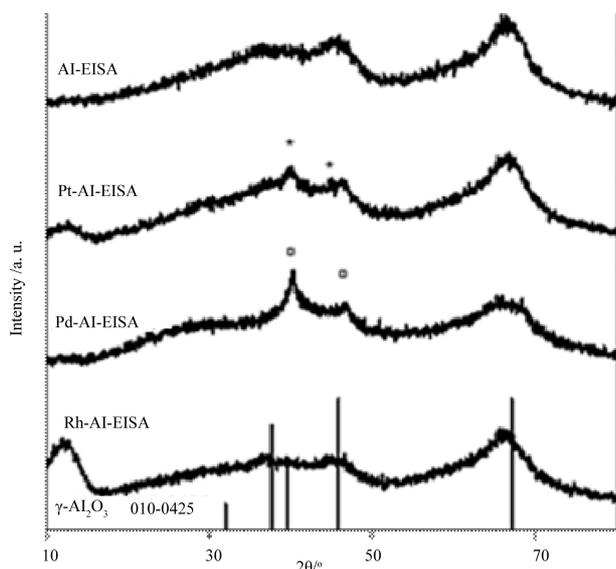
method, aluminas with higher  $S_{\text{BET}}$  can be obtained,  $\sim 400 \text{ m}^2\cdot\text{g}^{-1}$  [38]. However, the reproducibility and scaling up of these processes remain difficult, due to: 1) the necessity to carefully control the precursor concentration, generally low; 2) the use of inorganic solvents; 3) the increase in pressure during thermal crystallization.

The synthesis of ordered aluminas via classical Evaporation Induced Self Assembly has been first proposed by Niesz *et al.* [3] in 2005. The method of preparation the authors used is simple and reproducible, as evidenced thereafter by the numerous studies dealing with the synthesis of ordered aluminas during the past few years. In addition, highly ordered mesoporous aluminas with high surface areas, that means compatible with a use as catalysis support or adsorbent, can be obtained [4,42]. Yuan *et al.* [4] reported aluminas with  $S_{\text{BET}}$  as high as 434  $\text{m}^2\cdot\text{g}^{-1}$ , after thermal stabilization at 400°C. By comparing the physical properties of *NM*-aluminas to the alumina alone, it appears that the mean pore diameter slightly increases when incorporating noble metals and the pore volume is still the same than without noble metal. Generally, the samples synthesized by EISA process exhibit large pore size when prepared using voluminous triblock copolymers as templates. Pore sizes obtained in this work, c.a. 3.2 - 3.9 nm, are smaller than those classically reported for EISA synthesis, generally ranging from 5 to 7 nm. This can be explained, first of all by the chain length of the ionic liquid used: ten carbons which will confer a limited size at the organized phase. Indeed, the RTILs are known to form micelles in aqueous solutions [43,44]. The diameter of the micelles as formed, depends on the alkyl chain length: around 1.3 nm to 2.7 nm for alkyl chains containing respectively from 4 to 10 carbon atoms [45,46]. In contrast, Pluronic P123 forms a micelle with an approximate diameter of 18 nm [46,47]. In addition, the double role of the ionic liquid, solvent and porogen, makes the prediction of the pore size very difficult.

The wide angles XRD patterns of the alumina and noble metal functionalized materials show the characteristics of a  $\gamma\text{-Al}_2\text{O}_3$ . The crystallization of the alumina phase is preferable, since it confers to the solid a better thermal stability than in an amorphous material [36], as well as well-known surface properties [48]. Compared to the alumina synthesis by EISA where crystallization of the  $\gamma$ -phase is generally observed to occur at higher temperature, *i.e.* amorphous until 700°C in the Wan's work, crystallized at 800°C in the Yuan's work.

While no supplementary diffraction peak is observed for the Rh functionalized alumina, the diffraction patterns of the Pt-Al-EISA and Pd-Al-EISA show weak reflections attributed to the  $\text{Pt}^0$  and  $\text{Pd}^0$  phase respectively (annotated by \* and  $\square$  respectively in **Figure 4**).

These results, the formation of an external phase and



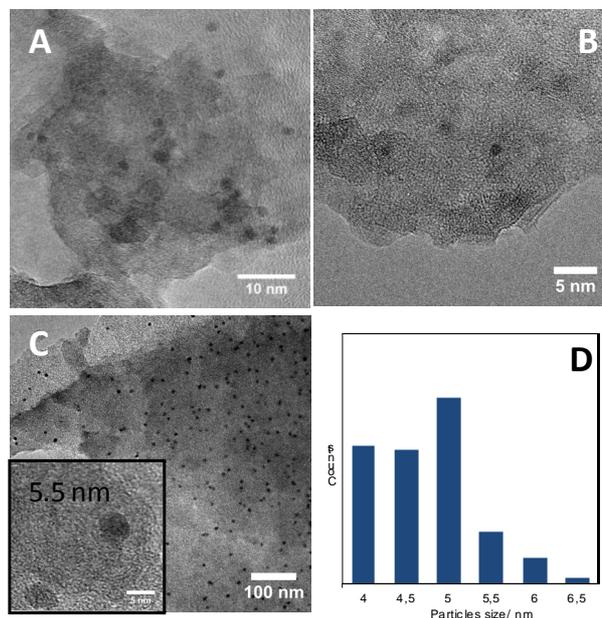
**Figure 4.** Wide angles XRD patterns of the aluminas.

its possible reduction, confirm that at least a part of the metal (case of Pd and Pt) is not incorporating into the alumina framework, and is accessible for gas phase (possibility to reduce them). The particles sizes evaluated by XRD, using the Debye-Scherrer equation after Warren's correction for instrumental broadening, are 1.8 nm and 4.9 nm for Pt-Al-EISA and Pd-Al-EISA respectively. Supported noble metal nanoparticles are then obtained in the case of the Pd and Pt based composites. The small Pt particle size evaluated by this method strongly suggests that the particles are dispersed inside the porosity with no difficulty of access due to the larger pore size of the support. For Pd-Al-EISA, the mean Pd particle size is evaluated at a size very close to that of the pore size support. Some support pore plugging by the metal nanoparticles can then occur in this solid, even if the metal loading remains low.

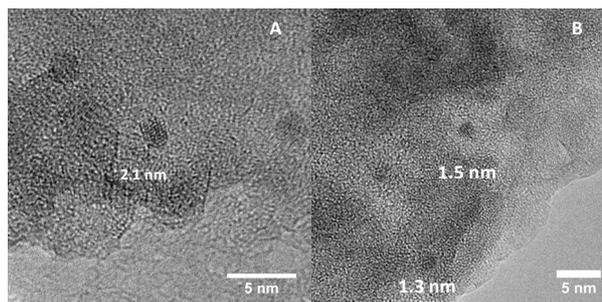
TEM analysis was performed on the materials to confirm the presence of metallic nanoparticles and their size in the alumina support. Representative TEM pictures are presented **Figure 5**. Some differences are easily observable:

For Pt-Al-EISA (**Figure 5(A)**), a homogeneous size and dispersion of the metallic particles in the alumina aggregates is observed. In addition, the mean size of 2 nm (**Figure 6(A)**) is close to the size evaluated from X-ray line broadening.

For Rh-Al-EISA (**Figure 5(B)**) metallic nanoparticles are observed at high magnification even if no reflection was detected by XRD. The particles are however very small, with most of them presenting sizes below 2 nm (**Figure 6(B)**), that can explain the lack of reflection in XRD pattern.



**Figure 5.** TEM images of  $NM-\gamma-Al_2O_3$  (A) Pt, (B) Rh, (C) Pd and (D) Size distribution histogram of Pd.



**Figure 6.** TEM images of Pt (A) and Rh (B) clusters in  $Al_2O_3$  matrix.

For Pd-Al-EISA (**Figure 5(C)**), 4 - 6 nm palladium nanoparticles with homogeneous size and dispersion are visible located in the alumina aggregates. Focusing on the metallic particles allows the size measurement, which is observed to be mainly ranging from 4 to 5 nm (histogram of size distribution is given **Figure 5(D)**). This result is then in accordance with that obtained by XRD.

By a classical post grafting it is not easy to observe metallic particles with homogeneous size and dispersion [48-50].

For example, Osaki *et al.* [52] present a comparison between a one-pot sol-gel synthesis of  $Pt-Al_2O_3$  and Pt post grafting. They show that by post grafting method, the metallic particle size is 2.5 times higher than that by the one-pot synthesis and the homogeneity of the noble metal is very low (<5%). At comparable calcination temperatures, it appears that  $NM-Al_2O_3$  exhibit  $S_{BET} < 200 \text{ m}^2 \cdot \text{g}^{-1}$  with  $NM$  particles sizes higher than 6 nm.

Wang *et al.* [53] compare the physical properties of

Pd-Al<sub>2</sub>O<sub>3</sub> synthesized by a one-pot sol gel method or post grafting method. The catalyst synthesized by post grafting method exhibits higher physical properties than the one obtained by the one pot synthesis. In their study the catalyst obtained in the latter case exhibits lower S<sub>BET</sub> and comparable pore diameter to our materials and contrary to our study, they demonstrate the necessity to use a stabilizer in the one pot synthesis in order to increase the physical properties of their catalyst.

By the one-pot synthesis described here, the incorporation of a metallic phase is possible at the first step of the synthesis, allowing the elimination of a preparation step (impregnation, grafting step). The as-obtained active phase is under the shape of dispersed nanoparticles in the alumina support. Even if palladium nanoparticles size is a little bit higher than for the other metals, an interesting homogeneity in size and dispersion is observed. These properties make these solids excellent model materials in the palladium chemistry field, including Suzuki cross coupling or Heck reactions [54-57]. In addition, all these materials present interesting physical properties like high surface area and pore size enough large for a use in gas phase reaction. These materials can also be considered for different applications such as hydrocarbons reforming, oxidation, hydrogenation or dehydrogenation reactions, NO<sub>x</sub> reduction [58-65].

To summarize, alumina supported noble metal nanoparticles are obtained using a simple way of synthesis. The ionothermal synthesis can advantageously replace the solvothermal process and facilitates the one-pot functionalization of the alumina support. The catalysts synthesized turned out interesting characteristics, like metallic nanoparticles well dispersed and homogeneous in size. In addition, whatever the noble metal used, the composites maintain competitive physical properties.

#### 4. Acknowledgements

M. Bonne thanks the Région Poitou-Charentes for her Ph. D grant.

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