



**Research/Technical Note**

# **Pine Wood Powder Treatment to $B_xH^+$ Homogeneous Catalyst ( $H^+/H_2SO_4$ ) Supported on Its Aromatics' and PNA' Alkenes – Application in Black Citric Acid Polymer Synthesis**

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**Abstract:** For a long time, many chemical reactions drew on catalysts, products used in smallest quantities compared to products-reagents, to accelerate their kinetics. In certain cases, one of the determining factors to improve these catalysts activities is the use of supports allowing dispersions and thereafter the effectiveness of its active sites. It is the goal of our study, to increase the pine wood powders value like support of active acid  $H^+$  sites of sulphuric acid molecules by hydrogen bond connection with alkenes of aromatics and polynuclear aromatics which were pine wood components and their derivatives obtained after sulphuric acid solution (98%) treatment. Among these derivatives we quote water molecules formed during dehydration and esterification of wood components. Thus, we obtained homogeneous catalysts  $B_xH^+$ , ( $H^+/H_2SO_4$ ) supported on pine wood powder which we tested by a test reaction: citric acid dehydration to prop-1-ene 1, 2, 3 acid- tricarboxylic acid. Also, the active acid sites ( $H^+/H_2SO_4$ ) contents and alkenes on  $B_xH^+$  catalysts were quantified by measuring out respectively with NaOH 0.05N and hydrofluoric acid (HF). This last measuring out enabled us to evaluate the nature of the aromatics and polynuclear aromatics which were the real supports contained in pine wood. At the end, we used these  $B_xH^+$  synthesized catalysts to catalyze the citric acid black polymer synthesis (PN). The soluble coke and insoluble coke in polar solvent dichloromethane and non-polar solvent hexane of citric acid black polymer synthesized by each catalyst were quantified.

**Keywords:** Supported Homogeneous Catalyst, Sulphuric Acid, Pine Wood, Alkene, Aromatics, PNA, Citric Acid Polymers, Coke

## **1. Introduction**

The first step of our study consisted in preparing catalysts  $B_xH^+$ , ( $H^+/H_2SO_4$ ) supported on pine wood powders which were treated with sulphuric acid solution (98%). Two kinds of pine wood powders were used: the first was dried pine wood powder and the second non-dried. After sulphuric acid solution (98%) treatment, we obtained two kinds of catalysts: the first was  $B_{NS}H^+$  catalysts, ( $H^+/H_2SO_4$ ) supported on non-dried pine wood powder and the second was  $B_SH^+$  catalyst, ( $H^+/H_2SO_4$ ) supported on dried pine wood powder.

Then, a part of dried pine wood powders was treated with methanol-sulphuric acid (98%) solution to obtain another type of catalyst:  $B_{SOH}H^+$  catalyst, ( $H^+/H_2SO_4$ ) supported on dried pine wood powder. The second step was to test these  $B_xH^+$  catalysts by a test reaction which was the citric acid dehydration to prop-1-ene 1, 2, 3 acid- tricarboxylic acid. Results showed that all these catalysts were very active and water molecules played probably significant role in transport of molecules present in the reactional environment during

each catalyst test reactions. That led us to the third step, using these catalysts to synthesize citric acid black polymer which their soluble and insoluble coke in dichloromethane and hexane solvents were quantified.

## 2. Wood General Points

### 2.1. Woods Structures and Porous Systems

Wood is a porous material resulting from vegetable and heterogeneous origin renewable source compared to other metallic (steel) and synthetics (plastic polymers) materials. The anatomical structure of wood consists of fibres directed in three directions, a longitudinal, and a transverse and radial section such as the tracheid, the parenchyma and the epithelial cells [1]. Tracheid constitute nearly 90% - 95% of the coniferous wood cells' (Stevanovic and Perrin 2009). The tracheid length is nearly 2mm – 3mm and his diameter 20 $\mu$ m to 50 $\mu$ m. They are connected by the ends and communicate through the areole punctuation located in the tracheid's lumen and wall with a major concentration in the ends. The wood cellular walls can be classified in two categories: the mesoporous which have diameters between 2nm to 50nm and the microporous which have diameter lower than 2nm. The smallest pores have diameter between 0.1nm to 1nm [2]. The knowledge of these wood's porous systems and are very important during the modification of wood by impregnation [1] and its compositions influenced the nature of the support obtained by sulfuric acid concentrated 98% treatment.

### 2.2. Wood's Compositions

Wood is constituted mainly of polysaccharides formed by polymerization of cellobiose units (cellulose and hemicellulose), phenolic polymers in particular lignin [3], extractible and minerals substances [4, 5, 6]. Extractible are free molecules being in wood porous structure and can be extracted by different solvents according to their nature. The various families of extractible chemical compounds are the waxes and greases; glucides in particular the gums polysaccharides, starch, disaccharides, simple sugars and glycosides; terpenes and terpénoïdes; phenolic compounds divided into simple phenols and tannins (condensed and hydrolysable) [7]. The wood chemical composition and its various compounds distribution varies according to the species shown by the following table 1 [6].

**Table 1.** Woods compounds distribution.

Components [%]	Resinous wood	Feuillus	Sylvestre Pine	Epicea
Cellulose	42 $\pm$ 2	45 $\pm$ 2	39	41
Hemicellulose	27 $\pm$ 2	30 $\pm$ 5	30	30
Lignin	28 $\pm$ 3	20 $\pm$ 4	27	27
Extractible	3 $\pm$ 2	5 $\pm$ 3	4	2

In our study and experimentations, because of cellulose and hemicellulose was said a non-negligible components, we adopted their values given by the following table 2 to the detriment of lignin and extractible contents.

**Table 2.** Pine wood powder compounds distribution.

Components [%]	Pine wood powder
Cellulose	40
Hemicellulose	33
Lignin	25
Extractible	2

## 3. The Sifting System

### 3.1. Sifting General Points and Procedure

The sifting is the action to separate and to retain the coarse parts of flour, ashes or chemical powder product through a sieve [8, 9]. It was said in the literature that to limit the pressure losses of the water filtration or purification columns, the balls ion exchanger diameters must be ranging between 0.3 [mm] and 1.2 [mm] [10]. For our wood powder sifting, we used simultaneously two sieves;  $T_S$ : the superior sieve and  $T_i$ : the lower sieve; whose meshes diameters was respectively 1.6 [mm] and 0.25 [mm]. The sieves with the pine wood powder are shaken on a vibration equipment for a minutes. We obtained the refusals indicating the part of the pine wood powder retained by the lower sieve ( $T_i$ : 0.25 [mm]) which we would use thereafter for the catalyst  $B_xH^+$  synthesis and tests. The refusal size that we obtained during this sifting was very important because it's one of the responsible of the well diffusion and well adsorption of the sulfuric acid molecules (98% - liquid) through the pine wood powder support (refusal) during the  $B_xH^+$  synthesis.

### 3.2. The Refusal Sifting Characteristics

From the sieves ( $T_S$  and  $T_i$ ) used dimensions, we calculated the refusal coefficient of uniformity (c.u), the refusal specific diameter ( $\phi_S$ ), the refusal fifty diameter ( $d_{50}$ ). We calculated also the external sphere surface correspondents. (Table 3)

**Table 3.** Refusal Pine wood powder sifting characteristics.

Refusal Characteristics	Formulas	Refusal Characteristics values
Coefficient of uniformity (c.u)	$c.u = \frac{T_S}{T_i}$	$c.u = 6.4$
Specific diameter ( $\phi_S$ )	$\phi_S = T_i \times (1 + 2 \log c.u)$	$\phi_S = 0.65[mm]$
Fifty diameter ( $d_{50}$ )	$d_{50} = T_i \times c.u^{0.834}$	$d_{50} = 1.176[mm]$
External surface by $\phi_S$	$S_{\phi_S} = \pi \times \phi_S^2$	$S_{\phi_S} = 1.33[mm^2]$
External surface by $d_{50}$	$S_{d_{50}} = \pi \times d_{50}^2$	$S_{d_{50}} = 4.345[mm^2]$

## 4. Citric Acid

### 4.1. Citric acid General Points

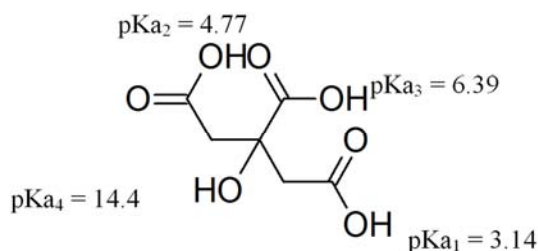


Figure 1. 3-hydroxybutane-1, 2, 4-tricarboxylic acid (Citric Acid).

Citric acid is solid with monoclinic as crystal structure, white, odorless and excessively sour flavor (Table 4) [11]. Citric acid exists in hydrates forms, the monohydrate melts towards 343.15 °K and the anhydrous state melting point is 426.15°K. Citric acid is soluble in alcohol, ether, ethyl

acetate and DMSO and insoluble in  $C_6H_6$ ,  $CHCl_3$ ,  $CS_2$ , and toluene. Its solubility in ethanol at 298.15°K is 62g/100g. Citric acid is very soluble in water and its solubility increases with the temperature as shown the following table (Table 5) [12].

Table 4. Citric acid physicochemical properties.

Physicochemical Properties	CITRIC ACID - $C_6H_8O_7$
Appearance	Crystalline white solid
Crystal structure	Monoclinic
Molar mass	192.12 [g.mol <sup>-1</sup> ]
Density	1.665 [g.cm <sup>-3</sup> ] anhydrous 1.542 [g.cm <sup>-3</sup> ] monohydrate at 291.15°K
Melting point	426.15°K anhydrous 343.15°K monohydrate
Boiling point	448.15°K
Solubility in ethanol	62g/100g
Solubility in water	59.20% at 293.15°K (Table 3)

Table 5. Evolution of the citric acid solubility in water (w/w) following to the temperature (°K).

T°K	283.15	293.15	303.15	313.15	323.15	333.15	343.15	353.15	363.15	373.15
Solubility (% g/100mg)	54.0	59.2	64.3	68.6	70.9	73.5	76.2	78.8	81.4	84.0

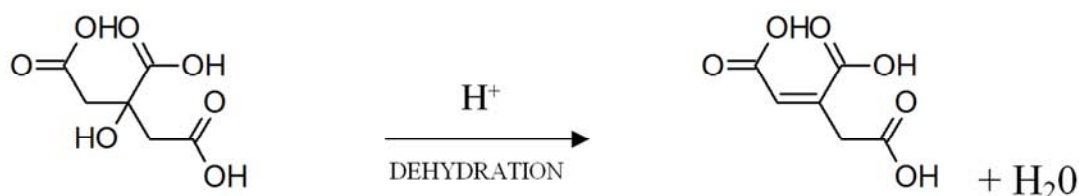
Citric acid  $C_6H_8O_7$  is a tricarboxylic acid  $\alpha$ -hydrolyzed. It contains three acids with pKa such as  $pK_{a1} = 3.14$ ,  $pK_{a2} = 4.77$  and  $pK_{a3} = 6.39$  and a  $\alpha$ -alcohol function with  $pK_a = 14.4$  [11, 13, 14, 15] "Figure 1". By its reactivity, the citric acid was the object of several studies and was used in several fields like the cosmetics, the food one, the chemistry and others [7]. We noticed that the acid form is AH with  $pK_a(AH)$ . It was shown that if the  $pH \leq [pK_a(AH) - 2]$ , the quantity of basic  $A^-$  associated to the acid/base couple  $AH/A^-$  is negligible in

comparison with the AH quantity. And if the  $pH \geq [pK_a(AH) + 2]$ , the quantity of acid AH associated to the acid/base couple  $AH/A^-$  is negligible in comparison with the  $A^-$  quantity [16]. For  $[pK_a(AH) - 2] \leq pH \leq [pK_a(AH) + 2]$ , the basic  $A^-$  and the acid AH forms coexist but if  $[pK_a(AH) - 2] \leq pH \leq pK_a(AH)$  the acid form AH dominate and if  $pK_a(AH) \leq pH \leq [pK_a(AH) + 2]$  the basic form  $A^-$  dominate [16]. Consequently, for the citric acid we noted in the following Table 6 the acids and basics forms according to the pKa and pH:

Table 6. Dominant Forms of "Citric Acid" According to the pH.

pH	Acid/base couple	pKa	Acid/Base reactions	Dominant forms	Dominant molecules/Ions
$pH \leq 3.14$	$AH_3/AH_2^-$	3.14	$AH_3 \rightleftharpoons AH_2^- + H^+$	$AH_3$	Citric Acid
$3.14 \leq pH \leq 4.77$	$AH_2^-/AH^{2-}$	4.77	$AH_2^- \rightleftharpoons AH^{2-} + H^+$	$AH_2^-$	Di-Hydrogenocitrate
$4.77 \leq pH \leq 6.39$	$AH^{2-}/A^{3-}$	6.39	$AH^{2-} \rightleftharpoons A^{3-} + H^+$	$AH^{2-}$	Mono-Hydrogenocitrate
$6.39 \leq pH$	$AH^{2-}/A^{3-}$	6.39	$AH^{2-} \rightleftharpoons A^{3-} + H^+$	$A^{3-}$	Citrate

### 4.2. Citric Acid Molecule Dehydration – Black Citric Acid Polymers (PN) Formation



(a) 2-hydroxypropane-1, 2, 3-tricarboxylic acid (citric acid)

(b) prop-1-ene-1, 2, 3-tricarboxylic acid – White monomer

Figure 2. 3-hydroxybutane-1, 2, 4-tricarboxylic acid (Citric Acid – (a)) dehydration to white monomer (b).

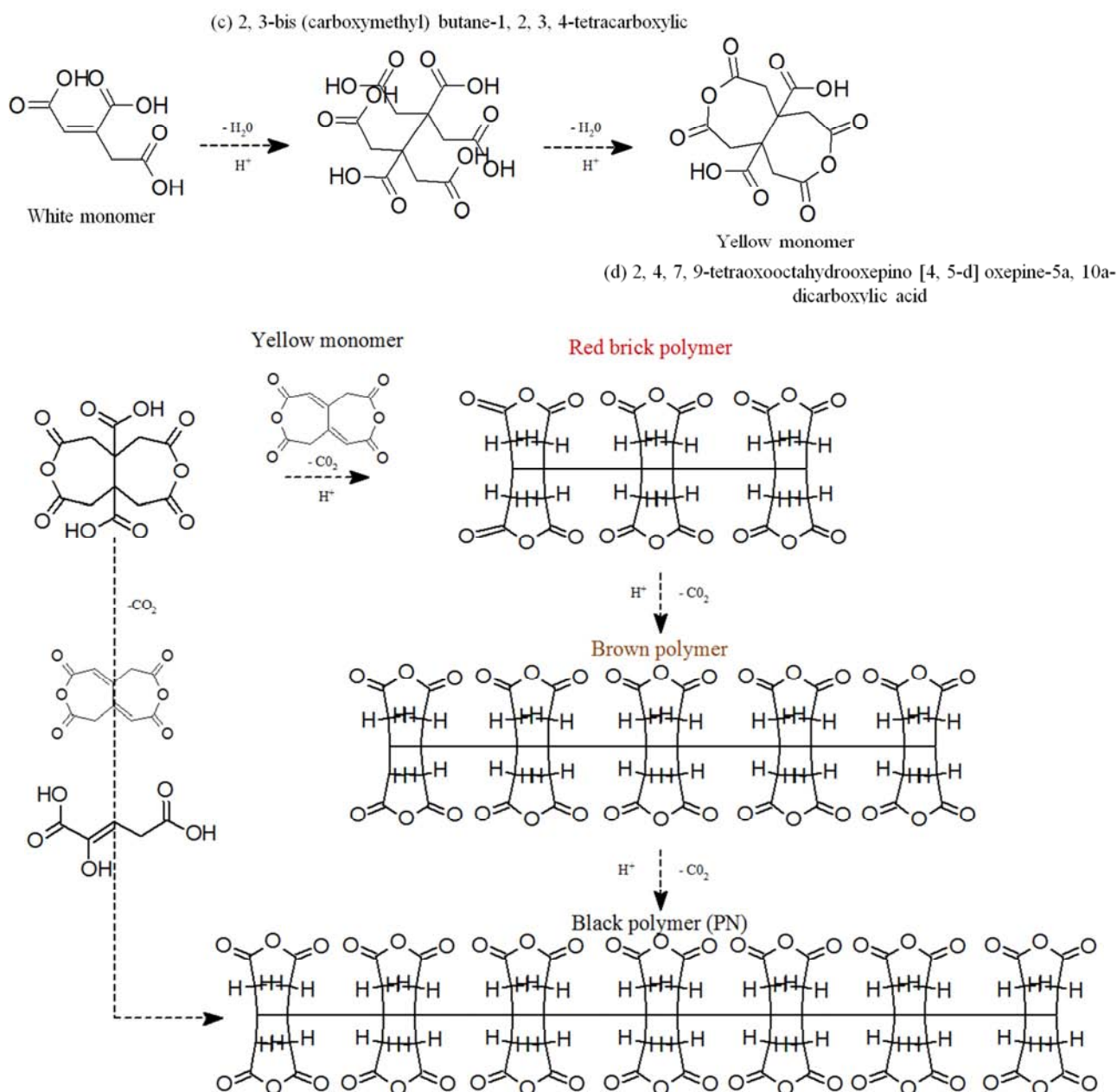


Figure 3. Black citric acid polymers (PN) formation.

The first step is the dehydration of citric acid molecules (a) to obtain prop - 1 - ene - 1, 2, 3-tricarboxylic acid (b) (Figure 2). This reaction was catalyzed by acid catalysts like sulfuric acid [18] or metal catalysts like iron [18]. Then, these monomers (White monomer) combined to form 2, 3 - bis (carboxymethyl) butane - 1, 2, 3, 4 - tetracarboxylic acid (c) which will be transformed to hydracids 2, 4, 7, 9-tetraoxooctahydrooxepineo [4, 5 - d] oxepine-5a, 10a-dicarboxylic acid (d) by two dehydration per molecule [18, 19]. The carboxylic acids of this last monomer was transformed to carbon dioxide at high temperature before they entered in reaction together to form polymers of citric acid. It was shown that the citric acid polymers color changed with the degree of polymerization such as red brick polymer, brown polymer and black polymer (PN) [18]. Black was the last color

which characterize the black citric acid polymer (PN) (e). (Figure 3). It was shown that black citric acid polymer (PN) was a good fuel oil additive [20].

## 5. Sulfuric Acid ( $H_2SO_4$ )

### 5.1. Sulfuric Acid $pK_a$ 's

We noticed that the acid form is AH with  $pK_a$  (AH). It was shown that if the  $pH \leq [pK_a (AH) - 2]$ , the quantity of basic  $A^-$  associated to the acid/base couple AH/ $A^-$  is negligible in comparison with the AH quantity. And if the  $pH \geq [pK_a (AH) + 2]$ , the quantity of acid AH associated to the acid/base couple AH/ $A^-$  is negligible in comparison with the  $A^-$  quantity [16]. For  $[pK_a (AH) - 2] \leq pH \leq [pK_a (AH) + 2]$ , the basic  $A^-$  and the acid AH forms coexist but if  $[pK_a (AH) - 2] \leq pH \leq$

pKa (AH) the acid form AH dominate and if  $pK_a(AH) \leq pH \leq [pK_a(AH) + 2]$  the basic form  $A^-$  dominate [16]. Consequently, for the sulfuric acid we noted in the following

Table 7 the acids and basics forms according to the pKa and pH [18]. On the table 8 we noted the used sulfuric acid characteristics.

Table 7. Dominant forms of "sulfuric acid" according to the pH.

pH	Acid/base couple	pKa	Acid/Base reactions	Dominant forms	Dominant molecule/Ions
$pH \leq -9$	$H_2SO_4/HSO_4^-$	$\approx -9$	$H_2SO_4 \rightleftharpoons HSO_4^- + H^+$	$H_2SO_4$	Sulfuric acid
$-9 \leq pH \leq 1.9$	$H_2SO_4/HSO_4^-$	$\approx -9$	$H_2SO_4 \rightleftharpoons HSO_4^- + H^+$	$HSO_4^- (H^+)$	Hydrogenosulfate ion
$1.9 \leq pH$	$HSO_4^-/SO_4^{2-}$	1.9	$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	$SO_4^{2-} (H^+)$	Sulfate ion

## 5.2. Used Sulfuric Acid Characteristics – The One Drop Sulfuric Acid $nH^+$ Moles

Table 8. Physicals and chemicals characteristics of used sulfuric acid and the one drop sulfuric acid  $nH^+$  moles.

PHYSICALS AND CHEMICALS CHARACTERISTICS	$H_2SO_4$
Density [g.ml <sup>-1</sup> ]	1.8357
Molar Mass [g.mol <sup>-1</sup> ]	98.07
Purity [%]	98
Volume	1 [drop]      0,1 [ml]
Mass [g]	0.1799
$H_2SO_4$ (n) moles quantity [moles]	$1.8344 \times 10^{-3}$
$H^+$ moles quantity at pH=2 [moles $H^+$ ]	$\approx 2.7516 \times 10^{-3}$
Molecular diameter [Å] [21]	4.87
Maximum size of a sulphuric acid molecule (Internuclear distance of the most distant oxygen atom and hydrogen atom) [19]	$3.289 \text{Å} \times 3.293 \text{Å}$

## 6. $B_xH^+$ Catalyst ( $H^+/H_2SO_4$ ) Supported on Pine Wood Powder Preparation Procedure

### 6.1. $B_{NS}H^+$ Catalyst ( $H^+/H_2SO_4$ ) Supported on Non-Dry Pine Wood Powder Preparation Procedure

By referring to the pine wood principal organic molecules components, its structure and porosity and the pine wood powders size importance for the sulfuric acid solution (98%) diffusion; we took 35 [g] of the pine wood powder filtered and non-dried in a beaker. Then, we added gradually and uniformly 62.97 [ml] of sulphuric acid solution (98%) by paying particular attention to the sulphuric acid molecules diffusion through the wood structure and porosity marked by the intense black coloring of the pine wood. After having mixed the mixture with a glass spatula if it's really necessary, the intense black coloring was uniform. We obtained the homogeneous catalyst  $H^+/H_2SO_4$  supported on non-dried wood:  $B_{NS}H^+$ . According to the sulphuric acid molecule sizes (Table 8) and the wood porosity diameters varying between 1Å to 500Å, the sulphuric acid molecules diffusion was fluid.

### 6.2. $B_sH^+$ Catalyst ( $H^+/H_2SO_4$ ) Supported on Dry Pine Wood Powder Preparation Procedure

By referring to the pine wood principal organic molecules components, its structure and porosity and the pine wood powders size importance for the sulfuric acid solution (98%) diffusion; we took 35 [g] of the pine wood powder filtered and dried in a beaker. Then, we added gradually and uniformly 62.97 [ml] of sulphuric acid

solution (98%) by paying particular attention to the sulphuric acid molecules diffusion through the wood structure and porosity marked by the intense black coloring of the pine wood. After having mixed the mixture with a glass spatula if it's really necessary, the intense black coloring was uniform. We obtained the homogeneous catalyst  $H^+/H_2SO_4$  supported on dried wood:  $B_sH^+$ . According to the sulphuric acid molecule sizes (Table 8) and the wood porosity diameters varying between 1Å to 500Å, the sulphuric acid molecules diffusion was fluid.

### 6.3. $B_{SOH}H^+$ Catalyst ( $H^+/H_2SO_4$ ) Supported on Dry Pine Wood Powder Preparation Procedure

By referring to the pine wood principal organic molecules components, its structure and porosity and the pine wood powders size importance for the sulfuric acid solution (98%) diffusion; we took 9.146 [g] of the pine wood powder filtered and dried in a beaker. Then, we prepared a sulphuric acid solution diluted with methanol such as  $\frac{n_{H_2SO_4}}{n_{CH_3OH}} = 1.042$  obtained by 16.45 [ml] of  $H_2SO_4$  (98%) in 12 [ml] of  $CH_3OH$ . Then, we added gradually and uniformly 62.97 [ml] of sulphuric acid solution (98%) by paying particular attention to the sulphuric acid molecules diffusion through the wood structure and porosity marked by the intense black coloring of the pine wood. After having mixed the mixture with a glass spatula if it's really necessary, the intense black coloring was uniform. We obtained the homogeneous catalyst  $H^+/H_2SO_4$  supported on dried wood prepared with methanol:  $B_{SOH}H^+$ . According to the sulphuric acid molecule sizes (Table 8), methanol molecular diameter 4.08Å [22] and the wood porosity diameters varying between 1Å to 500Å, the sulphuric acid molecules diffusion was fluid.

## 7. Chemicals and Physicals

### Characteristics of Catalyst $B_XH^+$ Supported on Pine Wood Powder

#### 7.1. $B_XH^+$ Catalysts ( $H^+/H_2SO_4$ ) Supported on Pine Wood Powder Accessible $H^+$ Ions Measuring out Procedure by NaOH Solution

Took approximatively 0.1 [g] of the  $B_XH^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder. Prepare a 0.05N NaOH solution. Dilute the sample in a beaker with 45 [ml] of distilled water, then add two or three drops of helianthine. The solution turn immediately to red intense. Place the 0.05N NaOH solution in an oilcan and the beaker on the magnetic stirrer. The measuring out can begin by falling into the beaker drip the oilcan 0.05N NaOH solution and mixing the beaker solution with the magnetic stirrer. When the beaker solution turn to orange yellow, closed the oilcan and record the equivalent 0.05N NaOH volume which correspond to the equivalent point. Then, we can calculate the  $B_XH^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder accessible  $H^+$  ions content and their  $H^+$  density (Table 9).

**Table 9.**  $B_XH^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder accessible  $H^+$  ions content.

$B_XH^+$ catalysts	$[H^+]$ [mol.l <sup>-1</sup> ]	nH <sup>+</sup> [moles]	$H^+$ Density [mol.g <sup>-1</sup> ]
$B_SH^+$	38.55E-3	1.735E-3	16.670E-3
$B_{SOH}H^+$	25.76E-3	1.159E-3	11.546E-3
$B_{NS}H^+$	23.51E-3	1.058E-3	10.580E-3

**Table 10.**  $B_XH^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder accessible  $H^+$  ions and alkene contents.

$B_XH^+$ catalysts	Weight catalysts [g]	Alkene function quantity [moles]	nH <sup>+</sup> [moles]	Alkene/nH <sup>+</sup>
$B_SH^+$	0.0106	9.9667E-4	1.7670E-4	5.64
$B_{SOH}H^+$	0.0308	2.1017E-3	3.5562E-4	5.91
$B_{NS}H^+$	0.0108	1.5859E-3	1.1426E-4	13.88

Compared with the nH<sup>+</sup> quantity, for all the  $B_XH^+$  catalysts, the alkene function quantity were largely more important (Table 10): approximatively six times (×6) more important for  $B_SH^+$  and  $B_{SOH}H^+$  catalysts and thirteen times more important for the  $B_{NS}H^+$  catalyst ( $H^+/H_2SO_4$ ) supported on non-dry pine wood powder.

**Table 11.**  $B_{NS}H^+$  catalyst ( $H^+/H_2SO_4$ ) supported on pine wood powder weight after (- C<sup>-</sup>) measuring out by HF.

$B_{NS}H^+$ catalyst	Initial $B_{NS}H^+$ weight	After alkene function (- C <sup>-</sup> ) measuring out $B_{NS}H^+$ mass
Weight [g]	0.0305	0.0039
$\Delta m$ [g]	0.0266 (87.21%)	

This 87.21% ( $H^+/H_2SO_4$ ) catalysts  $B_{NS}H^+$  supported on pine wood powder weight reduction confirms that the alkene function (- C<sup>-</sup>) measuring out by hydrofluoric acid (HF) destroyed certain molecular structure base of the pine wood porosity [1, 2] and allowed the ( $H^+/H_2SO_4$ ) molecules trapped inside to exit. The measuring out of these ( $H^+/H_2SO_4$ ) molecules trapped inside will be see in the 7.3 paragraph.

For the moment, the black color formed during the catalyst preparation confirmed the oxygenated aromatics and

#### 7.2. Alkenes Moles of Oxygenated Aromatics and Polynuclear Aromatics (PNA) Formed After Preparation Measuring out Procedure by Hydrofluoric Acid (HF) – Aromatics and PNA Formed Families' Characteristics

Took approximatively 0.0305 [g] of the  $B_{NS}H^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder. Prepare a 2.6E-3 [mol.l<sup>-1</sup>] HF solution [23]. Wash abundantly the sample with three times of 30 [ml] distilled water at the maximum to eliminate the  $H_2SO_4$  molecules. Then, dilute the washed catalysts in a beaker with 30 [ml] of distilled water. Then add two or three drops of bromophenol blue. The solution turn immediately to yellow. Place the 2.6E-3 [mol.l<sup>-1</sup>] HF solution in an oilcan and the beaker on the magnetic stirrer. The measuring out can begin by falling into the beaker drip the oilcan 2.6E-3 [mol.l<sup>-1</sup>] HF solution and mixing the beaker solution with the magnetic stirrer. When the beaker solution turn to blue, closed the oilcan and record the equivalent 2.6E-3 [mol.l<sup>-1</sup>] HF volume which correspond to the equivalent point. Then, we can calculate the  $B_XH^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder accessible alkene (- C<sup>-</sup>) function content (Table 10). After some minutes at rest, the baker solution after measuring out return to yellow that is to say it became to be acid solution which showed that there was ( $H^+/H_2SO_4$ ) ions trapped in the pin wood porous by the aromatics and polynuclear aromatics (PNA) formed during the  $B_XH^+$  preparation.

After the alkene function (- C<sup>-</sup>) measuring out, we weighted the rest of  $B_{NS}H^+$  catalyst in the following procedure: filter the solution containing the catalyst rest on filter paper, then dry the filter paper holding the catalyst rest in a drying oven at 338 [°K] during at least one hour. At the end, weigh the mass of the catalyst rest. We show in the following table 11 the result.

oxygenated polynuclear aromatics (PNA) formations according to the mechanisms presented and clarified in the following paragraphs and whose alkene function (- C<sup>-</sup>) contents were shown and measuring out previously. These aromatics molecules were obtained by esterification and dehydration molecules catalyzed by ( $H^+/H_2SO_4$ ) molecules accompanied with water and steams formations. Thus, accessible and inaccessible sulphuric acid molecules in solution can be physically adsorbed and move over these

aromatics and polynuclear aromatics oxygenated molecules and confirmed that  $B_XH^+$  catalysts were homogeneous catalysts supported on pin wood powder. The maximum

quantity of  $H^+$  is equal to the  $H_2SO_4$  moles number because of the electroneutrality and global electric charge conservation law.

**Table 12.**  $B_{NS}H^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder accessible and trapped  $H^+$  contents.

$B_{NS}H^+$ [g]	Alkene function $C^-$ [moles]	$nH^+$ ( $nH_2SO_4$ – accessible)[moles]	$nH^+$ ( $nH_2SO_4$ – trapped)[moles]	$nH^+$ ( $nH_2SO_4$ – Total)[moles]	Weight ( $H_2SO_4$ – accessible)[g]	Weight ( $H_2SO_4$ – trapped)[g]	Weight $B_{NS}H^+$ Corrected [g]
0.0305	1.5859E-3	1.5859E-3	3.276E-5	1.6187E-3	1.5572E-3	3.2105E-3	0.0257
0.0305	$nH^+$ (density)			3.2269E-4			
			10.15 [%]				

According to the weight conservation law, the aromatics and polynuclear aromatics oxygenated (PNA) formed weight was estimated at 0.0218 [g] equivalent to 84.82% of the pin wood powder initial weight (Table 13).

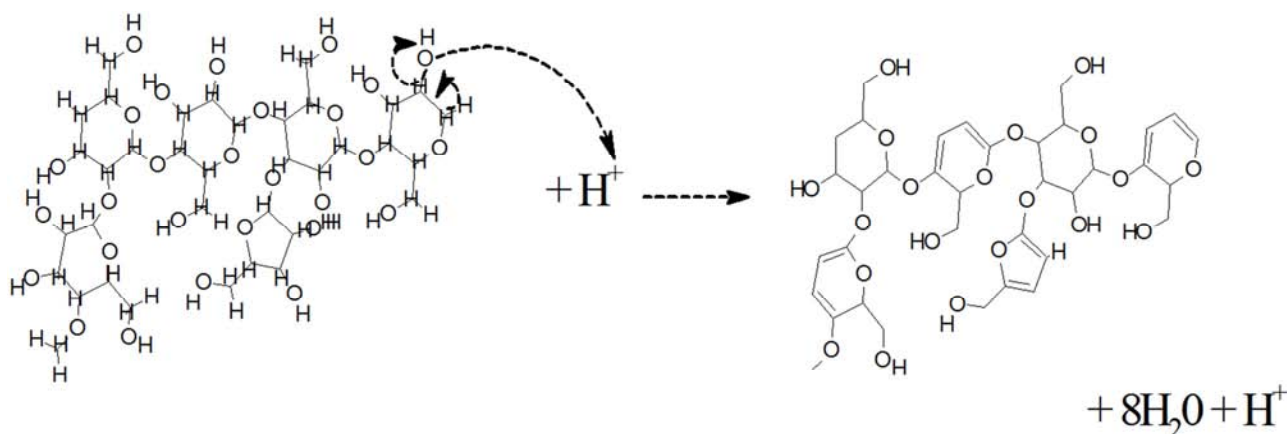
**Table 13.** Aromatics and Polynuclear aromatics oxygenated percentage compared with the cumuled pin wood components percentage.

PIN WOOD COMPONENTS	0.0257 [g]	Weight cumuled (Extractible to cellulose) [g]	Cumuled percentage (Extractible to cellulose) [%]	Weight of Aromatics and PNA [g]	A-PNA Percentage compared with the pin wood weight [%]
Cellulose (40%)	0.0103	25.7E-3	100		
Hemicellulose (33%)	0.0085	15.4E-3	59.94		15.18
Lignin (25%)	6.4E-3	6.906E-3		0.0218	
Extractible (2%)	5.06E-4	5.06E-4	26.88		84.82

According to the table 13, the most pin wood components had been transformed into aromatics and polynuclear aromatics oxygenated (PNA) (84.82% - Table 12). On the other hand, a non-negligible part of these components remained intact (15.18% - Table 12) and confirmed the non-deterioration and non-transformation of all pin wood structure trapping thus under the formed aromatics and polynuclear aromatics oxygenated (PNA) a non-negligible ( $H^+/H_2SO_4$ ) molecules corresponding to 2.02% of the total ( $H^+/H_2SO_4$ ) molecules that is to say 10.15% of the total  $B_{NS}H^+$  ( $H^+/H_2SO_4$ ) molecules. That is to say, significant amounts of sulphuric acid molecules in solution carrying the active sites

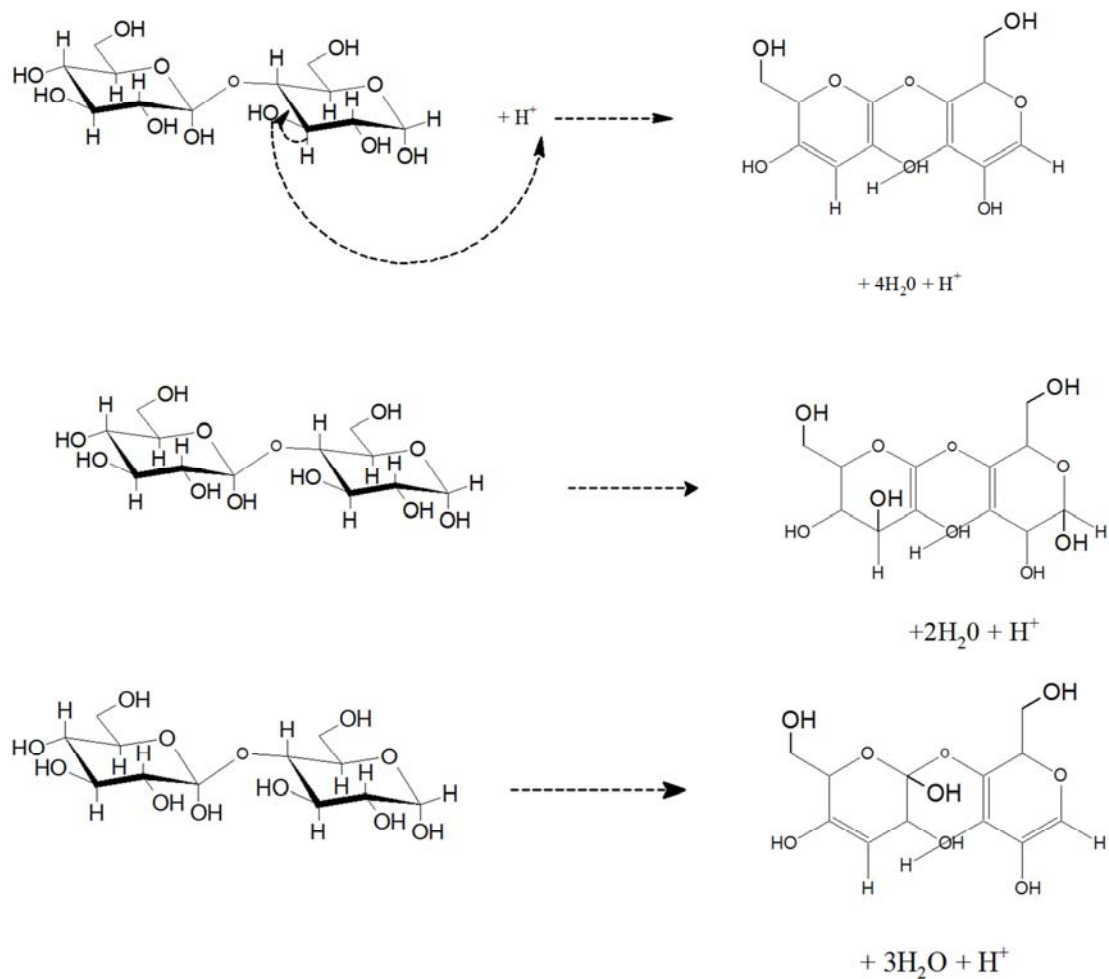
$H^+$  were accessible on surface and could be adsorbed and can move preferentially on the alkene functions which were many (Table 10) and may be on others aromatics and polynuclear aromatics oxygenated (PNA) functions by hydrogen bonds [24, 25]. What led us to suggest various possible transformations of pin wood components to aromatics and polynuclear aromatics oxygenated (PNA) with non-negligible alkene functions measuring out by hydrofluoric acid (HF – Table 12, Table 10). These transformations are catalyzed in solution by the  $H^+$  ions of ( $H^+/H_2SO_4$ ) molecules.

1.  $8nC=$  alkenes formed by hemicellulose dehydration



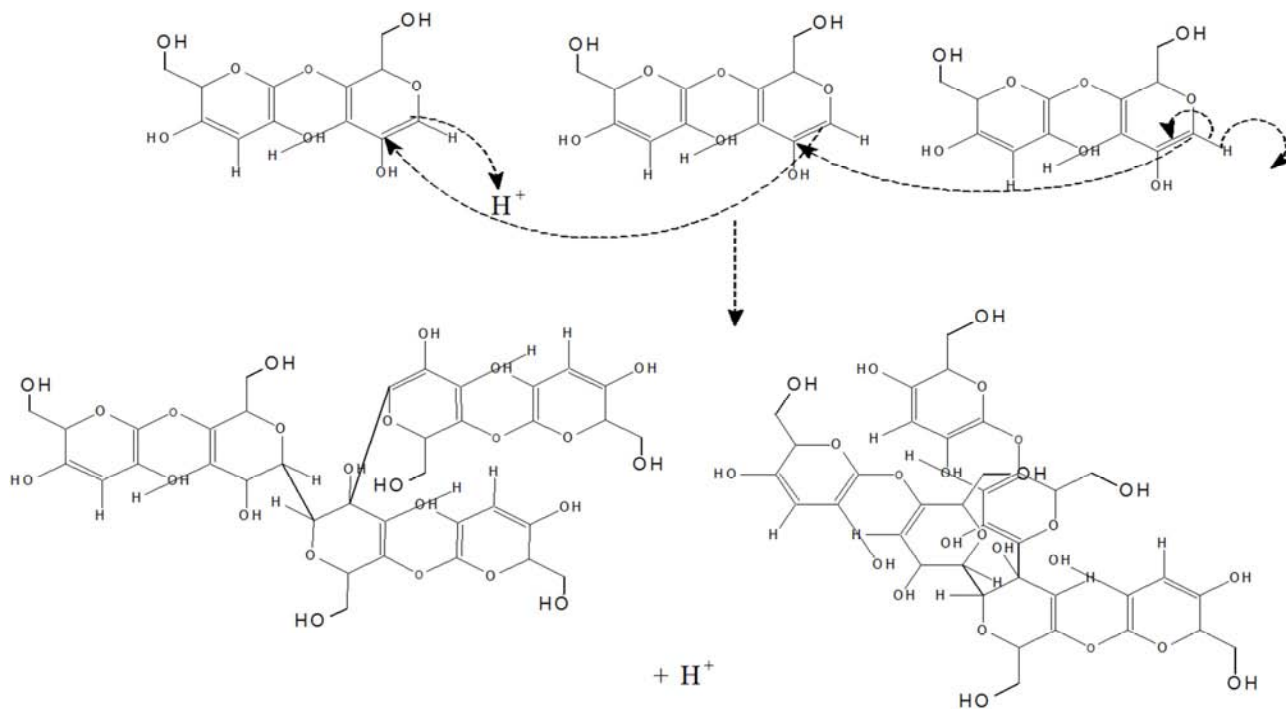
**Figure 4.**  $8nC=$  alkenes formed by hemicellulose dehydration.

2. Cellobiose (cellulose macromolecule unit) dehydration to form aromatics oxygenated with  $2nC=$ ,  $3nC=$  and  $4nC=$  alkenes



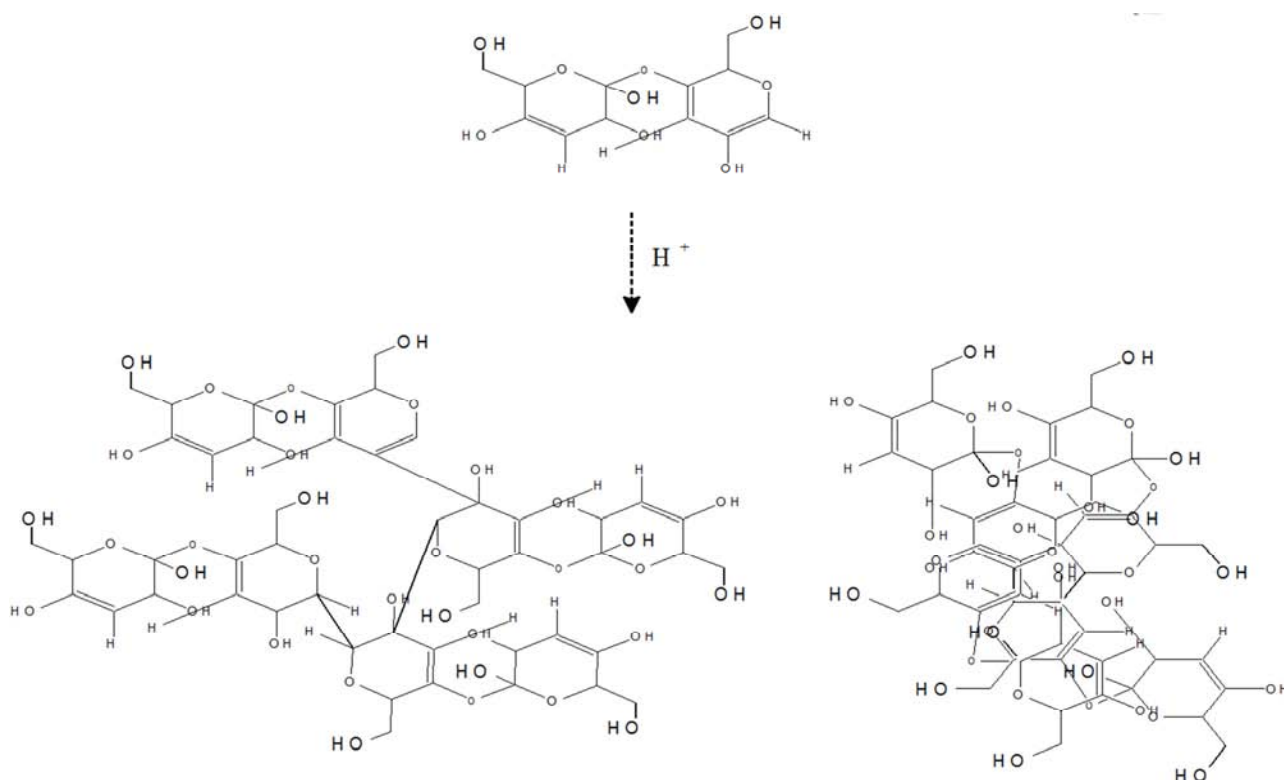
**Figure 5.** Aromatics with 2nC<sup>-</sup>, 3nC<sup>-</sup> and 4nC<sup>-</sup> alkenes formed by cellobiose (cellulose macromolecule unit) dehydration.

### 3. Three dehydrated cellobiose unities polymerization to form 10nC= alkenes of PNA oxygenated



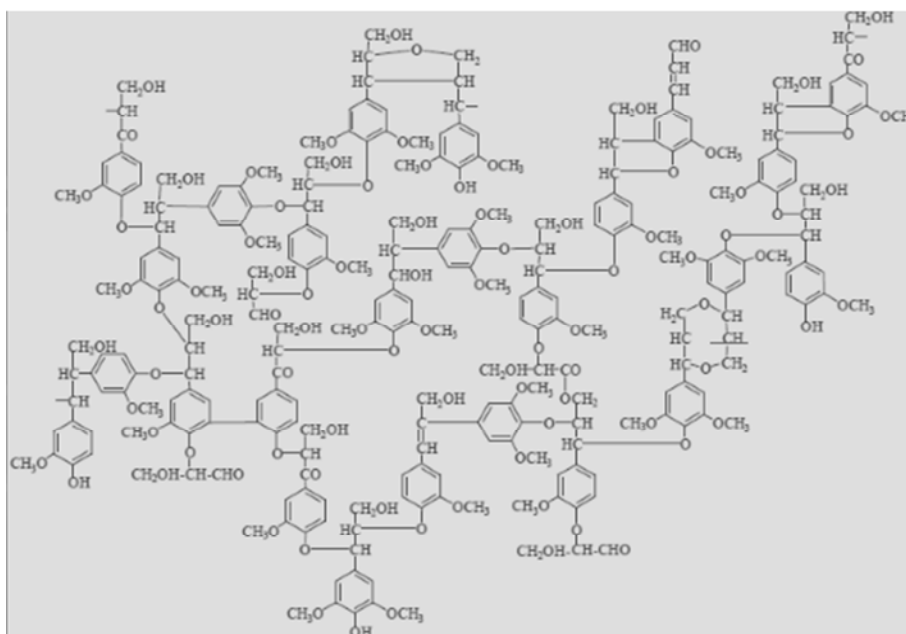
**Figure 6.** Three monomers dehydrated cellobiose unities polymerization to form 10nC<sup>-</sup> alkenes of PNA oxygenated.

#### 4. Four cellobiose unities polymerization to form 9nC= alkenes of PNA oxygenated



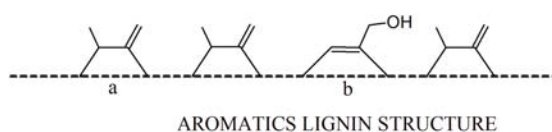
**Figure 7.** Four monomers dehydrated cellobiose unities polymerization to form 9nC<sup>-</sup> alkenes of PNA oxygenated.

#### 5. Alcohol's lignin functions dehydration to form C= alkenes function

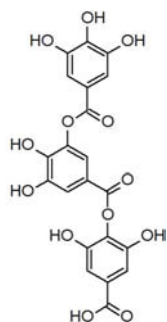


**Figure 8.** Lignin molecule [1, 7, 26].

Alcohol functions of the lignin molecule (figure 8) can be dehydrated also to generate alkene functions which were localised and scattered in majority on the tips of lignin structure (a) (figure 9).



**Figure 9.** Alkene functions a and b scattered on the lignin structure.



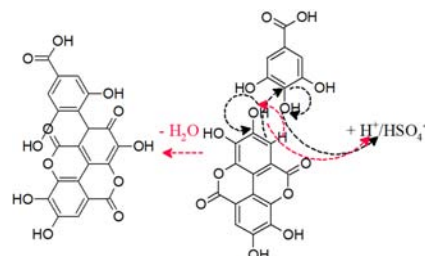
**Figure 10.** Digallic acid esterification by the alcohol function of gallic acid to form oxygenated aromatics

6. Esters functions formed by extractible molecules like gallic acid, digallic acid or ellagic acid esterification – Higher PNA molecules formation with alkene functions

The transformation of extractible phenolic compounds, in particular the gallic acid, the digallic and the ellagic acid, to

unsaturated polynuclear aromatics oxygenated by esterification with water molecules formation was also possible as shown in the following figure 10-11 and table 14 according to the alkenes quantity measuring out by hydrofluoric acid (§ 7.3).

7. Terpenes and sesquiterpenes transformation to form PNA molecules with alkenes function



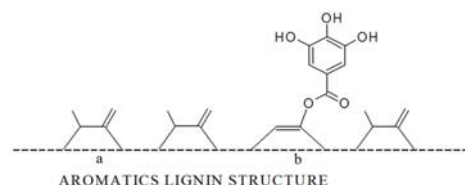
**Figure 11.** Nucleophile addition between ellagic acid and gallic acid catalyzed by  $H^+$  to form PNA with alkene functions and water formation.

**Table 14.** Aromatics and Polynuclear aromatics with alkene function formed by terpenes and sesquiterpenes according to the alkenes quantity (Table 12 - § 7.2).

n-C <sup>+</sup> [moles]	Equivalent n-benzene [moles]	Equivalent n-benzene entity stuck ( $\times 1.023E+23$ ) [entity]	Equivalent possible molecules
1.5859E-5	7.9295E-6	8.1119E+17	 Digallic acid esterification with occidenol
 Nucleophile addition between ellagic acid and gallic acid catalyzed by $H^+$ to form PNA with alkenes function and water formation			
 PNA oxygenated with alkenes function formed by Poly-esterification between gallic acids			
 Digallic acid esterification with nootkatine			
 Digallic acid esterification with nérolidol			

8. Esters functions formed by extractible molecules like gallic acid, digallic acid or ellagic acid esterification with alcohol scattered on the lignin structure – Higher PNA molecules formation with alkene functions

Then, it was also possible that alcohol function on the lignin structure (Figure 9) esterified the gallic acid (Figure 12) or digallic acid to form a higher PNA molecules with alkene functions.



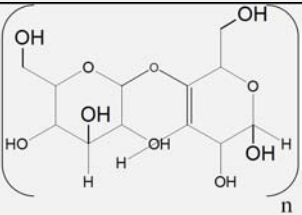
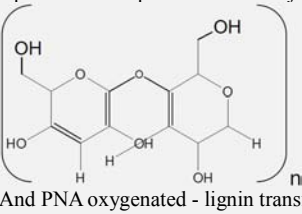
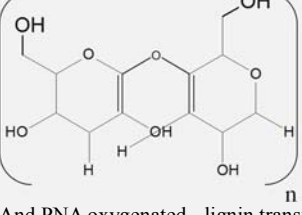
**Figure 12.** Alkene functions a and b and esters functions scattered on the lignin structure.

### 7.3. $B_XH^+$ catalysts ( $H^+/H_2SO_4$ ) Supported on Pine Wood Powder $H^+$ Ions Trapped Measuring out Procedure

It was shown before that the  $B_XH^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder alkene function ( $-C^=$ ) measuring out by hydrofluoric acid (HF) destroyed certain molecular structure base of the pine wood porosity [1, 2] and allowed the ( $H^+/H_2SO_4$ ) molecules trapped inside to exit. The goal was to measuring out these ( $H^+/H_2SO_4$ ) molecules trapped. So, when the alkene function ( $-C^=$ ) measuring out by hydrofluoric acid (HF) equivalent point was achieved, add immediately 1 [ml] to 2 [ml] of hydrofluoric acid in excess. Then add two or three drops of bromophenol blue. The

solution color in the beaker was blue. Place the 0.05N of NaOH solution in an oilcan and the beaker on the magnetic stirrer. The measuring out can begin by falling into the beaker drip the oilcan 0.05N NaOH solution and mixing the beaker solution with the magnetic stirrer. When the beaker solution turn to transparent yellow, closed the oilcan and record the equivalent 0.05NaOH volume which correspond to the equivalent point. Then, we can calculate the  $B_XH^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder trapped ( $H^+/H_2SO_4$ ) ions (Table 15) considering the 1 [ml] to 2 [ml] of hydrofluoric acid in excess.

Table 15.  $B_XH^+$  catalysts trapped alkenes quantity measuring out by hydrofluoric acid.

$B_XH^+$ catalysts	Weight catalysts [g]	Trapped ( $H^+/H_2SO_4$ ) [moles]	Alkene function quantity [moles]	Alkene/Trapped $nH^+$	Equivalent Aromatics and polynuclear aromatics formed
$B_SH^+$	0.0106	1.1844E-4	9.9667E-4	8.42	 <p>And PNA oxygenated - lignin transformed with equivalent multiples <math>N C^=</math> entities just as <math>N = 1 \times n / n \in N</math></p>
$B_{SOH}H^+$	0.0308	1.512E-5	2.1017E-3	139.35	 <p>And PNA oxygenated - lignin transformed with equivalent multiples <math>N C^=</math> entities just as <math>N = 3 \times n / n \in N</math></p>
$B_{NS}H^+$	0.0108	3.276E-5	1.5859E-3	48.41	 <p>And PNA oxygenated - lignin transformed with equivalent multiples <math>N C^=</math> entities just as <math>N = 2 \times n / n \in N</math></p>

This table 15 showed that alkenes quantity were all the time largely numerous than the trapped ( $H^+/H_2SO_4$ ). The large value of (Alkene/Trapped  $nH^+$ ) for the  $B_{SOH}H^+$  catalyst informed us not only the existence of trapped alkenes (accordingly the presence of aromatics and polynuclear aromatics trapped or on surface) but also their measuring out and their moving became easy by the methanol molecules. That was the same for the non-dried catalyst  $B_{NS}H^+$  where water molecules facilitated molecules moving and trapped  $H^+$  measuring out, so the Alkene/Trapped  $nH^+$  values was non-negligible equal to 48.41. However, the lowest value (8.41) for the dried catalyst  $B_SH^+$  showed that the drying procedure (cf. §11) eliminated a large part of extractible molecules. In the over wise, extractible molecules played an important role for the alkenes function formation (cf. §7.2). All these results

confirmed that alkenes function formed during the catalysts  $B_XH^+$  preparation were very important and played an important role in the  $B_XH^+$  activities.

### 7.4. $B_XH^+$ Catalysts ( $H^+/H_2SO_4$ ) Supported on Pine Wood Powder Density and Specific Surface Calculated by Empirical Formula - $B_{SOH}H^+$ Catalyst Specific Surface Correction by Determining the Methanol Molecules Quantity on Surface and Trapped using Calculations and Acetic Acid 99% Measuring out

#### 7.4.1. $B_XH^+$ Catalysts ( $H^+/H_2SO_4$ ) Supported on Pine Wood Powder Density and Specific Surface

$B_XH^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder specific surface,  $S_{\text{specific}}$ , were calculated by empirical formula  $\frac{3}{\rho \times r}$  such as was the catalyst density and  $r$  the

spoke corresponding to the specific diameter  $\phi_s$  (c.f § 3.2).

**Table 16.**  $B_XH^+$  catalysts density and specific surface calculated by empiric formula.

$r = 0,325$ [mm]	Wood Powder $B_s$	$B_sH^+$ Catalyst	$B_{Ns}H^+$ Catalyst	$B_{SOH}H^+$ Catalyst
[g.ml <sup>-1</sup> ]	0.9081	0.8987	2.191	1.6881
$S_{specific}$ [m <sup>2</sup> .g <sup>-1</sup> ]	10.165	10.2712	4.2130	5.4681

#### 7.4.2. $B_{SOH}H^+$ Catalyst Specific Surface Corrections and Observations

The moles quantity of methanol deposited and/or accessible on the  $B_{SOH}H^+$  catalyst and the methanol quantity trapped inside was measuring out by two methods: measuring out by acetic acid 99% and measuring out by hydrofluoric acid followed by acetic acid. The aim was to correct the  $B_{SOH}H^+$  density and specific surface.

##### (i) $B_{SOH}H^+$ Catalyst Accessible Methanol Quantity Measuring out by Acetic Acid 99%

Take approximatively 0.0308 [g] of  $B_{SOH}H^+$  catalyst. Dissolve ( $H^+/H_2SO_4$ ) and methanol molecules accessible in a baker with 15 [ml] of distilled water. Then, add 10 [ml] of dichloromethane solvent to extract methanol molecules accessible. Allow to settle the solution in a funnel a few minutes, then recover the organic phase in a beaker and add two or three drops of helianthine. The solution turn to orange yellow. Place the 99% acetic acid in an oilcan and the beaker on the magnetic stirrer. The measuring out can begin by falling into the beaker drip the oilcan 99% acetic acid solution and mixing the beaker solution with the magnetic stirrer. When the beaker solution turn to bluish pink, closed the oilcan and record the equivalent 99% acetic acid volume which correspond to the esterification of all acetic acid molecules by methanol molecules in solution. Finally, we calculated the corresponding accessible methanol quantity.

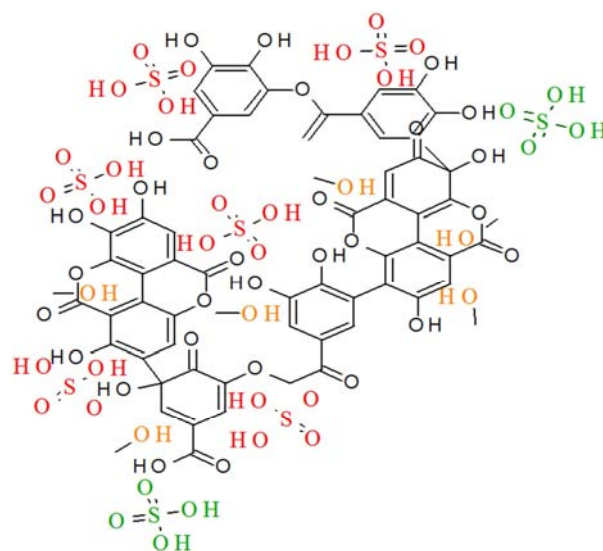
##### (ii) $B_{SOH}H^+$ Catalyst Trapped Methanol Quantity Measuring out by Acetic Acid 99%

Take approximatively 0.0308 [g] of  $B_{SOH}H^+$  catalyst. Begin to measuring out the alkene functions by the procedure

described in paragraph §7.2. Then, begin the measuring out of methanol molecules trapped inside the catalyst which were now in solution by 99% acetic acid solution according to the procedure described in paragraph §7.4.2.1 without adding the 15 [ml] of distilled water. Finally, we calculated the corresponding trapped methanol quantity.

##### (iii) $B_{SOH}H^+$ Catalyst Accessible and Trapped Methanol Quantity – Observations and Discussions

Also, the moles quantity of accessible and trapped methanol molecules quantity were estimated according to the alkenes functions moles quantity (measuring out by hydrofluoric acid-c.f§7.2) which can have hydrogen bond liaisons with sulphuric acid molecules and methanol molecules according to the cases considered in the following table (Table 17) showing the results. Indeed, during the homogeneous catalyst  $B_{SOH}H^+$  supported on pine wood the relationship between the moles of ( $H^+/H_2SO_4$ ) (pH≈2) and the moles of methanol was 1.5622 (figure 13).



**Figure 13.** Hydrogen bond between a polynuclear aromatics oxygenated with alkenes functions, four (4) methanol molecules and six (6) sulphuric acid molecules.

**Table 17.** Comparative table of density and specific surface values of  $B_{SOH}H^+$  determined by calculations of different caes and by measuring out.

N°CASES		Trapped methanol quantity [moles]	Trapped methanol weight [g]	Accessible methanol on surface quantity [moles]
N°1	$B_{SOH}H^+$ Without corrections	-	-	-
N°2	$B_{SOH}H^+$ With consideration of the molecules of MeOH trapped compared to its proportion (% $H^+$ of $H_2SO_4$ - $nH^+$ (Measuring out)/ $n_{MeOH} = 1.5622$ )	9.6787E-6	3.0972E-4	-
N°3	$B_{SOH}H^+$ With consideration of the MeOH molecules trapped and accessible on the surface compared to its proportion (% $H^+$ of $H_2SO_4$ ) without overlapping between the molecules of MeOH and $H_2SO_4$ on the sites of alkene functions C= on surface (Measuring out) [or the functions hydroxyls (- OH)] accessible on the surface by hydrogen bond	9.6787E-6	3.0972E-4	2.4608E-5
N°4	Measuring out results	1.0899E-4	3.4877E-3	1.8165E-5
N°5	$B_{SOH}H^+$ With consideration of the MeOH molecules trapped and accessible on the surface compared to its proportion (% $H^+$ of $H_2SO_4$ ) without overlapping of the molecules of MeOH and $H_2SO_4$ on the sites of alkene functions C= on surface (Measuring out) [or the functions hydroxyls (- OH)] accessible on the surface ] by hydrogen bond and that the numbers of moles on the surface of MeOH were four twice (4×) the moles of $H_2SO_4$ per hydrogen bond	9.6787E-6	3.0972E-4	1.5377E-4

Table 17. Continued.

N°CASES		Accessible methanol on surface weight [g]	Corrected weight of $B_{SOH}H^+$ catalyst [g]	Corrected density [g.ml <sup>-1</sup> ]	Corrected specific surface [g.m <sup>-2</sup> ]
N°1	$B_{SOH}H^+$ Without corrections	-	1.0095	1.6825	5.4863
N°2	$B_{SOH}H^+$ With consideration of the molecules of MeOH trapped compared to its proportion (% $H^+$ of $H_2SO_4-nH^+$ (Measuring out)/ $n_{MeOH}$ = 1.5622)	-	1.0092	1.6831	5.4844
N°3	$B_{SOH}H^+$ With consideration of the MeOH molecules trapped and accessible on the surface compared to its proportion (% $H^+$ of $H_2SO_4$ ) without overlapping between the molecules of MeOH and $H_2SO_4$ on the sites of alkene functions C= on surface (Measuring out) [or the functions hydroxyls (- OH)] accessible on the surface by hydrogen bond	7.8745E-4	1.0084	1.6846	5.4795
N°4	Measuring out results	5.8128E-4	1.0054	1.6881	5.4681
N°5	$B_{SOH}H^+$ With consideration of the MeOH molecules trapped and accessible on the surface compared to its proportion (% $H^+$ of $H_2SO_4$ ) without overlapping of the molecules of MeOH and $H_2SO_4$ on the sites of alkene functions C= on surface (Measuring out) [or the functions hydroxyls (- OH)] accessible on the surface ] by hydrogen bond and that the numbers of moles on the surface of MeOH were four times (4×) the moles of $H_2SO_4$ per hydrogen bond	4.9206E-3	1.0043	1.6925	5.4539

By comparing corrected specific surfaces of the considered model cases and that obtained after measuring out methanol quantities (case N°4), we had the following table 18 which shown the absolute

Value  $|\Delta| = |Value\ Case_{N^{\circ}4} - Value\ Case_{N^{\circ}i}|$  such as  $i=1, 2, 3, 5$ .

Table 18. Comparative table of  $B_{SOH}H^+$  specific surfaces values.

Specific surface Case N°4 (Measuring out) [g.m <sup>-2</sup> ]	5.4681			
Specific surface Case N°i [g.m <sup>-2</sup> ]	Case N°1 5.4863	Case N°2 5.4844	Case N°3 5.4795	Case N°5 5.4539
$ \Delta $	0.0182	0.0163	0.0114	0.0142

First, we noted that the case N°3 specific surface is the most approached value of the specific surface obtained by measuring out methanol quantities. That confirmed that methanol molecules were trapped inside the  $B_{SOH}H^+$  catalyst and other methanol molecules were adsorbed with the alkene functions on surface by hydrogen bond (figures 9-12-13). In that case (N°3), each aromatics or polynuclear aromatics formed hydrogen bond connection one by one with either a methanol molecule, either a sulphuric acid molecule without overlapping. What didn't exclude the possibility of hydrogen bond connection between alcohols or sulphuric acids hydrogen atom and sulphuric acids or alcohols oxygen atom and vis-versa (figure 13) - [25].

On the other hand, we noted that the trapped and on surface methanol quantities obtained by measuring out were more important than the evaluations obtained on the cases N°3 and N°5 (Table 19). However, the on surface methanol quantities estimated by the case N°3 gets close to measuring out values (Table 19).

Table 19. Comparative table of  $B_{SOH}H^+$  trapped and on surface methanol quantities.

N°of CASES [ESTIMATIONS% $H^+$ measuring out]	Trapped methanol molecules quantity [moles]	On surface methanol molecules quantity [moles]
N°3	9.6787E-6	2.4608E-5
N°4 (Measuring out)	1.0899E-4	1.8165E-5
N°5	9.6787E-6	1.5377E-4
$ \Delta _{N^{\circ}3\%N^{\circ}4}$	9.9311E-5	6.443E-6
$ \Delta _{N^{\circ}5\%N^{\circ}4}$	9.9311E-5	1.35605E-4

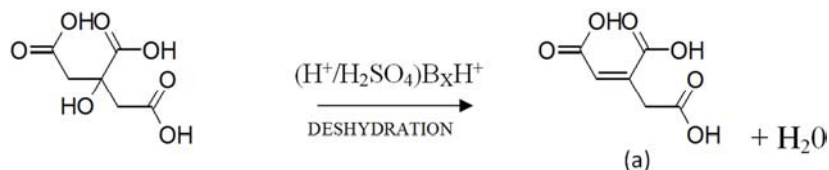
These results still confirmed that for the  $B_{SOH}H^+$  catalyst,

the on surface each alkene functions (measuring out) were connected by hydrogen bond with either one methanol molecule (measuring out), either one sulphuric acid molecule and the ( $H^+/H_2SO_4$ ) quantity (measuring out) is equal to 1.5622 times the methanol quantity.

## 8. $B_XH^+$ Catalysts ( $H^+/H_2SO_4$ ) Supported on Pine Wood Powder Test Reaction

### 8.1. Test Reaction Procedure – Citric Acid Dehydration

The  $B_XH^+$  homogenous catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder test reaction consisted of citric acid dehydration according to the mechanism presented on figure 14. This dehydration started with fast formation of citric acid's alkene functions (figure 14) under the ( $H^+/H_2SO_4$ ) ions supported on pine wood powder. The three acid functions of each citric acid molecule (figure 1) remainder in majority intact whereas the alcohol function (figure 1) disappeared quickly in the interest of alkene function formation (figure 14) with ( $H^+/H_2SO_4$ ) ions supported on pine wood powder regeneration. The rest of citric acid molecules that hadn't react were soluble in water. Then, we carried out the samples taking in terms of time and their treatments to follow up the citric acid conversion rate evolution. The rest of citric acid was measuring out by acetic acid (99%) esterification or by NaOH. These procedures would be elaborate in details in the following paragraphs (§8.2).



**Figure 14.** Citric acid dehydration catalyzed by  $B_XH^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder.

The test reaction proceeded as follows: first, put in a 250 [ml] beaker, which have  $\phi = 6.5$  [mm] diameter, 65 [g] of citric acid and the weight of  $B_XH^+$  homogenous catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder to test and to characterize. Then, add 200 [ml] of distilled water. Heat the whole on a hotplate at temperature more than 448.15 [°K] (Reaction temperature approximatively between 448°K and 523.15°K). We witnessed in the beaker, from the base to the top, a fast formation of a layer whose height increased with time. This corresponds to the phase containing the dehydrated citric acid [Figure 14 - (a)]. Whereas, the aqueous phase on the top which height X decrease with time contained not only the regenerated ( $H^+/H_2SO_4$ )  $B_XH^+$  supported on pine wood powder but also the rest of citric acid molecules not having reacted. Finally, we proceed to the rest of citric acid molecules measuring out.

## 8.2. The Rest of Citric Acid Molecules Measuring out by 0.05N NaOH Solution Procedure

After x minutes of reaction, took 1 [ml] to 1.5 [ml] sample of the on top aqueous phase (§8.1) using a 10 [ml] graduated pipette. Pay great attention not to take the catalyst grain  $B_XH^+$  during the sampling test. At the same time, took the measure X of this phase using a graduated ruler to calculate thereafter its volume  $V_{\phi a}$  equals to  $\{\prod \times (\phi/2) \times X\}$  and its total citric acid not having reacted content. Then, put the sample in a beaker and add 15 [ml] of distilled water, 10 [ml] of dichloromethane solvent to extract the rest of citric acid molecules in the sample. After a few minutes of decantation in a funnel, two phases appeared: an organic phase containing the citric acid molecules below and an aqueous phase in top containing the sulphuric acid molecules. Then, recover the organic phase in a beaker and wash then allow twice with 15 [ml] of distilled water to remove the possible remains of sulphuric acid molecules. Then, recover the washed organic phase in a beaker and add 15 [ml] of distilled water with two or three drops of helianthine. The solution turned to red. Place the 0.05N of NaOH solution in an oilcan and the beaker on the magnetic stirrer. The measuring out can begin by falling into the beaker drip the oilcan 0.05N NaOH solution and mixing the beaker solution with the magnetic stirrer. When the beaker solution turn to yellow, closed the oilcan and record the equivalent 0.05NaOH volume which correspond to the equivalent point. Then, we can calculate the total quantity (moles) of the rest of citric acid molecules in the  $V_{\phi a}$  volume at x minutes such as:

$$C_{NaOH} \times V_{NaOH} = C_{Ac} \times V_{Ech}$$

$$n_{Ac} = C_{Ac} \times V_{\phi a}$$

$$V_{\phi a} = \{\prod \times (\phi/2) \times X\}$$

And

- $C_{NaOH}$ : NaOH concentration
- $V_{NaOH}$ : NaOH volume at the equivalent point
- $C_{Ac}$ : Citric acid concentration
- $V_{Ech}$ : Sample volume
- $V_{\phi a}$ : Total aqueous phase volume
- $\phi$ : 250 [ml] beaker diameter
- X: Aqueous phase height
- $n_{Ac}$ : Total citric acid moles in the X aqueous phase

## 8.3. The Rest of Citric Acid Molecules Measuring out by Acetic Acid 99% Procedure – Results and Discussions

After x minutes of reaction, took 5 [ml] sample of the on top aqueous phase (§8.1) using a 10 [ml] graduated pipette. Pay great attention not to take the catalyst grain  $B_XH^+$  during the sampling test. In the same time took the total volume of mixed solution ( $V_{solution}$ ). Then, put the sample in a beaker and add 15 [ml] of distilled water, 10 [ml] of dichloromethane solvent to extract the rest of citric acid molecules in the sample. After a few minutes of decantation in a funnel, two phases appeared: an organic phase containing the citric acid molecules below and an aqueous phase in top containing the sulphuric acid molecules. Then, recover the organic phase in a beaker and wash then allow twice with 15 [ml] of distilled water to remove the possible remains of sulphuric acid molecules. Then, recover the washed organic phase in a beaker and add with two or three drops of helianthine. The solution turned to orange yellow. The base of this measuring out was to esterify selectively the acetic acid (99%) by the rest of citric acid. Place the acetic acid (99%) solution in an oilcan and the beaker on the magnetic stirrer. The measuring out can begin by falling into the beaker drip the oilcan acetic acid (99%) solution and mixing the beaker solution with the magnetic stirrer. When the beaker solution turn pink purplished, closed the oilcan and record the equivalent acetic acid (99%) volume which correspond to the equivalent point. Then, we can calculate the total quantity (moles) of the rest of citric acid molecules in the sample at x minutes such as:

$$C_{AA} \times V_{AA} = C_{Ac} \times V_{Ech}$$

$$n_{Ac} = C_{Ac} \times V_{solution}$$

And

- $C_{AA}$ : acetic acid concentration
- $V_{AA}$ : acetic acid volume at the equivalent point

- $C_{Ac}$ : citric acid concentration
- $V_{Ech}$ : sample volume
- $V_{solution}$ : total volume of mixed solution
- $n_{Ac}$ : Total citric acid moles in the mixed solution

#### 8.4. Results and Discussions

We presented in the following table 20 the results comparison obtained of the two measuring out procedures after 15 [mn] of test reaction.

Table 20. Comparative table of NaOH and acetic acid measuring out.

Catalyst weight 0.0577 [g]	$C_{NaOH} - C_{AA}$ [mol.l <sup>-1</sup> ]	$V_{Ech}$ [l]	$V_{qa} - V_{solution}$ [l]	$V_{NaOH} - V_{AA}$ [l]	$n_{Ac}^{Corrigé} - n_{Ac}$ [moles]	$\Delta n_{Ac}$
NaOH measuring out	0.050	1E-3	4.9775E-2	2.08E-3	3.4300E-3	
Acetic acid measuring out	0.0173	5E-3	235E-3	3.1E-3	2.5206E-3	0.9094E-3
$\Delta V_{AA} = 1.11842E-3$						

We obtained a difference of 0.9094E-3 moles which corresponded to a acetic acid volume difference equal to  $\Delta V_{AA} = 1.11842E-3$  [l]. This light difference can-being due to the fast formation of the ester molecules in citric acid and thereafter their possibility of réhydrolyse which under thus evaluates the full number of acid citric in the solution.

Another very important explanation was: the calculated pH of the initial test solution was 1.38. According to the Table 6 (§4 – Table 6 Dominant Forms of “Citric Acid” According to the pH), the dominant form is  $AH_3$  which correspond to the citric acid molecule. So, according to the  $pK_{a-2}$  and  $pK_{a+2}$  theory [16], only approximatively 5.97% of the  $pK_{a1}=3.14$  citric acid's acid form could presents in its basic form liable to be esterified by the measuring out by acetic acid (99%) solution. What is statistically and really negligible and confirmed what was said as previously that the alcohol citric acid dehydration reaction which lead to the alkene formation is dominant. So, we attended a 0.9094E-3 citric acid moles differences between the measuring out by the acetic acid (99%) solution and the measuring out by NaOH 0.05N. The acetic acid (99%) solution citric acid molecules measuring out underevaluation could be explained by the auto-esterification of a negligible quantity of citric acid molecules. What led us to choose the NaOH – 0.05N measuring out procedure to quantify the rest of citric acid molecules.

#### 8.5. Test Reactions Results

##### 8.5.1. The Reaction Time Effect on the Citric Acid Molecules Dehydration – Comparison with the Sulfuric Acid

##### Dehydration Without the Pine Wood Powder Support

All  $B_XH^+$  catalysts were more active than the sulphuric acid drop except for the  $B_{NS}H^+$  0.2 [g] catalyst which was conglomerated (figure 14 – figure 15). That took us to study the unsticking conglomeration effects on the catalysts before their uses in the test reaction. We also noticed that the  $B_{SOH}H^+$  catalyst prepared with methanol-sulphuric acid (98%) solution was initially less active than other catalysts.

##### 8.5.2. The $B_XH^+$ Catalysts ( $H^+/H_2SO_4$ ) Supported on Pine Wood Powder Preparation Effect – the Methanol Effect as Sulfuric Acid Solvent

In comparison to the  $B_{NS}H^+$  trend curve (figure 16), the  $B_{SOH}H^+$  catalyst prepared with methanol-sulphuric acid (98%) solution was initially (5' to 10') less active. But, we noticed

that the total conversion of the citric acid molecules by the  $B_{SOH}H^+$  catalyst was reached as soon as 20 [mn] against 25 [mn] for the  $B_{NS}H^+$  catalyst. These results showed that the non-dried catalyst  $B_{NS}H^+$  was much more active than the  $B_{SOH}H^+$  catalyst which was dried beforehand. This case will be discussed on the next paragraph (§11).

Now, the total conversion reached early for the  $B_{SOH}H^+$  catalyst showed an important activity from 5 [mn] surely due to the drying treatment of the pine wood powders which led to the porous system formation before its sulphuric acid-methanol solution treatment supporting the test reaction and the system ( $H^+/H_2SO_4$ ) catalysts-reactant citric acid movement (c.f. §7.2 – Table 17). Whereas, the non-dried catalyst  $B_{NS}H^+$  remained initially more active because of the important formation of aromatics and polynuclear aromatics with alkene functions coming from the extractible, lignin and cellobiose units transformation (c.f. §7.2).

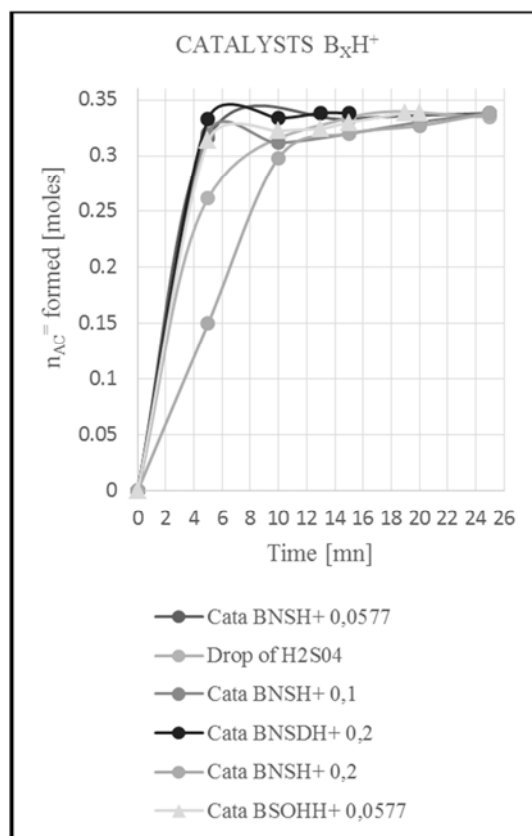


Figure 14. Dehydrated citric acid formed according to time evolution.

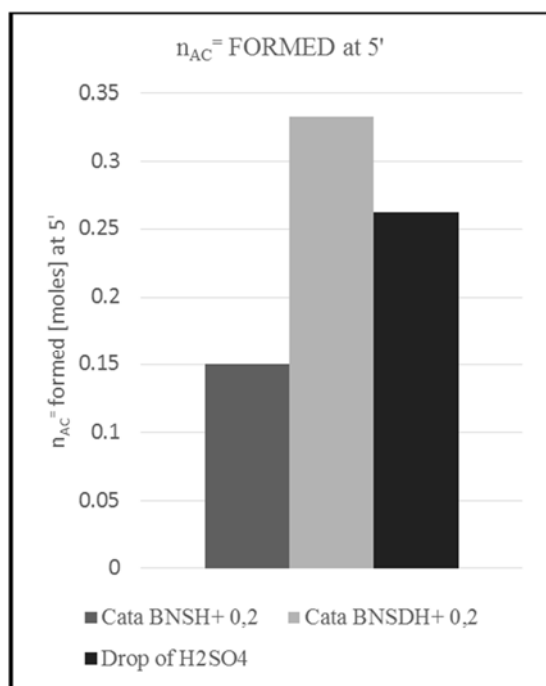


Figure 15. Dehydrated citric acid formed at 5'.

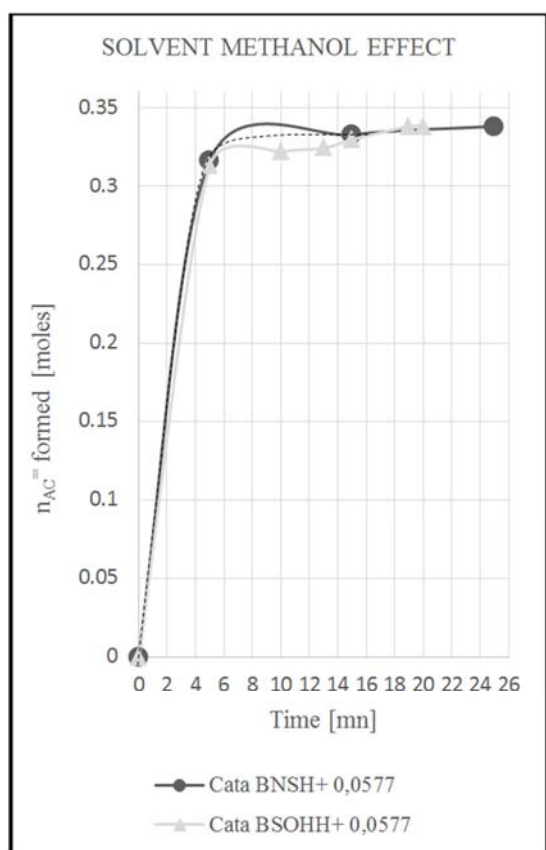


Figure 16. Dehydrated citric acid formed by 0.0577 [g] of  $B_{NS}H^+$  and  $B_{SOH}H^+$  - Methanol solution effect.

Now, we will see the solvent methanol effect itself by comparing the dried catalysts 0.0577 [g]  $B_S H^+$  treated with the sulphuric acid 98% and  $B_{SOH}H^+$  treated with sulphuric acid-methanol solution.

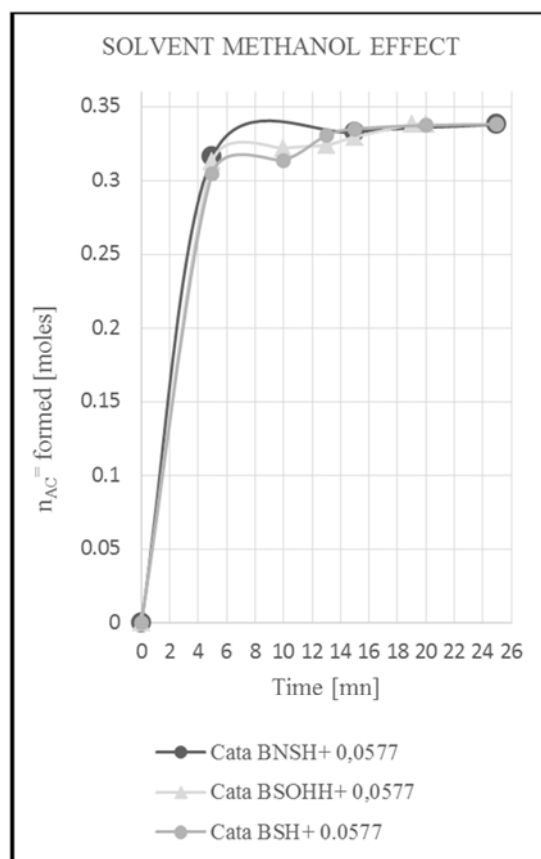


Figure 17. Dehydrated citric acid formed by 0.0577 [g] of  $B_{NS}H^+$ ,  $B_S H^+$  and  $B_{SOH}H^+$  - Methanol solution effect.

$B_{SOH}H^+$  Catalyst was initially more active than the  $B_S H^+$  (figure 18 - figure 19) and led to the maximum conversion in advance for the  $B_{SOH}H^+$  (figure 20-(b)). Let us notice nevertheless that at 15 minutes, the  $B_S H^+$  catalyst activity became higher than the  $B_{SOH}H^+$  (figure 20-(a)). These results agreed with the additional porous system formation due to the drying treatment of the pine wood powder causing the elimination of extractible and the transformation of part of lignin molecules by dehydration (before treatment) supporting the sulphuric acid or sulphuric acid-methanol solution treatment before the test reaction. Consequently, methanol molecules and sulphuric acid molecules carrying active sites ( $H^+/H_2SO_4$ ) (during the treatment) as well as water molecules during the test reaction could enter and leave the pores formed or existing on the dried pine wood structure. That explained not only the low content of trapped sulphuric acid molecules carrying active sites ( $H^+/H_2SO_4$ ) for the  $B_{SOH}H^+$  catalyst ( $1.512E-5$  [moles]) compared to those  $B_{NS}H^+$  and  $B_S H^+$  (respectively  $3.276E-5$  and  $1.1844E-4$ ) (Table 15) but also the effectiveness of methanol as vector liquid by hydrogen bond during the sulphuric acid (98%) solution treatment and the test reaction without to exceed and to substitute the effectiveness of alkene function of aromatics and polynuclear aromatics to support methanol, sulphuric acid and citric acid molecules (§7.2 – figure 9 – figure 12). Indeed, the following curve (figure 21 – figure 22) which presented the citric acid moles converted according to total

( $H^+/H_2SO_4$ ) and the ( $H^+/H_2SO_4$ ) density for  $B_{NS}H^+$ ,  $B_S H^+$  and  $B_{SOH}H^+$  catalysts showed that the  $B_{SOH}H^+$  activity was less

than the non-dried  $B_{NS}H^+$  catalyst and the activity of dried catalyst  $B_S H^+$  was definitely lower.

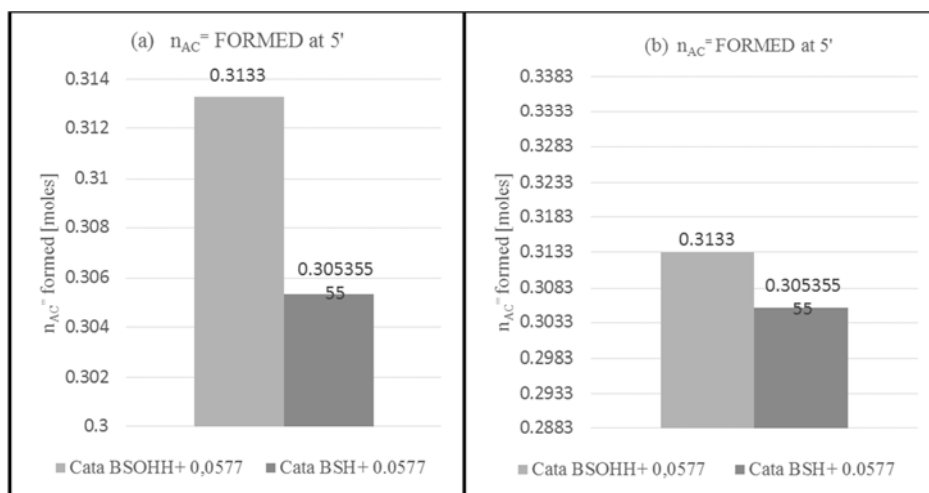


Figure 18. (a) (b). Dehydrated citric acid formed by 0.0577 [g] of  $B_S H^+$  and  $B_{SOH}H^+$  - Methanol solution effect at 5 minutes.

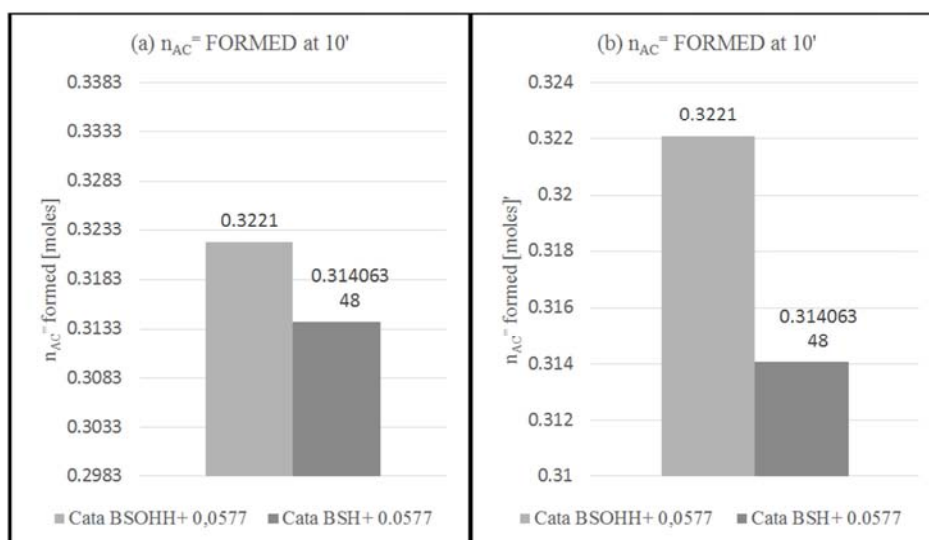


Figure 19. (a) (b). Dehydrated citric acid formed by 0.0577 [g] of  $B_S H^+$  and  $B_{SOH}H^+$  - Methanol solution effect at 10 minutes.

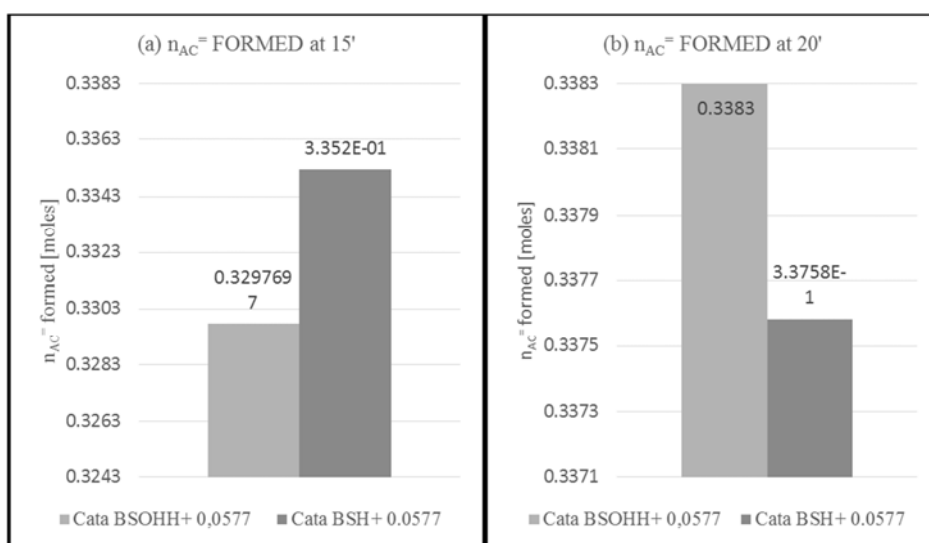


Figure 20. Dehydrated citric acid formed by 0.0577 [g] of  $B_S H^+$  and  $B_{SOH}H^+$  - Methanol solution effect at 15 minutes (a) and at 20 minutes (b).

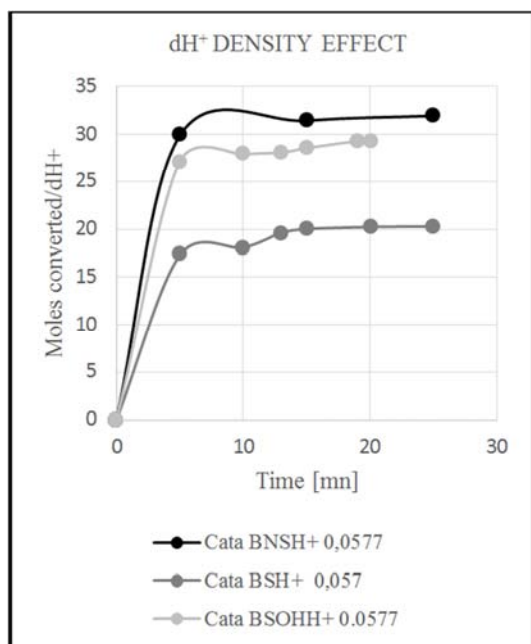


Figure 21. Dehydrated citric acid formed by 0.0577 [g] of  $B_SH^+$ ,  $B_{NS}H^+$  and  $B_{SOH}H$  according to each density.

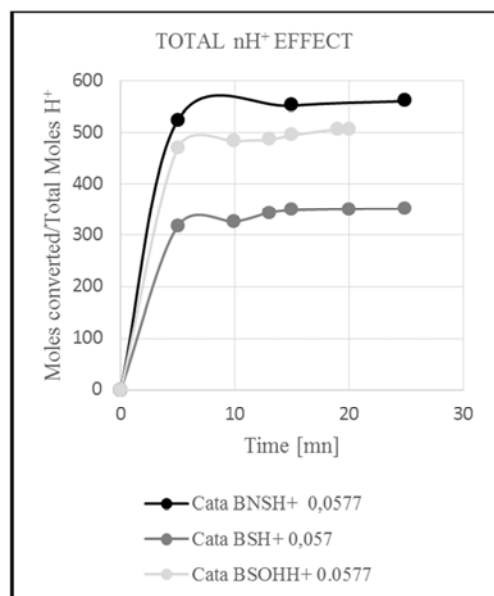


Figure 22. Dehydrated citric acid formed by 0.0577 [g] of  $B_SH^+$ ,  $B_{NS}H^+$  and  $B_{SOH}H$  according to each total ( $H^+/H_2SO_4$ ) quantity.

### 8.5.3. The Support pine Wood Powder Drying Effect Before Their Use for Preparing the $B_XH^+$ Catalysts

#### (i) Drying Support Pine Wood Powder Procedure

Take 65 [g] of pine wood powder and divided it into three parts in three 250 [ml] beakers such as the thickness of each sample was between 1 [cm] to 1.5 [cm] maximum. In order to be careful not to burn or to char the wood, the oven was programed to 338 [°K] and the beakers was introduced to be dried during x hours. Then, the treatment of the dried pine wood powder with sulphuric acid (98%) solution to obtain the ( $H^+/H_2SO_4$ ) catalysts  $B_SH^+$  supported on pine wood powder

was done. We presented in the following table 21 the drying results such as the wood moisture content [27].

Table 21. Drying procedure results.

Drying Time [h]	17	106
Pine wood powder weight [g]	11.6660	11.6667
Pine wood powder weight after drying treatment [g]	9.1833	9.1495
$\Delta m$ [g]	2.4827	2.5172
Drying rate [%]	21.28	21.58
Wood moisture content [%]	27.03	27.51

Water in wood takes two forms: free water and bound water. Free water exists as liquid and vapor in cell cavities (lumens). Bound water is part of the cell wall materials. Water easily binds with the cellulose fibers by hydrogen bounds in the cell wall [27]. As wet wood dries, free water leaves firstly the lumens (cell cavities). After all the free waters is gone only bound water remains, the cell has reached its fiber saturation point (fsp). At this point, no water is present in the cell lumen, but the cell wall is completely saturated. It was sure that drying procedure led to porous formation besides those existing in the initial wood structure [2] and a non-negligible amount extractible water soluble volatile elimination. As wood is dried further, bound water leaves the cell wall, and cells start to lose moisture below the fsp. As water leaves and the microfibrils come closer together, shrinking occurs. That is to say, an amount of lignin which were the polynuclear aromatic precursor could be transformed.

#### (ii) $B_SH^+$ and $B_{NS}H^+$ Catalysts Comparison

The drying procedure contributed largely to water molecules and extractible substance eliminations in the interest of porous formation besides those existing in the initial wood structure. These were important by facilitating the ( $H^+/H_2SO_4$ ) molecules accessibility during the sulphuric acid treatment and consequently the formation of polynuclear aromatics with alkenes function which were particularly less unsaturated (Table 15 –  $B_SH^+$ ) by cellobiose unit dehydration then polymerization for example. In this way, for the dried  $B_SH^+$  catalyst, aromatics molecules, water molecules could enter and go out of the porous system. Polynuclear aromatics formed couldn't wedge totally the existent porous and explain its important initial activity and the maximum conversion reaching early (figure 23-b).

However, for the non-dried  $B_{NS}H^+$  catalyst, extractible substances and lignin were all transformed on surface to aromatics and polynuclear aromatics more saturated (Table 15 -  $B_{NS}H^+$ ) by cellobiose unit dehydration then polymerization for example and could block or fill the wood porous system by sprawling on its surface. Seeing that sulphuric acid molecules carrying active acid sites  $H^+/H_2SO_4$  formed one by one hydrogen bond connection (§7.4.2.3) with alkene function of aromatics or polynuclear aromatics and their quantity were important for the non-dried  $B_{NS}H^+$  catalyst, it was normal that its initial activity was definitely higher than the  $B_SH^+$  catalyst (figure 24).

Consequently, a relatively important sulphuric acid molecules quantity ( $B_{NS}H^+$  catalyst trapped moles  $H_2SO_4$  were

$3.276\text{E-}5$  [moles] and  $\text{B}_\text{S}\text{H}^+$  catalyst trapped moles  $\text{H}_2\text{SO}_4$  were  $1.1844\text{E-}4$  [moles] – Table 15) were trapped inside the porous structure with aromatics or polynuclear aromatics after sulphuric acid treatment. The trapped moles quantity for the  $\text{B}_\text{S}\text{H}^+$  catalysts were more important than for the non-dried  $\text{B}_\text{NS}\text{H}^+$  catalyst. That explain its maximum conversion reaching not early. Indeed, it could be possible that the non-dried  $\text{B}_\text{NS}\text{H}^+$  catalyst porous system wasn't completely blocked by aromatics formed by sulphuric acid treatment. However, the drying procedure which led to porous formations favored the molecules ( $\text{H}^+$  and/or aromatics) trapping phenomena and explained its lower initial activities

from 5 [mn] to 13 [mn] (figure 25). So, water molecules formed (§7.2) could play not only the pH regulator but also a liquid vector able to transport by hydrogen bond connection sulphuric acid molecules carrying active acid sites  $\text{H}^+/\text{H}_2\text{SO}_4$  and/or citric acid molecules from a place or site to another place or site explaining the greatness of the non-dried  $\text{B}_\text{NS}\text{H}^+$  catalyst initial activities.

In general, we noticed an important initial activity for the whole of the  $\text{B}_\text{X}\text{H}^+$  catalysts except for that  $\text{B}_\text{XND}\text{H}^+$  which contained grain conglomeration causing a reduction of aromatics and polynuclear aromatics surface able to carry hydrogen bond connection. Details will be see in §12.

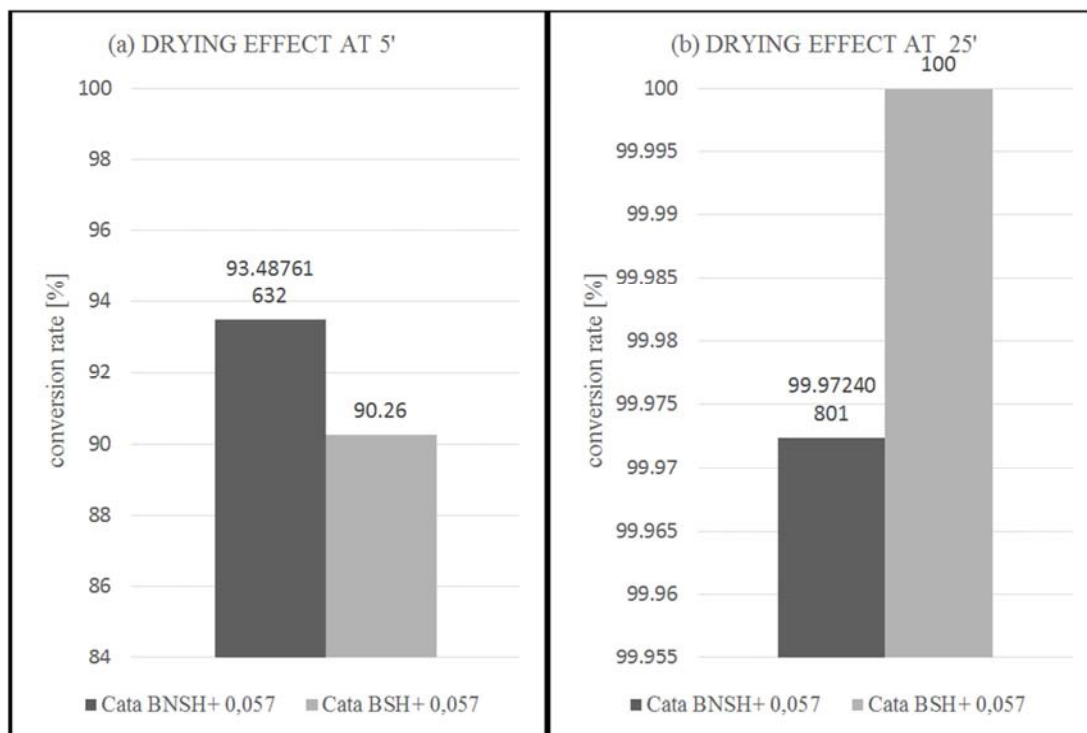


Figure 23. Citric acid conversion by 0.0577 [g] of dried  $\text{B}_\text{S}\text{H}^+$  and non-dried  $\text{B}_\text{NS}\text{H}^+$ .

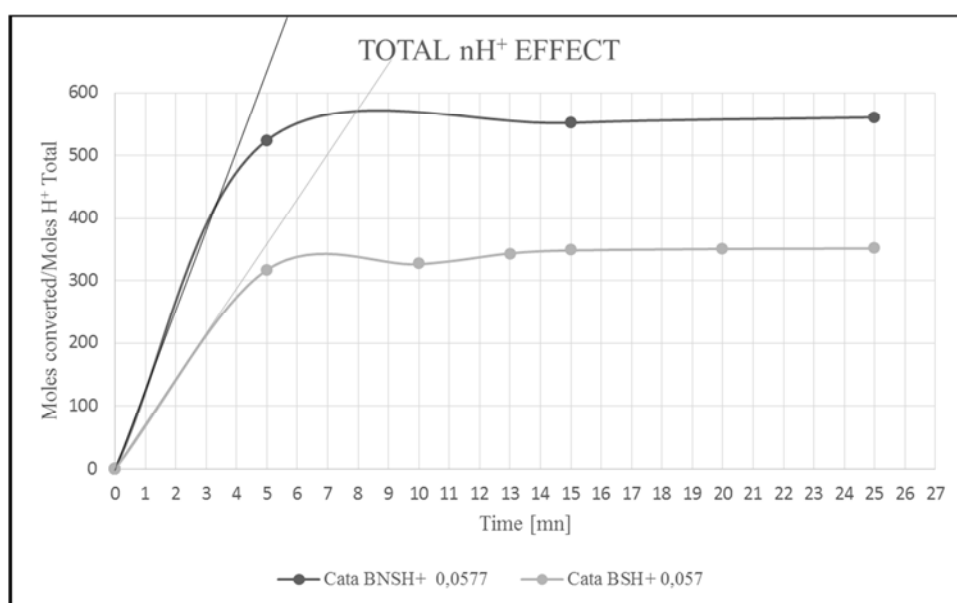
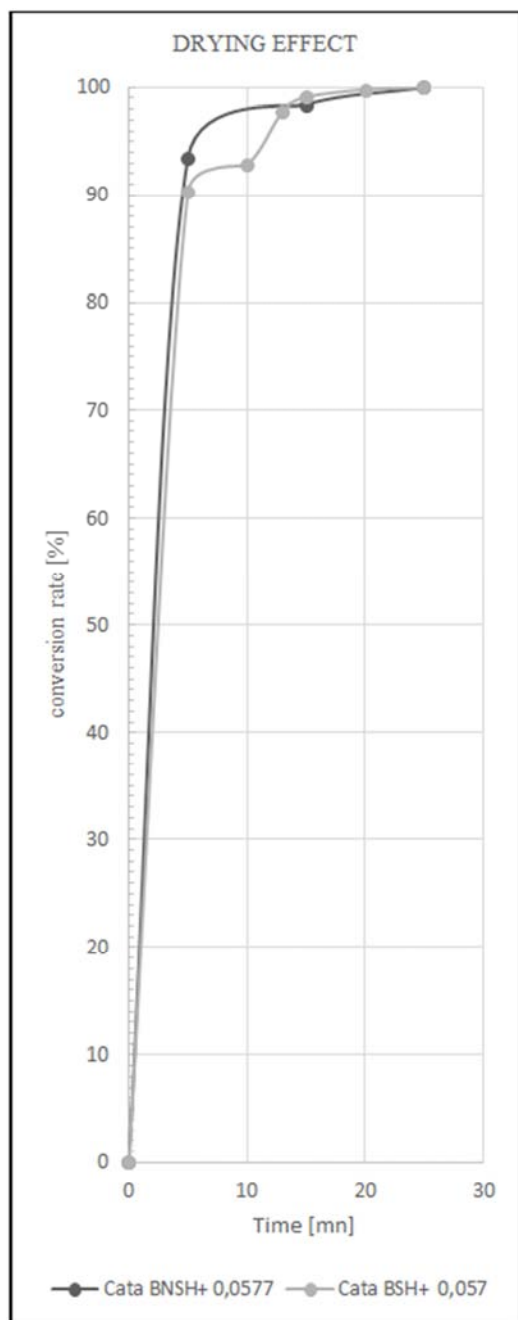


Figure 24. Total  $\text{nH}^+$  quantity effect on citric acid conversion by 0.0577 [g] of dried  $\text{B}_\text{S}\text{H}^+$  and non-dried  $\text{B}_\text{NS}\text{H}^+$ .



**Figure 25.** Citric acid conversion by 0.0577 [g] of dried  $B_SH^+$  and non-dried  $B_{NS}H^+$  catalysts evolution according to time.

Initial activity of  $B_{NS}H^+$  catalyst calculated at 3 [mn] was 130 [moles converted/moles  $H^+/mn$ ] or 2.17 [moles converted/moles  $H^+/s$ ]. Initial activity of  $B_SH^+$  catalyst calculated at 4 [mn] was 72.5 [moles converted/moles  $H^+/mn$ ] or 1.21 [moles converted/moles  $H^+/s$ ]. The  $B_{NS}H^+$  catalyst was initially 1.79 times more active than the  $B_SH^+$  catalyst and confirmed the drying effect explicated before. These results also showed the water molecules role which were not only the solution pH regulator in the vicinity of one supporting the citric acid dehydration selectivity but also its liquid vector role able to transport by hydrogen bond connection sulphuric acid molecules carrying active acid

sites  $H^+/H_2SO_4$  and/or citric acid molecules from a place or site to another place during the treatment and the test reaction. Indeed, the turnover number of non-dried  $B_{NS}H^+$  catalyst was almost twice more important than its dried  $B_{NS}H^+$  catalyst. These results justify that  $B_XH^+$  were homogeneous catalyst with ( $H^+/H_2SO_4$ ) active sites supported on pine wood powder.

#### 8.5.4. The $B_{XD}H^+$ Catalysts Unsticking Conglomeration Effects Before the Test Reaction

##### (i) The $B_{XD}H^+$ Catalyst Unsticking conglomeration Procedure

After sulphuric acid 98% solution treatment and conservation in a desiccator with sulphuric acid concentrated (98%) safe from moisture, part of prepared catalysts were stuck. Reaction tests were carried out on unsticked  $B_{XD}H^+$  and stuck  $B_{XND}H^+$  ( $H^+/H_2SO_4$ ) catalyst supported on pine wood powder. The unsticking procedure was done quite simply by screening stuck  $B_{XND}H^+$  catalyst through a fine plastic sieve. We thus obtained uniformly unsticked  $B_{XD}H^+$  catalyst.

The stuck  $B_{XND}H^+$  catalyst was all the time definitely less active than the unsticked  $B_{XD}H^+$  catalyst (figure 26). Initial activity of unsticked  $B_{XD}H^+$  catalyst calculated at 3 [mn] was 36 [moles converted/moles  $H^+/mn$ ] or 0.6 [moles converted/moles  $H^+/s$ ]. Initial activity of stuck  $B_{XND}H^+$  catalyst calculated at 5 [mn] was 14 [moles converted/moles  $H^+/mn$ ] or 0.23 [moles converted/moles  $H^+/s$ ]. The unsticked  $B_{XD}H^+$  catalyst was initially 2.6 times more active than stuck  $B_{XND}H^+$  catalyst (figure 27). The pine wood powder used was non-dried before the treatment to obtain the samples stuck  $B_{XND}H^+$  and unsticked  $B_{XD}H^+$  catalysts. We had shown on paragraph 11 (§11) that for the non-dried powder, during its sulphuric acid (98%) solution treatment to obtain the  $B_{NS}H^+$  catalyst, extractable substances, lignin and others were still present and being transformed into aromatics, polynuclear aromatics with alkene functions (§7.2) which could lay out side by side and arrived easily filling, even partially, the pine wood porous structure, by spreading on the catalyst surface. That explain the low activity of the stuck  $B_{XND}H^+$  catalyst which was due to one or more aromatics and polynuclear aromatics (supports) responsible not only of the hydrogen bond connection with sulphuric acid carrying out active sites ( $H^+/H_2SO_4$ ) putting down but also their dispersion and their accessibility. Consequently, putting down layers of aromatics and polynuclear aromatics cause not only one additional active acid sites trapping but also definitely a possible reduction of the total support surface which had been reflected in the initial activity of the stuck  $B_{XND}H^+$  catalyst. Indeed, according to the results above (figure 27), the unsticked  $B_{XD}H^+$  catalyst a mole of active sites ( $H^+/H_2SO_4$ ) transformed 36 moles of citric acid per minute (A turnover number of 36 or 2160 respectively per minute or per hour) whereas the stuck  $B_{XND}H^+$  catalyst turnover number was only 14 or 840 respectively per minute or per hour.

(ii) Unsticked  $B_{XD}H^+$  and Sticked  $B_{XND}H^+$  Catalysts Tests Reaction Results

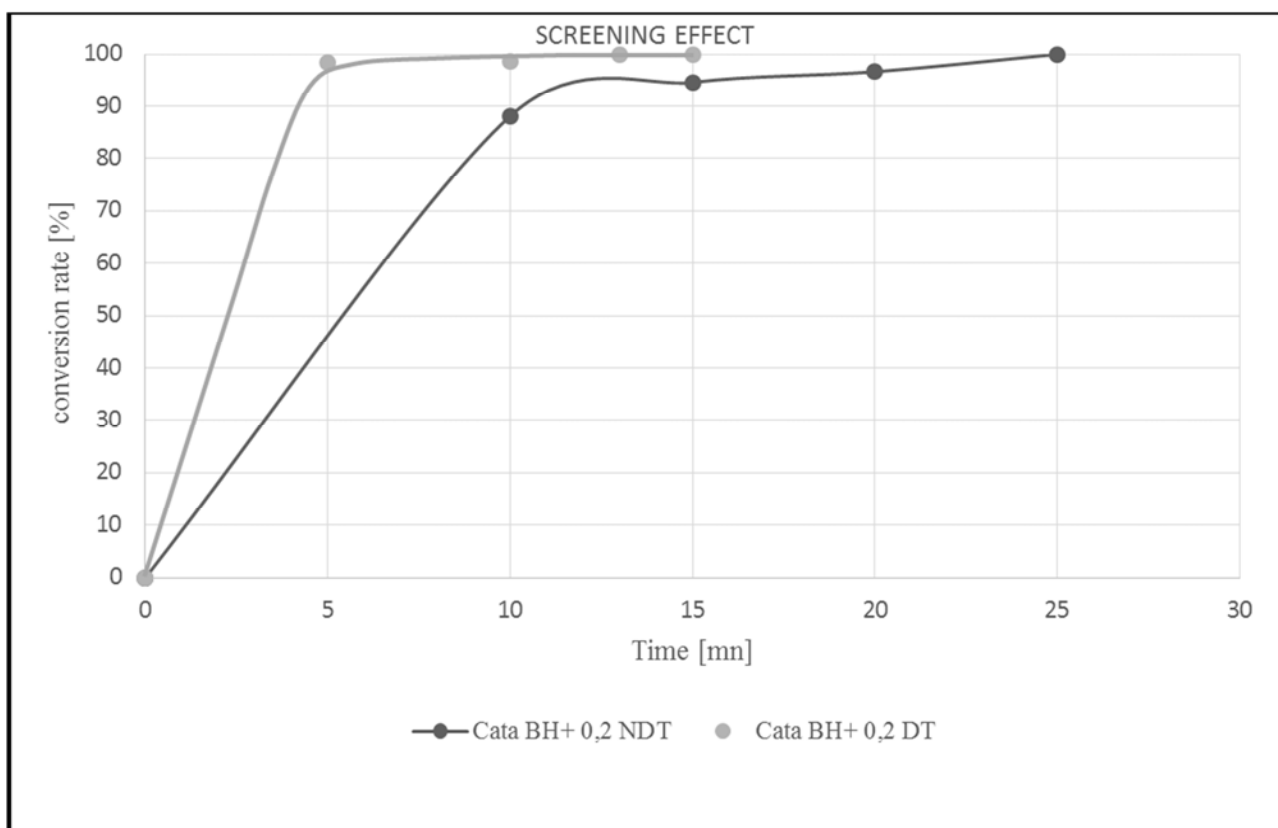


Figure 26. Citric acid conversion by 0.2 [g] of stucked  $B_{XND}H^+$  and unsticked  $B_{XD}H^+$  catalysts evolution according to time.

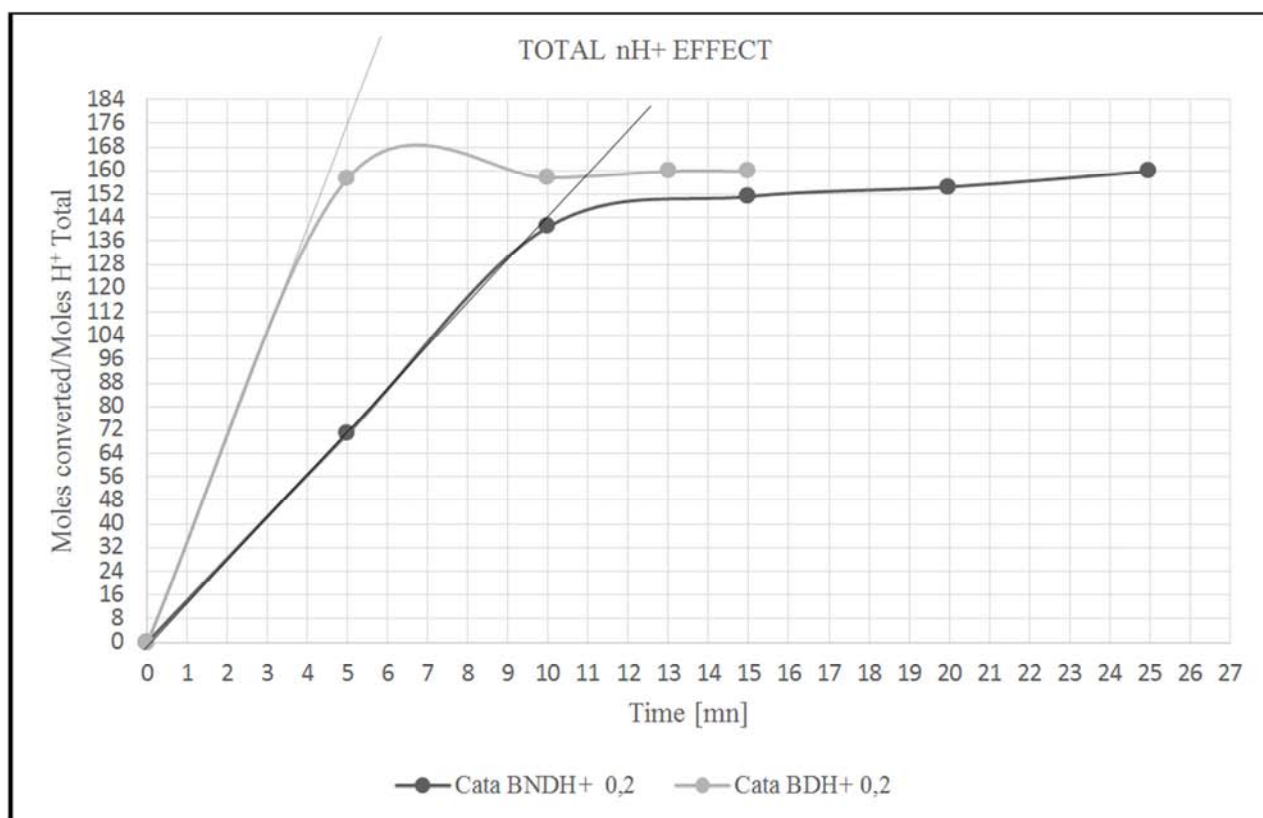


Figure 27. Total  $nH^+$  quantity effect on citric acid conversion by 0.2 [g] of stucked  $B_{XND}H^+$  and unsticked  $B_{XD}H^+$  catalysts.

### 8.5.5. $B_XH^+$ Catalysts Quantity Effects

The increase in catalyst weight increased the conversion rate which was all the time over 90% for all catalysts (figure 28). This result is surely due to the increase of not only the sulphuric acid molecules carrying active acid sites ( $H^+/H_2SO_4$ ) (figure 29) but also the increase of the aromatics and polynuclear oxygenated aromatics with alkene function molecules (figure 30) which were responsible for the hydrogen bond connections of these active acid sites, their dispersions and their accessibilities.

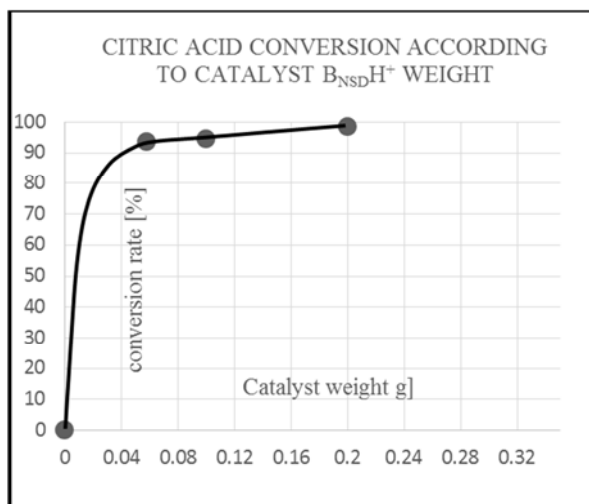


Figure 28. Citric acid conversion evolution according to the catalyst  $B_{NSD}H^+$  weight.

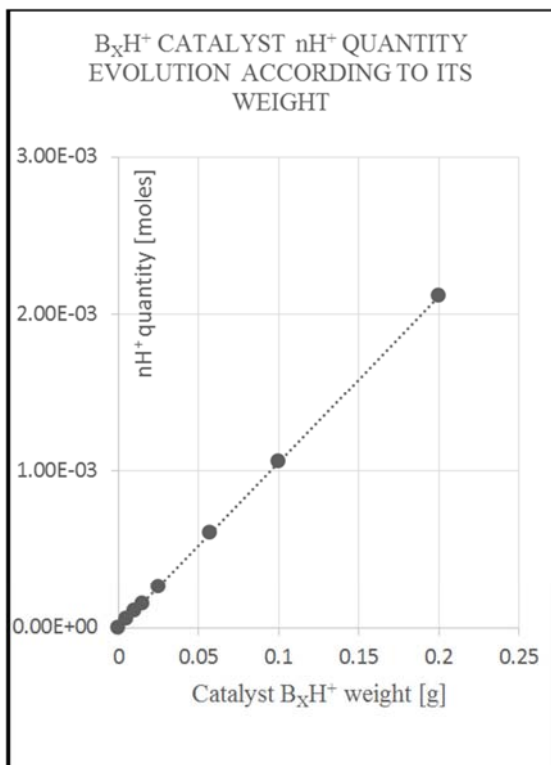


Figure 29.  $B_XH^+$  active acid sites quantity evolution according to its weight.

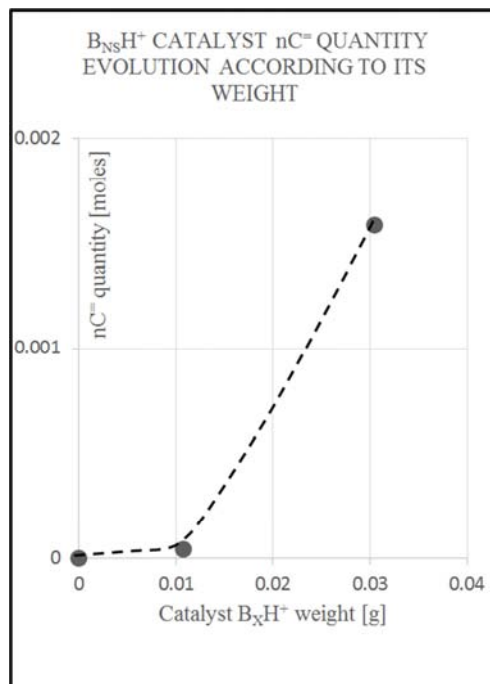


Figure 30.  $B_{NSH}H^+$  alkene function quantities evolution according to its weight.

### 8.5.6. $B_XH^+$ Catalysts Specific Surface Calculated by Empirical Formula Effects

$B_XH^+$  ( $H^+/H_2SO_4$ ) catalysts supported on pine wood powder specific surface,  $S_{specific}$ , were calculated by empirical formula  $\frac{3}{\rho \times r}$  such as  $\rho$  was the catalyst density and  $r$  the spoke corresponding to the specific diameter  $\phi_s$  (c.f § 3.2). The rather important density of these catalysts  $B_XH^+$  were due not only to the consideration of aromatics and polynuclear aromatics with alkene function formation but also and mostly with the consideration of sulphuric acid molecules carrying active acid sites ( $H^+/H_2SO_4$ ) which were connect one by one with aromatics and polynuclear aromatics with alkene functions by hydrogen bond.

These results confirmed the noticed above. The non-dried  $B_{NSH}H^+$  and with methanol  $B_{SOH}H^+$  ( $H^+/H_2SO_4$ ) supported on pine wood powder catalysts whose density were rather important and thus their calculated specific surface were low had much more activities at 5 minutes (figure 31 (a) and (b)). Those one were still confirmed by the following table 23 which showed the  $B_XH^+$  catalysts initial activity taking account of each total specific surface.

These results confirmed that alkene functions quantities, sulphuric acid quantities were two important parameters for the  $B_XH^+$  catalyst ( $H^+/H_2SO_4$ ) supported on pine wood powder, the non-dried  $B_{NSH}H^+$  and  $B_{SOH}H^+$  catalysts with more alkene functions and afterwards able to have good active acid sites by hydrogen bond connections were more active with respectively 53,333.33 [Moles  $Ac^-$  formed per  $m^2$  per moles of  $H^+$  and par minute] and 50,000.00 [Moles  $Ac^-$  formed per  $m^2$  per moles of  $H^+$  and par minute] initial activities than the dried  $B_SH^+$  with only 42,000.00 [Moles  $Ac^-$  formed per  $m^2$  per moles of  $H^+$  and par minute] initial activity.

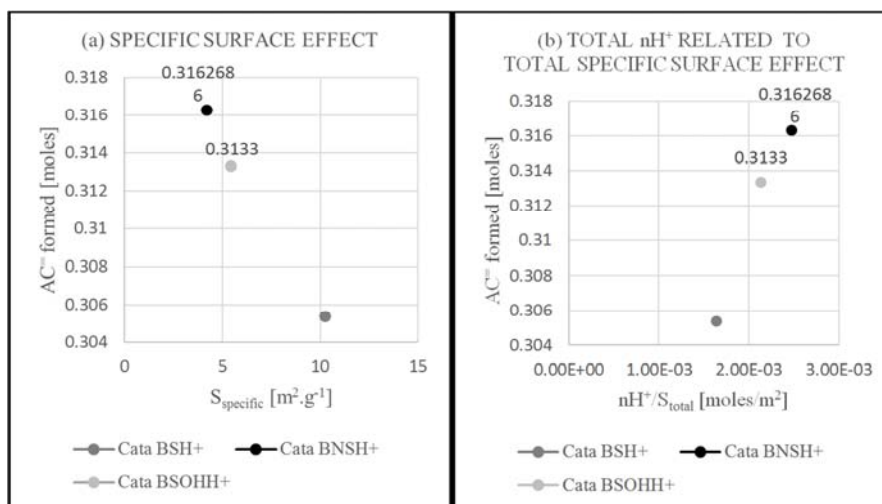


Figure 31. Specific surface (a) and (b) total active sites quantity related to total specific surface effects.

Table 22.  $B_xH^+$  catalysts density, specific surface, active acid sites quantity per specific surface and activity at 5'.

$r = 0.325$ [mm]	Wood Powder $B_s$	$B_sH^+$ Catalyst	$B_{NS}H^+$ Catalyst	$B_{SOH}H^+$ Catalyst
$[g.ml^{-1}]$	0.9081	0.8987	2.191	1.6881
$S_{specific} [m^2.g^{-1}]$	10.165	10.2712	4.2130	5.4681
$n_{AC^-}$ [moles] formed at 5' ( $m_{cata}=0.057$ [g])		0,3053556	0,3162686	0,3133
$nH^+[moles]/S_{Total} [m^2]$		1.64E-3	2.48E-3	2.14E-3

Table 23.  $B_xH^+$  initial activity taking account of each total specific surface and total active sites quantities.

ACTIVITIES/ $B_xH^+$ CATALYSTS	$B_sH^+$	$B_{NS}H^+$	$B_{SOH}H^+$
[Moles $Ac^-$ formed per $m^2$ per moles of $H^+$ and per minute]	40	32.5	31.25
[Moles $Ac^-$ formed per $m^2$ per moles of $H^+$ and par minute]	42,000.00	53,333.33	50,000.00

## 9. Black Citric Acid Polymers (PN) Synthesis Using $B_xH^+$ Catalysts ( $H^+/H_2SO_4$ ) Supported on Pine Wood Powder

### 9.1. PN Synthesis Procedure and Observations

Table 24. Black citric acid polymers (PN) synthesis using  $B_{NS}H^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder.

$B_{NS}H^+$ ( $m_{Cata}=2.0026$ [g]/ $nH^+=0.02119$ [moles] – $m_{Ac}=5.0024$ [g] – $V_{H_2O}=1.5$ [ml])						
Temperature – $T^\circ$ [°K]		Duration [mn]	Speed [°K.mn <sup>-1</sup> ]	Temperature rise duration [mn]	Cumulated duration [mn]	OBSERVATIONS
Start ( $T^\circ$ Displayed - Stable)	End ( $T^\circ$ Displayed - Stable)					
313.15	398.15	15	284.15	9	24	-At 17' Dehydration reaction (RDesh) of citric acid molecules (figure 14)
398.15	423.15 (433.15)	30	284.15	2	56	-At 30' Synthesis reactions of yellow-white monomer (RDesh – figure3). Red brick polymers formation (Decarboxylation – RDeca – figure3).
423.15 (433.15)	458.15 (473.15)	15	276.15	12	83	-At 45' Polymerization reactions (Decarboxylation - RDeca) lead to first black polymers (PN) formation surrounding $B_{NS}H^+$ catalyst. (figure 3)
458.15 (473.15)	473.15 (498.15)	18	276.15	5	106	-At 65' Polymerization reactions (Decarboxylation - RDeca) lead to brown and black polymers (PN) formation surrounding $B_{NS}H^+$ catalyst. (figure 3)
						-Obtaining black polymers (PN) and its derivatives such as poly- black polymers (PN-...-PN) probably by radical polymerization reaction of black polymers [20].

Weight (PN+Cata  $B_{NS}H^+$ ) = 2.7596 [g].

**Table 25.** Black citric acid polymers (PN) synthesis using  $B_{SOH}H^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder.

$B_{SOH}H^+$ ( $m_{Cata}=1.8353$ [g]/ $nH^+=0.02119$ [moles] – $m_{Ac}=5.0024$ [g] – $V_{H_2O}=1.5$ [ml])						
Temperature – $T^\circ$ [°K]		Duration [mn]	Speed [°K.mn-1]	Temperature rise duration [mn]	Cumulated duration [mn]	OBSERVATIONS
Start ( $T^\circ$ Displayed - Stable)	End ( $T^\circ$ Displayed - Stable)					
383.15	398.15 (423.15)	15	275.15	8	23	-At 8' Dehydration reaction (RDesh) of citric acid molecules (figure 14)-At 8' Synthesis reactions of red brick polymers formation (Decarboxylation – RDeca – figure3)
398.15 (423.15)	423.15 (433.15)	30	284.15	2	55	-At 27' Very important formations of red polymers bricks (Decarboxylation - RDeca)-At 40' Brown polymers formation – polymerization reaction (RDeca) -At 48' Black polymers (PN) formation - Polymerization reaction (Decarboxylation - RDeca)
423.15 (433.15)	458.15 (473.15)	15	284.15	3	73	-At 66' – 73' Polymerization reactions (Decarboxylation - RDeca) lead to melted black polymers (PN).
458.15 (473.15)	473.15 (498.15)	15	284.15	2	90	- Obtaining black polymers (PN) and its derivatives such as poly- black polymers (PN-...-PN) probably by radical polymerization reaction of black polymers [20].

Weight (PN+Cata  $B_{SOH}H^+$ ) = 4.0648 [g].

**Table 26.** Black citric acid polymers (PN) synthesis using  $B_SH^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder.

$B_SH^+$ ( $m_{Cata}=1.2712$ [g]/ $nH^+=0.02119$ [moles] – $m_{Ac}=5.0022$ [g] – $V_{H_2O}=1.5$ [ml])						
Temperature – $T^\circ$ [°K]		Duration [mn]	Speed [°K.mn-1]	Temperature rise duration [mn]	Cumulated duration [mn]	OBSERVATIONS
Start ( $T^\circ$ Displayed - Stable)	Start ( $T^\circ$ Displayed - Stable)					
313.15	398.15 (423.15)	15	284.15	8	22	- Dehydration reaction (RDesh) of citric acid molecules (figure 14)
398.15 (423.15)	423.15 (433.15)	30	284.15	2	55	-At 30' Synthesis reactions of white monomers (RDesh – figure3) and a bit of yellow monomers (RDesh – figure3)-At 45' Polymerization reactions (Decarboxylation - RDeca) lead to first black polymers (PN) formation surrounding $B_SH^+$ catalyst (figure 3)
423.15 (433.15)	458.15 (473.15)	15	276.15	12	82	-At 65' Red brick and brown polymers formation surrounding $B_SH^+$ catalyst (figure 3) – Polymerization reactions (Decarboxylation-RDeca) -At 77' Black polymers (PN) formation to the detriment of total brown polymers
458.15 (473.15)	473.15 (498.15)	3	3	5	90	-At 84' Obtaining black polymers (PN) and its derivatives such as poly- black polymers (PN-...-PN) probably by radical polymerization reaction of black polymers [20].

Weight (PN+Cata  $B_{SH}H^+$ ) = 1.8646 [g].

## 9.2. Results and Discussions

By comparing all observations seen on each PN synthesis we could say that: first, all the synthesis started with the dehydration reaction of citric acid molecules to form the white monomer with alkene function followed by the synthesis reactions of yellow monomers and red brick polymers at temperature lower than 433.15 [°K]. But, on the non-dried  $B_{NS}H^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder, the white and yellow monomers formation were clear and ordered whereas the brown polymer formation were not noticed, we have noticed immediately the red brick and black polymers (PN) as soon as 45 [mn] surrounding the non-dried catalyst. These results were due not only to the

presence of polynuclear aromatics and aromatics oxygenated with alkene function (§7.2 – Table15) which were the supports supporting the dispersion of the sulphuric acid molecules (carrying active acid sites ( $H^+/H_2SO_4$ )) by hydrogen bond connections one by one (figure 13), but also the water molecules presence formed by dehydration reactions or brought at the synthesis beginning which, let us recall it, played the role of pH regulator and liquid vector (§11). Thus, for the non-dried  $B_{NS}H^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder the synthesis black polymer (PN) mechanism would be rather the left one (figure 3).

Then, for the dried  $B_SH^+$ ,  $B_{SOH}H^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder, we noticed that the white monomers formation was immediately followed by rapid

formation of polymers either red brick, either brown or black (PN). Thus can be due to the drying procedure followed by sulphuric acid (98%) solution leading to the additional porous formation where polymerization reaction showed in the right of figure 3 were favored.

But, we noticed that for the  $B_{SOH}H^+$  catalysts ( $H^+/H_2SO_4$ ) supported on pine wood powder, the red brick polymers formation was very important as soon as 27 minutes. These results were probably due to the methanol molecules which, let us recall it, could also carry the sulphuric acid molecules (active acid sites ( $H^+/H_2SO_4$ )) by hydrogen bond connection as water molecules (§10 - §11).

### 9.3. Polymers Coke Soluble and Coke Insoluble in Hexane and $CH_2Cl_2$ Measuring out Procedure

We had also carried out the soluble and insoluble coke in dichloromethane (polar solvent) and hexane (non-polar solvent) according to the procedure described in the bibliography [20]. Only, we had also measuring out the alkene contents of soluble and insoluble coke in the dichloromethane, soluble coke in hexane by hydrofluoric acid [23].

We showed in the following table the results obtained (Table 27).

**Table 27.** Coke soluble and coke insoluble in dichloromethane and hexane of Black citric acid polymers (PN) synthesized by  $B_XH^+$  catalysts.

PN of $B_XH^+$ Catalysts/Coke		Coke soluble $CH_2Cl_2$	Coke insoluble $CH_2Cl_2$	Coke soluble Hexane
PN of $B_{NS}H^+$	Weight [g]	0.0231	0.0204	0.002
	Percentages [%]	53.10	46.90	26.67
	Alkene $C^=$ contents [moles.l <sup>-1</sup> ]	2.578E-3	-	1.3E-3
	Alkene $C^=$ contents [moles.g <sup>-1</sup> ]	-	44.2E-3	0.43E-3
PN of $B_{SOH}H^+$	Weight [g]	0.1817	0.0603	0.0063
	Percentages [%]	75.08	24.92	92.65
	Alkene $C^=$ contents [moles.l <sup>-1</sup> ]	4.875E-3	-	0.78E-3
	Alkene $C^=$ contents [moles.g <sup>-1</sup> ]	-	81.25E-3	0.23E-3
PN of $B_SH^+$	Weight [g]	0.0715	0.0141	0.0051
	Percentages [%]	83.53	16.47	76.12
	Alkene $C^=$ contents [moles.l <sup>-1</sup> ]	4.875E-4	-	2.17E-4
	Alkene $C^=$ contents [moles.g <sup>-1</sup> ]	-	1.99E-3	0.0582E-3

**Table 27.** Continued.

PN of $B_XH^+$ Catalysts/Coke		Coke insoluble Hexane	$\Delta =   \text{Coke insoluble Hexane} - \text{Coke soluble } CH_2Cl_2   =   \text{Coke insoluble } CH_2Cl_2 - \text{Coke soluble Hexane}  $
PN of $B_{NS}H^+$	Weight [g]	0.0055	
	Percentages [%]	73.33	20.23
	Alkene $C^=$ contents [moles.l <sup>-1</sup> ]	-	
	Alkene $C^=$ contents [moles.g <sup>-1</sup> ]	-	
PN of $B_{SOH}H^+$	Weight [g]	0.0005	
	Percentages [%]	7.35	67.73
	Alkene $C^=$ contents [moles.l <sup>-1</sup> ]	-	
	Alkene $C^=$ contents [moles.g <sup>-1</sup> ]	-	
PN of $B_SH^+$	Weight [g]	0.0016	
	Percentages [%]	23.88	59.65
	Alkene $C^=$ contents [moles.l <sup>-1</sup> ]	-	
	Alkene $C^=$ contents [moles.g <sup>-1</sup> ]	-	

Seeing that dichloromethane is a polar solvent, soluble coke in its solvent was composed of black polymers (PN) and/or red brick polymers and brown polymers (figure 3) with maybe its derivate especially black poly-polymers PN-...-PN (19). We noticed that the non-dried  $B_{NS}H^+$  and dried  $B_{SOH}H^+$  dichloromethane coke soluble solution color was black against intense brown for the dried  $B_SH^+$  which confirmed the presence of not only black polymers but also brown polymers and its derivate. But, we noticed that dried  $B_{SOH}H^+$  and  $B_SH^+$  catalysts black polymers with its derivate contents (respectively 78.05% and 83.53%) were largely higher than the dried  $B_SH^+$  catalyst one only 53.10% (Table 27) which firstly confirmed the pine wood drying procedure importance

followed by sulphuric acid (98%) solution treatment leading to the additional porous system formation where long-range left polymerization reactions (figure 3) were favored. Then, these results showed and confirmed also the aromatics-polynuclear aromatics with alkene function role and initial or formed water molecules role as supports for the active acid sites ( $H^+/H_2SO_4$ ) and molecules liquid vector (§11 - figure 13). These results were still confirmed by the alkene measuring out in dichloromethane soluble coke (Table 27) which showed generally that plus the alkene contents were low, plus higher was the Black polymer (PN) derivate such as Poly-black polymers contents (Table 27 – figure 32).

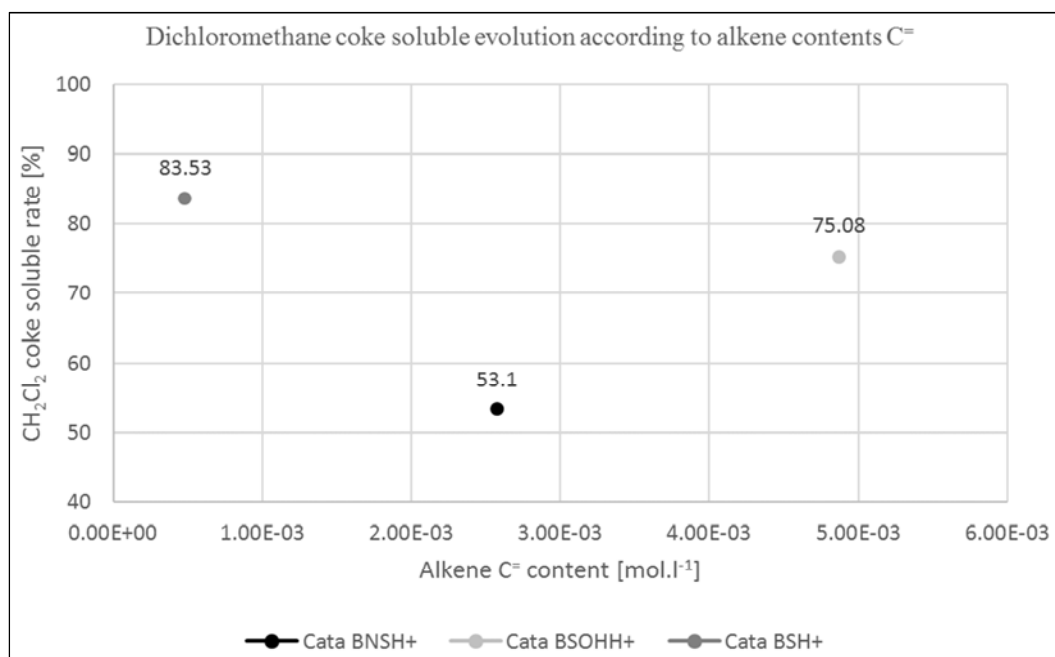


Figure 32. Dichloromethane coke soluble evolution according to alkene contents for  $BXH^+$  catalysts.

Also, we noticed that non-polar hexane soluble coke content was important enough for the three catalysts going of 26.67% ( $B_{NS}H^+$ ) to 76.12% ( $B_S H^+$ ) and 92.65% ( $B_{SOH}H^+$ ) (Table 27) confirming decarboxylation at high temperature (higher than 433°K) of the citric acid molecules to give propene molecules and its derivate more or less soluble in hexane obtained probably by its reactions with other reactants like polymers [20].

After measuring out, the alkene content were not very much for the three catalysts with a maximum value equals to 2.03 [%] compared with the initial citric acid molecules (0.02119 [moles]) showing that almost of these propene molecules reacted with other reactants present in the reactional environment to give its derivate more or less soluble in hexane. That allowed us to think of possible aromatics or polynuclear aromatics non-oxygenated formation, even with small quantity since their formations started only from 433 [°K], by propene molecules transformations. Among the molecules reactive presented in the reactional environment we quoted the white monomers, the yellow monomers, the red brick polymers, and brown polymers. Then, we noticed a rather important differences between hexane insoluble coke and dichloromethane soluble coke. ( $\Delta$  value – Table 27). These difference is also equal to the difference between dichloromethane insoluble coke and hexane soluble coke and corresponded indeed to the molecules formed by reactions between propene molecules (and its derivate) with reactive molecules presented in the reactional environment which we had quoted above. Indeed, during the dichloromethane extractions on all  $B_XH^+$  catalysts, a higher phase was above dichloromethane whose color varied from white (for  $B_{NS}H^+$  and  $B_{SOH}H^+$  catalysts) to brown (for BSH+ catalyst) corresponding to the propene molecules reactions with respectively white monomers (and/or yellow monomers) and brown polymers.

## 10. Conclusion

Alkenes of aromatics and polynuclear aromatics in unsticking homogeneous  $B_XH^+$  catalysts, ( $H^+/H_2SO_4$ ) supported on pine wood powder were efficient supports by hydrogen bond connection one by one not only with the sulphuric acid molecules carrying active acid sites  $H^+$  but also with molecules present in the reactional environment such as reactive molecules citric acid, liquid vector molecules water molecules and methanol molecules. Consequently,  $B_XH^+$  catalysts were initially very active even if the maximum activity (100% conversion) were different because of their alkene content reflecting their aromatics and their polynuclear aromatics nature, and also because of the additional porous formation for catalysts synthesized with dried pine wood powders. In all the cases, these catalysts  $B_XH^+$  enabled us to have citric acid black polymer (PN) as soon as 45 minutes ( $B_{NS}H^+$  -  $B_S H^+$ ) and 48 minutes ( $B_{SOH}H^+$ ) at only 433.15 [°K]. The soluble and insoluble coke extraction in polar solvent dichloromethane and polar solvent hexane enabled us to account not only for intermediate molecules leading to the citric acid black polymers (PN) formation such as white monomer, yellow monomer, red brick polymer and brown polymer but also the catalysts  $B_XH^+$  differentiations.

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