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Research Article

Study of the Use of Oxygenated Water as a Non-Toxic Molecule Model for Catalytic Testing of Pozzolana-PN and Iron-Based NOx Reducing Catalysts

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Abstract

During previous catalytic tests on the reducing power of NOx catalysts based on pozzolana and PN-black citric acid polymer, it was found that the use of the NO_2 model molecule poses a significant health and environmental risk. Thus, a project was launched to find another, much less harmful model molecule. Hydrogen peroxide H_2O_2 was chosen, a molecule naturally secreted by the body to prevent pigment synthesis, with disinfectant, antiseptic and whitening properties widely used in various activities, including cosmetics. Consequently, catalytic tests of NOx-reducing power using hydrogen peroxide H_2O_2 as a model molecule were carried out on two catalysts based on pozzolana and PN-black polymer of citric acid, PNP-Fe-water-15% and PNP-Fe-ethanol-15%, differing in the solvent used during their syntheses according to a procedure detailed in the bibliography and this manuscript. Pozzolana is a volcanic rock widespread in the volcanic mountains in the Vakinankaratra region of Madagascar. Its use as a support for catalysts based on PN-black polymer of citric acid and Iron-Fe enabled us to synthesize various catalysts, the characteristics and synthesis methods of which are detailed in this manuscript. In short, the catalytic test with hydrogen peroxide was conclusive, enabling a pragmatic comparison of the two catalysts tested, with the result that the catalyst synthesized with water PNP-Fe-water-15% is more active than the catalyst synthesized with ethanol PNP-Fe-ethanol-15%. This is due to the quality and difference in dispersion of the PN-black polymer molecules depending on the solvent used, which can have an impact on the nature of the catalyst surfaces and certain characteristics such as porosity. This dispersion is confirmed and viewed using an optical microscope to visualize the surface of a catalyst grain. Kinetic results from two proposed mechanisms for the reduction of H_2O_2 hydrogen peroxide molecules using PNP-Fe catalysts also confirmed not only the proposed mechanisms, but also the higher activity of PNP-Fe catalysts synthesized with water, whose kinetic constants are much higher than those synthesized with ethanol.

Keywords

Pozzolana, PN-Black Polymer Citric Acid, PNP-Fe Catalyst, Catalytic Test, Porosity, Dispersion, Optical Microscope, Mechanism

1. Introduction

The first part of this manuscript deals with the details of the procedures for synthesizing PNP-Fe catalysts using PN-black polymer of citric acid and pozzolana, including the determination of the quantities of Fer-Fe, PN, pozzolana and solvents to be used. Then, the second part deals with the various physico-chemical characteristics of PNP-Fe catalysts, in particular the catalysts to be tested, PNP-Fe-water-15% and PNP-Fe-ethanol-15%. Finally, the last part of the manuscript deals with the details of the catalytic tests as well as the exploitation of the kinetic results followed by their interpretations and discussions leading to the conclusion that hydrogen peroxide is an efficient, environmentally friendly and health-friendly model molecule that can be used to evaluate and compare the catalytic activity of Iron-pozzolana-PN-black polymer citric acid, NOx reduction catalysts. The materials used in the experimental tests are pozzolana, citric acid, PN-black polymer citric acid, beaker, iron chloride $FeCl_3$, hydrogen peroxide H_2O_2 50%, distilled water, ethanol, grinder, sieve, magnetic stirrer, containers, test tube, helianthin and bromophenol blue indicator, pipette, burette, magnetic bar, oven, MOTICAM 3+ 3.0 MP/USB3.0 optical microscope.

2. Synthesis Procedures for PNP-FeCl₃ Catalyst Precursor Salts and PNP-Fe2 Catalysts

This synthesis of precursor salts and catalysts based on pozzolan, iron and black PN-polymer of citric acid used local raw materials from Madagascar. Indeed, the pozzolanas come from the pozzolanic site of Iavoko Ambohinaorina in the region of Vakinankaratra district of Antsirabe II; their oxide contents are given by the various bibliographical resources [1] and the equivalent black polymer contents of citric acid PNP - PNpozzolana used were determined by NaOH-0.05N titration [2]. This determination of the amount of black PN-polymer of citric acid in the synthesized PNP would be

used to evaluate the amount of $FeCl_3$ to be dispersed on this PNP support.

2.1. Determination of the FeCl₃ Amount Used During the Synthesis

The amount of $FeCl_3$ used in the synthesis of the PNP-FeCl$_3$ catalyst precursor salts was chosen so that not only the $FeCl_3$ were well dispersed by hydrogen bridge bonding on the black polymers of the PNP-black polymer pozzolana [3] but also so that its quantity would follow the definition of a catalyst whose mass quantity is low in relation to the total mass of the PNP-FeC1$_3$ precursor salt. As a result, two PNP-FeCl$_3$ precursor salts were synthesized, the first of which, PNP-FeCl$_3$×14, has a molar FeCl3 content fourteen times (×14) the PN content of the black pozzolana polymer support PNP, and the second, PNP-FeCl$_3$-15%, has a molar $FeCl_3$ content 15% by mass of the total mass of the synthesizer to be synthesized. Thus, for PNP-FeCl$_3$×14, two $FeCl_3$ molecules were to be deposited on each yellow monomer unit (Figure 1), the total number of which is seven (7), making up the black citric acid PN-polymer [4] (figure 2) of the support PNP.
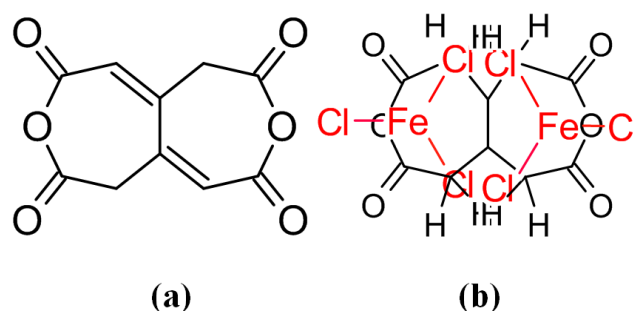

(a) **(b)**

Figure 1. Yellow monomers from citric acid polymerization (a) and the two molecules of FeCl₃ on the Yellow monomer of PN– Black citric acid polymer (b).
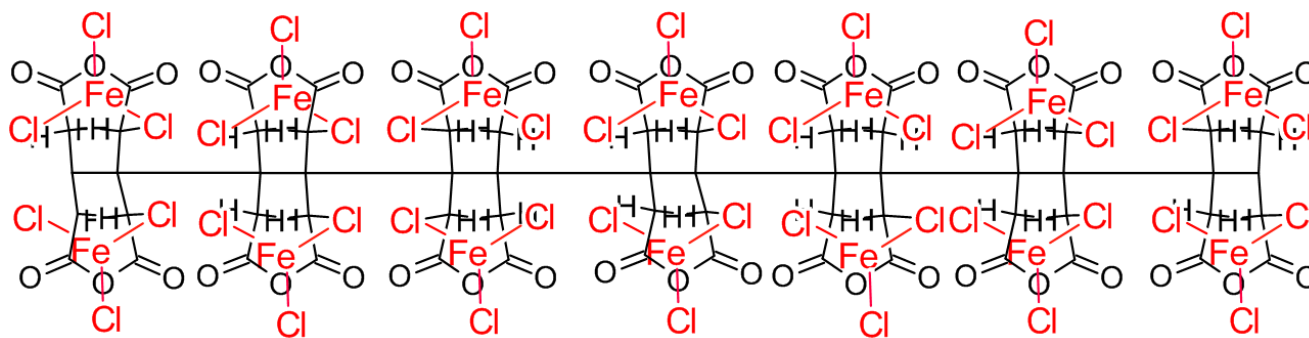

Figure 2. Molecules of FeCl₃ on the PN – Black citric acid polymer.

2.2. The Choice of Solvent Used in the Synthesis of PNP and PNP-FeCl₃

Two solvents were chosen for the synthesis of PNP and PNP-FeCl₃ catalyst precursor salts. The first solvent was water, which had been used and described in the literature [2, 3] whose molar volume at 20 ℃ $MV^{20}*$ is 18.0 ± 3.0 cm^3, its density at 20 ℃ $d^{20}*$ is 0.998 ± 0.06 g/cm^3, its surface tension at 20 ℃ $\gamma 20*$ was 72.2 ± 3.0 dyne/cm and the boiling temperature is 100 ℃ while the second solvent used is ethanol, whose molar volume at 20 ℃ $MV^{20}*$ is 59.0 ± 3.0 cm^3, its density at

20 ℃ $d^{20}*$ is 0.780 ± 0.06 g/cm^3, its surface tension at 20 ℃ $\gamma 20*$ is 22.3 ± 3.0 dyne/cm and the boiling temperature is 78.4 ℃; it is one of the most widely used solvents in the synthesis of catalyst precursor salts, especially for the preparation of colloidal solutions of these catalyst precursor salts. (*values given by ACD/ChemSketch FREEWARE application file – version 2023 24).

The following table 1 shows the characteristics of PNP-Black citric acid polymer Pozzolana synthesized according to the procedure described in the bibliography.

Table 1. Characteristics of raw materials and synthesized PNP- Black citric acid polymer Pozzolana.

CHARACTERISTICS	WATER SOLVENT	ETHANOL SOLVENT
Weight PN used [g]	2.6037	2.613
Weight pozzolana used [g]	2.0251	2.01
Solvent volume [ml]	15	15
Weight PN-pozzolana PNP – synthesized [g]	4.2476	4.2987
Weight concentration in PN-surface of PNP [moles/g]	3.6443E-5	4.7619E-5
PN-surface content of PNP [%]	18.14	23.99
PN-interne content of PNP [%]	81.86	78.01

2.3. Synthesis of PNP-FeCl₃ Catalyst Precursor Salts

Once the characteristics of the synthesized PNP-Pozzolana Black citric acid polymer have been determined (Table 1), the quantities of solid raw materials PNP and FeCl₃ are weighed to achieve the desired proportions described in §2.1. In a 250ml beaker, dissolve the ferric chlorides in the chosen solvent, then add the PNP carrier. In the case of the ethanol solvent, the whole is stirred magnetically at room temperature

for at least 8 hours until a colloidal phase is obtained; in the case of the water solvent, the impregnation process is carried out at a moderate temperature 45 ℃ to a maximum 90 ℃ in a water bath, as for the synthesis of PNP-Pozzolana Black citric acid polymer [2, 3]. At the end, complete evaporation of the solvents can be carried out either on a sand plate at the boiling temperature of the solvent used, or in an oven at 75 ℃ for one to two hours at most, until solid PNP-FeCl₃ is achieved. These catalysts precursor salts are then ground and sieved using an ASTM-N °60 sieve so that the catalyst grain size is less than 250 microns.

Table 2. Characteristics of raw materials used during catalyst precursor salt synthesis PNP-FeCl₃.

CHARACTERISTICS	WATER SOLVENT		ETHANOL SOLVENT	
	PNP-FeCl₃×14	PNP-FeCl₃-15%	PNP-FeCl₃×14	PNP-FeCl₃-15%
Weight PNP used [g]	1.0032	2.0052	1.0032	2.0004
Weight FeCl₃ used [g]	0.4587	0.3545	0.4546	0.3545

2.4. The Synthesis Procedure for the PNP-Fe Catalysts

PNP-Fe catalysts are synthesized by heat treatment of PNP-FeCl$_3$ catalyst precursor salts in an oven at 200 ℃ for one (1) hour. In this process, chlorine atoms are removed in the form of chlorine gas Cl$_2$ (Equation 1 - figure 3) according to a radical mechanism similar to the heat treatment of

Fe-(OEt) deposited on PN-pozzolana (PNP) in order to generate Fe dispersed on PN-pozzolana (PNP-Fe).

$$1PNP - 14FeCl_3 \xrightarrow{\Delta°C} 1PNP - Fe + 21Cl_2^{\uparrow} \quad (1)$$

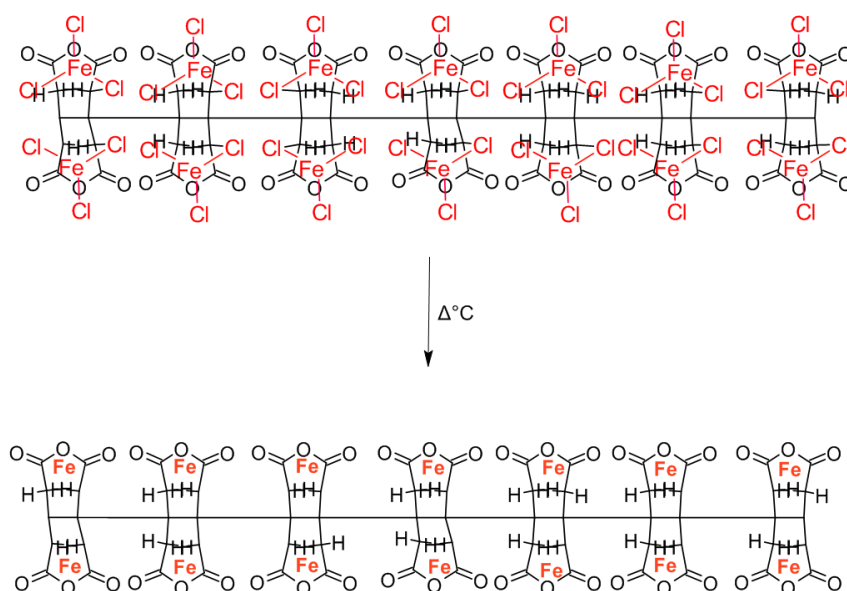Equation 1- Réaction de formation du PNP-Fe par traitement thermique.

Figure 3. Formation of the PNP-Fe catalysts by heat treatment of PNP-FeCl$_3$ catalyst precursor salts.

3. Characterization of Catalyst Precursor Salts PNP-FeCl$_3$ and the Catalysts PNP-Fe

3.1. Measuring the Density Apparent of Precursor Salts and Catalysts

Determining the apparent density ρ_a of precursor salts PNP-FeCl$_3$ and the catalysts PNP-Fe is determined gravimetrically. To do this, first weigh a small, well-dried 5 ml vacuum test tube m_e; then weigh the previously sieved catalyst grains into a small 5ml test tube, piling them up to the 1ml unit (cf. §2.3), this weight is noted $m_{catalyseur+éprouvette}$. Thus, the density of the catalyst sample is given by equation 2.

$$\rho_a \, [g.cm^{-3}] = \frac{(m_{catalyseur+éprouvette} - m_e)}{1} \quad (2)$$

Equation 2 – Formula for determining the apparent density ρ_a

Determining density ρ_s equal to the gravity center of the raw material-reagent densities used during their synthesis is

assimilated to the specific density of the precursor salts PNP-FeCl$_3$ and the catalysts PNP-Fe.

$$\rho_s \, [g.cm^{-3}] = \frac{\sum m_i \times \rho_i}{\sum m_i} \quad (3)$$

Equation 3 – Formula for determining density ρ_s assimilated to the specific density.

3.2. Specific Pore Volumes and Porosity of Precursor Salts and Catalysts Determination

Specific pore volumes V_g and porosity ε of the precursor salts and catalysts synthesized are deduced from the above densities. (cf. §3.1) from the above densities by the following equations 4 and 5 [5].

$$V_g = \left(\frac{1}{\rho_e} - \frac{1}{\rho_s}\right) \quad (4)$$

Equation 4 – Specific pore volume formula

$$\varepsilon = \frac{\left(\frac{1}{\rho_e} - \frac{1}{\rho_s}\right)}{\frac{1}{\rho_e}} = V_g \times \rho_e \quad (5)$$

Equation 5 – porosity formula

3.3. Determining the Iron Fe Content of Precursor Salts and Catalysts

Quantifying the iron-Fe content of precursor salts PNP-$FeCl_3$ and of the catalysts PNP-Fe synthesized after heat treatment of the previously synthesized precursor salts was carried out by EDTA complexometric titration. To do this, the solution to be titrated is prepared in a 250ml beaker by adding a sample weight $m_e - [g]$ approximately 0.01g of precursor or catalyst into 15ml of distilled water; then add 5ml of a pH-10 buffer solution to maintain the solution at this Ph-10. Next, add twenty drops of NET color indicator, which will turn wine-red to indicate the presence of iron-Fe molecules complexed with it. Then place the EDTA-0.03N titrant solution in a 25ml precision burette and begin the titration. s reached when the solution to be titrated turns blue-green, marking the freedom of the EDTA molecules. Thus, the weight concentration of iron-Fe [Fe] of the sample is given by equation 6 below:

$$[Fe] - [moles - Fe/g_{catalyseur}] = \frac{(V_e \times 0.001 \times 0.03)}{m_e} \quad (6)$$

Equation 6 – Formula for Determining the Iron-Fe Mass Concentration of Catalyst Precursors and Catalysts.

Note that the pH-10 buffer solution had been prepared by dissolving a 0.0008g sodium ethanoate salt in 600ml ethanol-90°.

3.4. Determining the Equivalent Alkene Content of PNP-Fe Catalysts

The quantity - weight concentration of equivalent alkenes into the synthesized catalysts is determined by the method described in the bibliography [6]. In this case, take a weight of catalyst sample $m_e - [g]$ approximately 0.0066g and place it in a 250ml beaker. Then add 15ml of distilled water and 3 drops to 4 drops of bromophenol blue indicator, the solution to be titrated turns into purplish blue. Next, place the hydrofluoric acid titrant solution in a burette HF-0.0026N and start the titration. After this, the equivalent volume point Ve-[ml] is reached when the solution to be titrated turns a transparent chick-yellow. Thus, the amount - weight concentration - of equivalent alkene in the catalyst PNP-Fe is given by equation 7;

$$[C^=] - [moleC^=/g_{catalyseur}] = \frac{(V_e \times 0.001 \times 0.0026)}{m_e} \quad (7)$$

Equation 7 – Determination of the alkene equivalent weight concentration of PNP-Fe catalysts.

3.5. Optical Microscope View of the Synthesized PNP-$FeCl_3$

An optical microscope whose trademark is MOTICAM 3+ 3.0 MP/USB3.0 was used to see not only the structure of the PN-Pozzolana support for the catalyst precursor salts PNP-$FeCl_3$ but also the quality and dispersion of the metals on the PN-Pozzolana support [7]. To do this, first the sample PNP-$FeCl_3$ to be characterized is placed and dispersed on the slide, with a small glass plate to hold it in place; then, the sample is protected by a cover slip placed on top. These are then fixed to the sample stage using the clamps. This optical microscope is brightfield. The sample is illuminated from below and observed from above, and the microscope is equipped with four $\times 4$ magnifications for an overall view of the sample; a $\times 10$ zoom for a closer overall view, a $\times 40$ zoom for an increasingly magnified and specific view of part of a sample particle, a $\times 60$ zoom for a highly magnified and specific view of part of a sample particle. So, after efficient focusing using the macro-metric and micrometric screws and thus a good fit with the light, images giving characteristics of the PNP-$FeCl_3$ precursor salt samples are viewed through the eyepiece of the optical microscope.

3.6. Characterizations Results and Interpretation/Discussions

The results of the various characterizations of the catalyst precursor salts and the synthesized catalysts are presented in Table 3.

It should be noted that we have also synthesized a product by dispersing the $FeCl_3$ on the PN to obtain a PN-$FeCl_3$ intermediate. As in the synthesis of catalyst precursors, two quantities of $FeCl_3$ had been chosen in relation to the equivalent moles number of PN in the PN-synthesized. The solvents used are water and ethanol, and the synthesis procedure is the same as that described in §2.3 and the bibliography [2, 3].

Table 3. *Characteristics of raw materials, precursor salts and synthesized catalysts.*

Products Characteristic	raw materials			Intermediate products		Products		Catalyst precursors				Catalysts			
	PN	Poz-zo-lana	FeCl$_3$	PNP-PN pozzolana – water	PNP-PN pozzolana - ethanol	FeCl$_3$PN×14 Water	FeCl$_3$PN-15% Water	FeCl$_3$PNP×14 – water	FeCl$_3$PNP×14 - ethanol	FeCl$_3$PNP-15% - ethanol	FeCl$_3$PNP-15% - water	FePNP×14 water	FePNP×14 - ethanol	FePNP-15% - ethanol	FePNP-15% - water
Weight solvent water [g]	2.6037	2.0251	-			0.3849FeC + 0.5713PN	0.3986FeC + 2.25PN								
Weight solvent ethanol [g]	2.6130	2.0100	-					1.0032PNP + 0.4587FeC	1.0032PNP + 0.4546FeC	2.0004PNP + 0.3545FeC	2.0052PNP + 0.3545FeC				
density apparent - ρ_a [g/cm^3]	1.0375	2.5467	2.9000	-	-	0.8054	0.8026	1.0457	1.0369	1.0633	1.0787				
Specific density - ρ_s [g/cm^3]	-	-		1.6978	1.6937	1.7872	1.3178	2.0750	2.0699	1.8753	1.8784				
Porosity volume [cm^3/g] (1)						0.6821	0.4871	0.4744	0.4813	0.4072	0.3947				
Porosity [%] (2)						54.94	39.10	49.60	49.90	43.30	42.57				
Insaturation C= of PNP quantity [mol/g]				1.57E-3	2.80E-3									2.8E-3	1.576E-3
PN-surface [%]				18.14	23.99										
PN-internal [%]				81.86	78.01										
Iron-Fe weight concentration before synthesis [mol/g]						2.4816E-03	9.2781E-04	1.9344E-03	1.9225E-03	9.2807E-04	9.2619E-04				
Iron-Fe weight concentration after synthesis [mol/g] (3)						2.4590E-03	8.5714E-04	6.2500E-04	5.5046E-04	2.4193E-04	2.6790E-04				
Fer-Fe weight concentration of the synthesis after heat treatment [mol/g]						7.2000E-04	4.7244E-04					4.5802E-04	3.7500E-04	2.3810E-04	2.4000E-04

Products Characteristic	raw materials			Intermediate products		Products		Catalyst precursors				Catalysts			
	PN	Pozzolana	$FeCl_3$	PNP-PN pozzolana – water	PNP-PN pozzolana - ethanol	$FeCl_3PN\times14$ Water	$FeCl_3PN$-15% Water	$FeCl_3PNP\times14$ – water	$FeCl_3PNP\times14$ - ethanol	$FeCl_3PNP$-15% - ethanol	$FeCl_3PNP$-15% - water	$FePNP\times14$ water	$FePNP\times14$ - ethanol	FePNP -15% - ethanol	FePNP -15% - water
Acid sites Weight concentration in the synthesis after heat treatment [mol/g]												9,1197E-03	6,5574E-04	2,2769E-03	3,5088E-03
Basic sites Weight concentration in the synthesis after heat treatment [mol/g]												2,4108E-03	4,0323E-03	4,6685E-04	2,2960E-03
Porosity at iso-level of $FeCl_3$ (2)/(3) [%]/[mol/g]				$FeCl_3$ 2.234E+02	Fe 7,630E+02	$FeCl_3$	Fe 8,275E+02	7,937E+02	9,066E+02	1,790E+03	1,589E+03	1,083E+03	1,331E+03	1,819E+03	1,774E+03
Pore volume at iso-level of $FeCl_3$ [cm^3]/[mol] (1)/(3)				$FeCl_3$ 2.7738E+02	Fe 9.4735E+02	$FeCl_3$ 5.6829E+02	Fe 1.0310E+03	7,5899E+02	8,7434E+02	1,6832E+03	1,4732E+03	1,0357E+03	1,2834E+03	1,7103E+03	1,6445E+03

Looking generally at the porosity and pore volume values (Table 3), the catalyst precursor salts and the catalysts PNP-FeCl₃×14 et PNP-Fe×14 are more porous than PNP-FeCl₃-15% et PNP-Fe-15%. However, when the porosity values are adjusted to FeCl₃ iso-levels, the catalyst precursor salts and catalysts, 15% PNP-FeCl₃-15% et PNP-Fe-15% are the most porous. Indeed, the porosities and pore volumes of PNP-FeCl₃-15% (water) et PNP-FeCl₃-15% (ethanol) respectively equals to 1.4732E+03 [cm³/mol] and 1.6832E+03 [cm³/mol] are much higher than those of PNP-FeCl₃×14 (water) et PNP-FeCl₃×14 (ethanol) respectively equals 7.5899E+02 [cm³/mol] et 8.7434E+02 [cm³/mol]. However, these differences due to the amount of Iron become less significant after heat treatment. These results indicate that the porosities were mainly due to the PNP support used, so the higher the FeCl₃ content, the lower the porosity and pore volumes. Nevertheless, heat treatment of catalyst precursor salts generally improves the porosity and pore volume of catalysts.

Concerning the effect of the solvent used, the results mentioned above and in Table 3 indicate that when using the solvent ethanol for precursor salt synthesis, the amount of porosity and pore volume is much greater than with the solvent water. Furthermore, heat treatment always has a positive effect on porosity and pore volumes during synthesis.

PNP-PNpozzolana synthesized with ethanol as solvent contains significantly more alkene equivalents than that synthesized with water. This certainly implies that the amount of alkene-equivalent in catalysts synthesized with ethanol as solvent is greater than that synthesized with water (Table 3), which is the case for FePNP-15% catalysts.

Since the molar volume of water is much smaller than that of ethanol, water molecules are easily released from the pores after boiling, which explains the large decrease in Fer-Fe mass concentration of catalysts synthesized with water as solvent.

Optical microscopy revealed the presence of black PN-polymer scattered over the light-brown to darker-brown pozzolana.
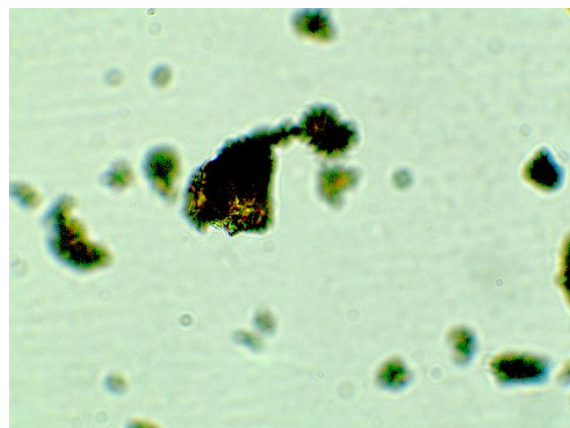
Figure 4. FeCl₃PNP solvent water magnifiedt×40.

Figure 5. FeCl₃PNP×14 solvent water magnified×10.
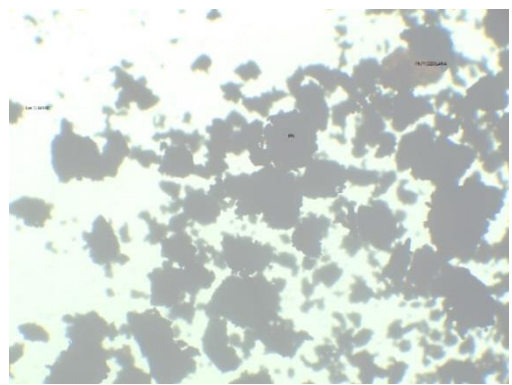
Figure 6. FeCl₃PNP×14 solvent ethanol magnified×10.
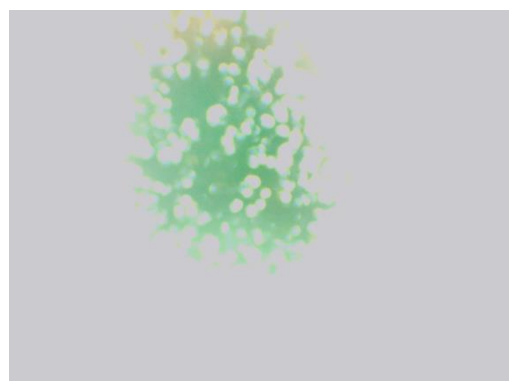
Figure 7. FeCl₃PNP-15 solvent ethanol magnified×40.

Figure 8. FeCl₃PNP-15 solvent water magnified ×60.

Comparing the figure 4 of the precursor salts synthesized with the water and ethanol solvents, it was noted that the ethanol solvent (Figure 6) produced a dispersion that was more spread out and evenly covering the pozzolana than the water solvent (Figure 5).

Figures 4 and 5 show the scattering of $FeCl_3$ molecules illuminated in white on the PNP (Figure 7) and as green speckles on the black PNP (Figure 8), while the pozzolana support is light to dark brown (Figure 8).

4. Catalytic testing of Fe-PNP-H₂0-15% and Fe-PNP-Ethanol-15% catalysts with hydrogen Peroxide H₂O₂

By definition, a catalytic test is a thermodynamically possible chemical reaction where the catalyst under test is used to catalyze the reaction. A kinetic study, i.e. monitoring the evolution of the catalytic reaction over time, would enable us to collect results that could be used to objectively assess the activity of the tested catalyst to produce a product or to catalyze a specific reaction.

Iron and black PN-Polymer catalysts have been shown to reduce NOx gases. Indeed, a catalytic test was carried out in a fixed-bed piston reactor using the PNP-Fe catalyst to reduce NO_2 [2]. The problem was that not only the implementation of the gas-phase catalytic test is difficult, but also the NO_2 model reagent used to represent NOx gases is very noxious and difficult to acquire, requiring great care in its synthesis and use. Since then, a project has been underway to find a model molecule that is less harmful but just as oxidizing as NO_2, and which can be effectively reduced using a catalyst to be tested.

Since then, the idea has turned to hydrogen peroxide H_2O_2. Indeed, hydrogen peroxide is an oxidized molecule that can be reduced by various mechanisms to hydrogen-H_2, with the formation of water-H_2O and/or the release of oxygen-O_2, depending on the experimental conditions and the catalysts used. In this case, the catalytic test is carried out in the liquid phase under atmospheric pressure at room temperature in an open reactor, using H_2O_2 diluted in water as the model reagent. The characteristics of

hydrogen peroxide are given in the following Table 4:

Table 4. *Characteristics of hydrogen peroxide H_2O_2.*

CARACTERISTIQUES	H_2O_2
Purity [%]	50
Concentration [mol/L]	15,9748

The first catalysts used to test this model reaction with hydrogen peroxide were the FePNP-15% - ethanol and FePNP-15% - water.

4.1. Description of the Hydrogen Peroxide Catalytic Test Procedure H_2O_2

The catalytic test was carried out in an uncovered glass container under atmospheric pressure. Firstly, the mass of catalyst to be tested was weighed and placed in the container. Then, the 15ml volume of H_2O_2 reagent used and to be transformed was measured using a pipette and placed in the reactor container, at the same time as the chronometer was started. We noticed the formation of gas bubbles right from the start, one of which was certainly hydrogen, which turned blue on contact with a lighter flame, and the other oxygen (Figure 9).


Figure 9. *Formation of gas bubbles right from the start.*

In fact, the literature shows that hydrogen peroxide can be broken down into water and oxygen [8, 9]. The proposed reaction mechanisms are described in §4.3 and compared with the experimental results. Then, for the kinetic study, one-drop samples are collected by pipette and transferred to 250ml beakers at 1mn, 3mn, 5mn, 7mn and 15mn to be assayed with

$KMnO_4$ for H_2O_2 concentrations.

The H_2O_2 molecule dosing procedure is as follows: once the drop of sample has been placed in the 250ml beaker, it is diluted in 10ml of distilled water, to which 10ml of 0.1N sulfuric acid is added as catalyst. The titrant solution KMnO4 - 0.0106N is added to the burette, and dosing can begin in accordance with the following global oxidation-reduction equation (equation 8) such that the equivalent point corresponding to the equivalent volume V_e is reached when the color of the solution to be titrated first changes from transparent white to persistent light purple.

$$2MnO_4^- + 6H^+ + 5H_2O_2 \leftrightarrows 2Mn^{2+} + 8H_2O + 5O_2 \quad (8)$$
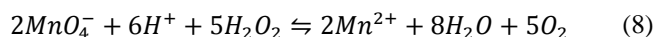
Equation 8 – Redox balance reaction: reduction of the $KMnO_4$ ($MnO^{4+}/Mn^2 - 1.51^+$) reduction by hydrogen peroxide ($O_2/H_2O_2 - 0.68$)

Thus, the H_2O_2 quantities in a drop sample is given by equation 9.

$$nH_2O_{2\,sample}[moles] = \frac{5}{2} \times 0,0106[\frac{moles}{l}] \times V_e[l] \quad (9)$$

Equation 9 – Quantity of hydrogen peroxide molecules in a drop sample.

During the reaction, it was taken that the reaction volume remain constant and equal to 15ml. Indeed, this was visually observed during the duration of the catalytic test in an uncovered 75ml glass vessel under atmospheric pressure. Thus, the total quantity of residues in moles of hydrogen peroxide (equation 10) and their concentrations at all times are deduced from this experimental condition, given that one drop corresponds to 0.05ml. Thus,

$$nH_2O_{2\,Total}[moles] = \frac{15}{0.05} \times nH_2O_{2\,échantillons}[moles] \quad (10)$$

Equation 10 - Total quantity of remaining hydrogen peroxide molecules in the reaction medium.

4.2. Catalytic Test Results, Interpretations and Discussions

Table 5 below shows the results of the evolution over time of the molar quantities of hydrogen peroxide molecules and, consequently, the evolution of their conversions for the two catalysts FePNP-15% - ethanol and the FePNP-15% - water.

Table 5. *Comparative conversion results from catalyst testing FePNP-15% - ethanol et FePNP-15% - water.*

H_2O_2 initial Quantity $= 0.239622$ [ml]		
Catalyst weight [g]	FePNP-15% ethanol	0.0346
	FePNP-15% water	0.0355

| H_2O_2 *initial Quantity* = 0.239622 [ml]						
[Fe] – [mol/g]	FePNP-15% ethanol	4.72E-04				
	FePNP-15% water	2.40E-04				
Initial Iron-Fe quantity [moles]	FePNP-15% ethanol	1.63E-05				
	FePNP-15% water	8.52E-06				
$[Fe]_0$ - [mol/L]]	FePNP-15% ethanol	1.09E-03				
	FePNP-15% water	5.68E-04				
TIME (mn)	Catalysts	1	3	5	7	15
nH_2O_2 SAMPLE [moles]	FePNP-15% ethanol	7.98E-04	7.31E-04	8.37E-04	1.59E-05	7.95E-06
	FePNP-15% water	7.34E-04	7.58E-04	1.30E-03	7.74E-04	6.89E-04
nH_2O_2 TOTAL [moles]	FePNP-15% ethanol	2.39E-01	2.19E-01	1.26E-01	4.77E-03	2.39E-03
	FePNP-15% water	2.20E-01	1.14E-01	9.72E-02	7.74E-02	6.89E-02
Conversion [%]	FePNP-15% ethanol	0,14%	8.10%	46.94%	97.02%	98.01%
	FePNP-15% water	8,10%	52.25%	58.82%	66.54%	69.94%
Total H_2O_2 converted per moles of initial Fe catalyst [moles H_2O_2 /molesFe]	FePNP-15% ethanol	2.00E+01	1.19E+03	6.88E+03	1.42E+04	1.44E+04
	FePNP-15% water	2.28E+03	1.47E+04	1.65E+04	1.87E+04	1.97E+04
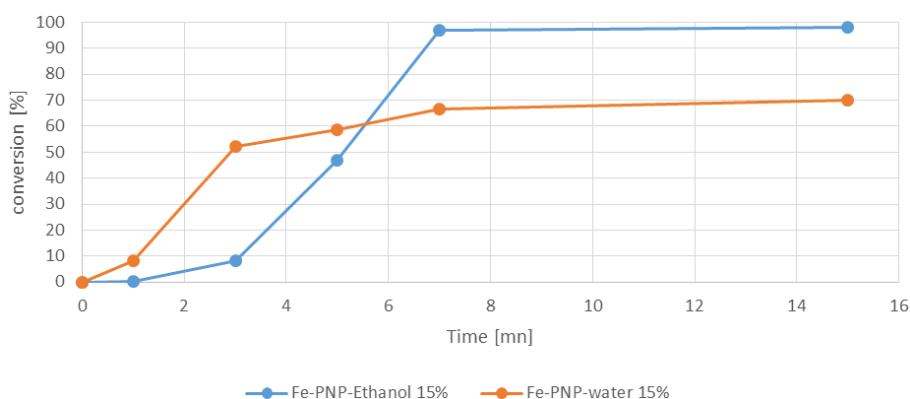
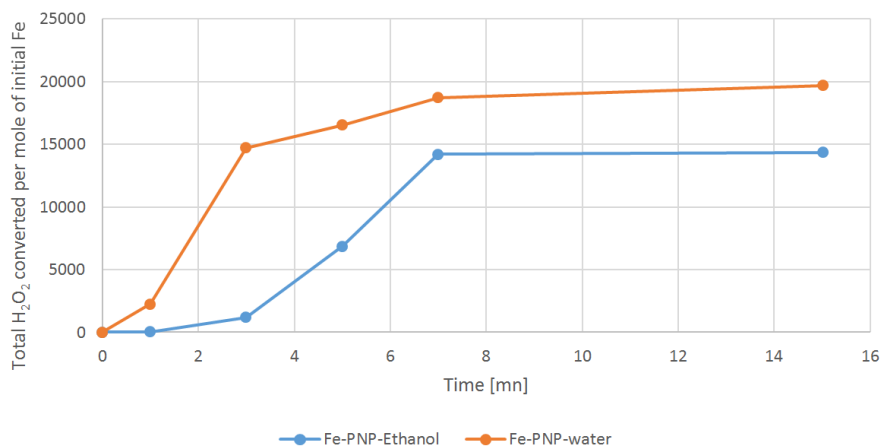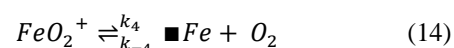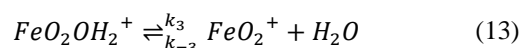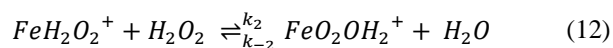**Figure 10.** *Evolution of conversion as a function of time for the two catalysts.*
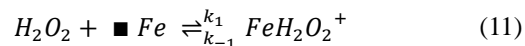

Figure 11. *Evolution of total H_2O_2 converted per mole of initial Fe [moles H_2O_2 /molesFe] for the two catalysts.*

The results and figures above show that the model reaction with hydrogen peroxide not only makes it possible to determine the activity of a heterogeneous catalyst in a reduction reaction, but also to compare its activity with that of another heterogeneous catalyst. In our study in this manuscript, Figure 11 shows that initially the catalyst Fe-PNP-Water 15% synthesized with water is more active than the catalyst Fe-PNP-Ethanol 15% synthesized with ethanol. By relating the quantities of H_2O_2 converted per moles of initial Fe catalyst for each catalyst, the figure showing the evolution of this quantity with reaction time clearly confirms the high activity of the catalyst Fe-PNP-Water 15% synthesized with water compared with that of the catalyst Fe-PNP-Ethanol 15% synthesized with ethanol. These differences in activity between the two catalysts could be explained by their black polymer content, by the dispersion of these NPs on pozzolana and by their equivalent alkene content, as well as by their porosity. First, the surface black polymer content of PNP-Ethanol (23.99% - Table 3) is higher than that of PNP-Water (18.14% - Table 3) and also it had been noticed on the optical microscopy pictures that the dispersion of these NPs on the pozzolana for Fe-PNP-Ethanol×14 (Figure 6) is more spread out and regularly covers the pozzolana than that of the solvent water (Figure 5). Then, the pore volume at iso-iron-Fe content of the Fe-PNP-Ethanol 15% (1.7103E+03 [cm^3/mol] – Table 3) is slightly larger than that of Fe-PNP-Water15% (1.6445E+03[cm^3/mol] – Table 3), which indicates that the iron molecules are better dispersed on the Fe-PNP-Ethanol 15% than on Fe-PNP-Water15%. Next, the alkene-equivalent content of the Fe-PNP-Ethanol 15% (2.800E-3[molC$^=$/g] – Table 3) is higher than that of Fe-PNP-Water 15% (1.576E-3 [molC$^=$/g] – Table 3). These differences in characteristics indicate that on the Fe-PNP-Water 15% These differences in characteristics indicate that on A, in addition to chemisorption, there is more physisorption of H_2O_2 reagents on the PN-free Pozzolana parts by hydrogen bridge bonding or low-energy Van Der Waals bonding, which This favors the formation of reaction intermediates with faster reactivity and desorption of their reaction products than Fe-PNP-Ethanol 15%, where the NPs are well dispersed, and favors the formation of reaction intermediates with more energetic binding of H_2O_2 reagents and its NPs by chemisorption. This is a phenomenon that is widely discussed and justified in the literature [5].

4.3. Confrontation of Catalytic Test Results with Proposed Reaction Mechanisms

According to the literature, hydrogen peroxide breaks down into water and oxygen (mechanism 1) However, during the catalytic test with the two catalysts mentioned above, the Fe-PNP-Ethanol 15% and the Fe-PNP-Water 15%, the formation of a blue flame in the presence of a flame was recorded,

which is none other than the formation and release of hydrogen during this catalytic test (mechanism 2). This prompts us to propose two reaction mechanisms for these catalytic tests, whose rates and kinetic constants are deduced and confronted with the experimental results.
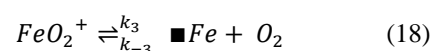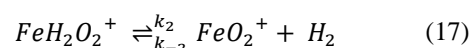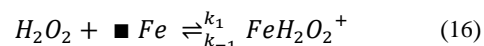
$$H_2O_2 + \ \blacksquare \ Fe \ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \ FeH_2O_2^+ \tag{11}$$

$$FeH_2O_2^+ + H_2O_2 \ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \ FeO_2OH_2^+ + H_2O \tag{12}$$

$$FeO_2OH_2^+ \ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \ FeO_2^+ + H_2O \tag{13}$$

$$FeO_2^+ \ \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \ \blacksquare Fe + O_2 \tag{14}$$

Mechanism 1 – Mechanism of hydrogen peroxide dismutation catalyzed by the heterogeneous catalyst FePNP

$$2H_2O_2 + Fe \rightarrow 2H_2O + O_2 + Fe \tag{15}$$
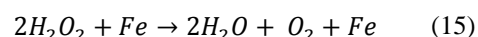
Equation 15 – General catalyzed hydrogen peroxide dismutation reaction by FePNP

This proposed first mechanism is characterized by a general hydrogen peroxide dismutation reaction catalyzed by FePNP involving the successive adsorption of two hydrogen peroxide molecules onto the heterogeneous FePNP catalyst, accompanied by the formation of intermediates and two water molecules, finalized by the formation of one oxygen molecule. (Mechanism 1).

$$H_2O_2 + \ \blacksquare \ Fe \ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \ FeH_2O_2^+ \tag{16}$$

$$FeH_2O_2^+ \ \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \ FeO_2^+ + H_2 \tag{17}$$

$$FeO_2^+ \ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \ \blacksquare Fe + O_2 \tag{18}$$

Mechanism 2 – Mechanism of hydrogen peroxide molecule decomposition into hydrogen and oxygen catalyzed by FePNP

$$H_2O_2 + Fe \rightarrow H_2 + O_2 + Fe \tag{19}$$
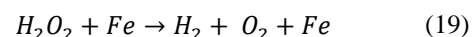
Equation 19 – General hydrogen peroxide decomposition reaction catalyzed by FePNP

This proposed second mechanism is characterized by a general decomposition reaction of hydrogen peroxide catalyzed by Iron-Fe via adsorption of the hydrogen peroxide molecule onto the catalyst to form a reaction intermediate that progressively decomposes into hydrogen and oxygen with regeneration of the catalyst. FePNP (Mechanism 2).

4.3.1. Expression of the Reaction Rate for the First Mechanism and Determination of the Kinetic Constants

Referring to the first mechanism, we'll choose equation 12 as the kinetically limiting step, so the overall reaction rate is that of this limiting step (Equation 12) equal to

$$v_{equation\ 12} = k_2[FeH_2O_2^+][H_2O_2] - k_{-2}[FeO_2OH_2^+][H_2O] \tag{20}$$

As a result, the other reactions in the first mechanism are practically at equilibrium, and their rates are zero, thus

$$v_{equation11} = k_1[H_2O_2][Fe] - k_{-1}[FeH_2O_2^+] = 0 \implies [FeH_2O_2^+] = \frac{k_1}{k_{-1}}[H_2O_2][Fe]$$

$$v_{equation\ 12} = k_3[FeO_2OH_2^+] - k_{-3}[FeO_2^+][H_2O] = 0 \implies [FeO_2OH_2^+] = \frac{k_{-3}}{k_3}[FeO_2^+][H_2O]$$

$$v_{equation\ 14} = k_4[FeO_2^+] - k_{-4}[Fe][O_2] = 0 \implies [FeO_2^+] = \frac{k_{-4}}{k_4}[Fe][O_2]$$

Given that the adsorption equilibrium constants are as follows: $K_1 = \frac{k_1}{k_{-1}}$, $K_2 = \frac{k_2}{k_{-2}}$, $K_3 = \frac{k_{-3}}{k_3}$, $K_4 = \frac{k_{-4}}{k_4}$ and by substituting the expressions for the concentrations of the reaction intermediates in equation 20 from the over equations, the reaction rate of mechanism 1 becomes,

$$v_{mechanism1} = v_{equation\ 12} = k_2K_1[H_2O_2]^2[Fe] - k_{-2}K_3K_4[Fe][O_2][H_2O]^2[Fe]$$

$$\iff v_{mechanism1} = v_{equation\ 12} = (k_2K_1[H_2O_2]^2 - k_{-2}K_3K_4[O_2][H_2O]^2)[Fe] \tag{21}$$

Applying the law of conservation to Iron-Fe, it can be written as follows

$$[Fe]_0 = [FeO_2OH_2^+] + [FeH_2O_2^+] + [FeO_2^+] + [Fe] \tag{22}$$

Eliminating [Fe] from the other side of the equation and replacing the concentrations of the reaction intermediates, the expression for the equation 22 will be as follows,

$$[Fe] = \frac{[Fe]_0}{1 + K_3K_4[O_2][H_2O] + K_1[H_2O_2] + K_4[O_2]} \tag{23}$$

Transferring this expression for Fe concentration (equation 23) to equation 21, the expression for the latter will be as follows,

$$v_{mechanism1} = v_{equation\ 12} = \frac{k_2K_1[H_2O_2]^2 - k_{-2}K_3K_4[O_2][H_2O]^2}{1 + K_3K_4[O_2][H_2O] + K_1[H_2O_2] + K_4[O_2]} \times [Fe]_0 \tag{24}$$

Assuming that oxygen- O_2 is not yet being formed and released in the initial instants
The expression in equation 24 will be as follows,

$$v_{mechanism1-initial} = v_{equation12-initial} = \frac{k_2K_1[H_2O_2]^2}{1 + K_1[H_2O_2]} \times [Fe]_0 \tag{25}$$

The speed expression is

$$v_{mechanism1-initial} = v_{equation12-initial} = -\frac{d[H_2O_2]}{dt} \tag{26}$$

By making a change of variable $x = [H_2O_2]$, The equivalence of equations 25 and 26 gives

$$-\frac{dx}{dt} = \frac{k_2K_1x^2}{1 + K_1x} \times [Fe]_0 \iff -\frac{(1 + K_1x)dx}{k_2K_1x^2} = [Fe]_0 dt$$

$$\iff \int -\frac{(1 + K_1x)dx}{k_2K_1x^2} = \int [Fe]_0 dt \iff \frac{1}{k_2K_1x} - \frac{1}{k_2}\ln x = [Fe]_0 t + C$$

At time t = 0, $x = x_0 = [H_2O_2]_0 \Rightarrow$ *the constant* $C = \frac{1}{k_2 K_1 x_0} - \frac{1}{k_2} \ln x_0$

As a result, the following expression for mechanism 1 at the initial instants is deduced,

$$\frac{1}{k_2 K_1}\left(\frac{1}{x} - \frac{1}{x_0}\right) - \frac{1}{k_2} \ln \frac{x}{x_0} = [Fe]_0 t \tag{27}$$

$$\Leftrightarrow \ln \frac{x}{x_0} = -k_2[Fe]_0 t + \frac{1}{K_1}\left(\frac{1}{x} - \frac{1}{x_0}\right) \tag{28}$$

By drawing, $\ln \frac{x}{x_0} = f(t)$ from the experimental results in table 5 §4.2, the curves in the following figure 12 was deduced

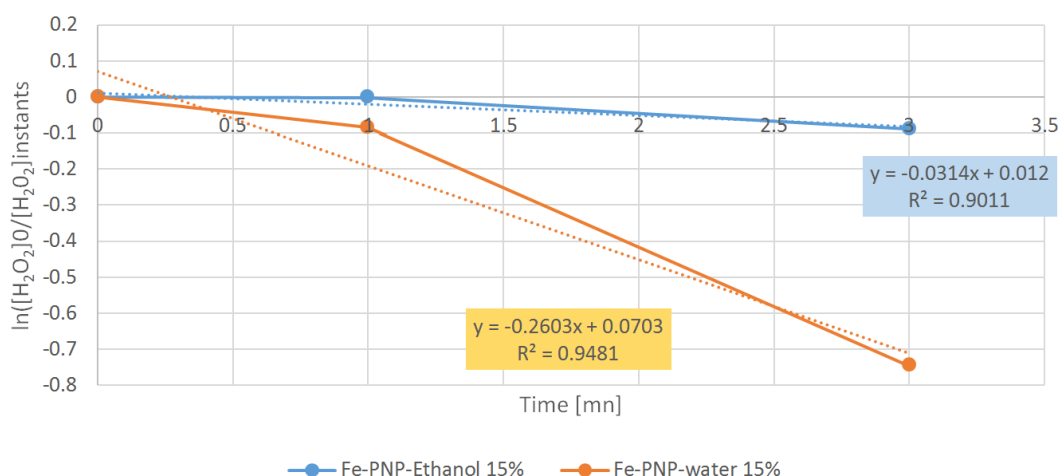**Figure 12.** *Evolution of ln([H₂O₂]ᵢᵢₙᵢₜᵢₐₗ/[H₂O₂]₀) with time reaction for the tested two catalysts.*

Figure 12 above clearly shows that there were straight lines from which it is possible to derive the values of the kinetic constants k_2 (*slope of straight lines*) and the constant K_1 (*from the* $y-intercept$) for the two catalysts tested FePNP-15% - ethanol and the FePNP-15% - water.

To evaluate K_1, the value of $\left(\frac{1}{x} - \frac{1}{x_0}\right)$ at the initial instant was determined by plotting the following figure 13 of its evolution as a function of time. Thus,
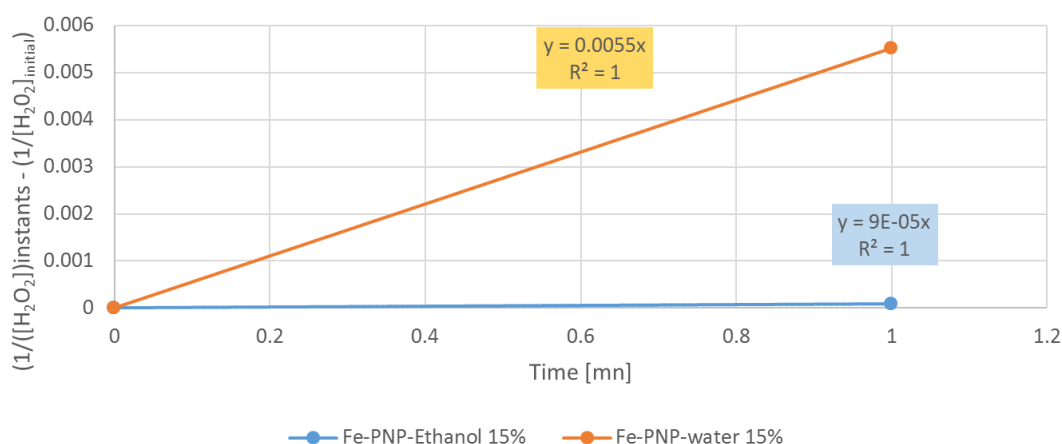

Figure 13. *Evolution of 1/([H₂O₂])ᵢₙₛₜₐₙₜₛ ᵢₙᵢₜᵢₐᵤₓ - (1/[H₂O₂]₀) with time reaction.*

Taking an initial time value t=0,006min, the initial values   of $\left(\frac{1}{x} - \frac{1}{x_0}\right)$ for the catalyst Fe-PNP-15%-Ethanol and for the

catalyst Fe-PNP-15%-water were respectively 5, 4E-07 et 3, 3E-05.

The various data and analyses of the above results allow to determine the values of the kinetics constants presented in table 6 below:

Table 6. The values of cinetic constants at the initial instants of the tested catalysts for mechanism1.

	K_1	k_2
Fe-PNP-15%-ethanol	154.320.988	28,8073
Fe-PNP-15%-water	431.053,063	363,204

These results in Table 6 show that not only the proposed mechanism number 1 agree and is confirmed by the experi-mental results, but also and more importantly the hydrogen peroxide catalytic test would allow a pragmatic comparison of catalysts and confirm that the Fe-PNP-15%-water catalyst is more active than the Fe-PNP-15%-ethanol catalyst for reduc-tion reactions.

4.3.2. Expression of the Reaction Rate for the Second Mechanism and Determination of the Speed Constants

Referring to the second mechanism, the equation 17 was choosen as the kinetically limiting step, so the overall reaction rate is that of this limiting step (Equation 17), equal to

$$v_{equation\ 17} = k_2[FeH_2O_2{}^+] - k_{-2}[FeO_2{}^+][H_2] \quad (29)$$

As a result, the other reactions in the second mechanism are practically at equilibrium, so their speeds are zero, thus

$$v_{equation\ 15} = k_1[H_2O_2][Fe] - k_{-1}[FeH_2O_2{}^+] = 0 \Rightarrow [FeH_2O_2{}^+] = \frac{k_1}{k_{-1}}[H_2O_2][Fe]$$

$$v_{equation\ 18} = k_3[FeO_2{}^+] - k_{-3}[Fe][O_2] = 0 \Rightarrow [FeO_2{}^+] = \frac{k_{-3}}{k_3}[Fe][O_2]$$

Given that the adsorption equilibrium constants are as follows: $K_1 = \frac{k_1}{k_{-1}}$, $K_2 = \frac{k_2}{k_{-2}}$, $K_3 = \frac{k_{-3}}{k_3}$ by substituting the expres-sions for the concentrations of the reaction intermediates in equation 29, the reaction rate for mechanism 2 will be,

$$v_{mechanism2} = v_{equation\ 17} = (k_2K_1[H_2O_2] - k_{-2}K_3[O_2])[Fe] \quad (30)$$

Applying the law of conservation to Iron-Fe, it can be written as follows

$$[Fe]_0 = [FeH_2O_2{}^+] + [FeO_2{}^+] + [Fe] \quad (31)$$

Eliminating [Fe] from the other side of the equation and replacing the concentrations of the reaction intermediates, the ex-pression for the Equation 31 will be

$$[Fe] = \frac{[Fe]_0}{1 + K_1[H_2O_2] + K_3[O_2]} \quad (32)$$

Transferring this expression for Fe concentration (equation 32) to equation 30, the expression for the latter will be as follows

$$v_{mechanism2} = v_{equation\ 17} = \frac{k_2K_1[H_2O_2] - k_{-2}K_3[O_2]}{1 + K_1[H_2O_2] + K_{-3}[O_2]} \times [Fe]_0 \quad (33)$$

Assuming that oxygen- O_2 is not yet being formed and released in the initial instants
The expression in equation 33 will be as follows

$$v_{mechanism2-initial} = v_{equation\ 17-initial} = \frac{k_2K_1[H_2O_2]}{1 + K_1[H_2O_2]} \times [Fe]_o \quad (34)$$

The speed expression is

$$v_{mechanism2-initial} = v_{equation\ 17-initial} = -\frac{d[H_2O_2]}{dt} \quad (35)$$

By making a change of variable $x = [H_2O_2]$, The equivalence of equations 34 et 35 gives

$$-\frac{dx}{dt} = \frac{k_2 K_1 x}{1+K_1 x} \times [Fe]_o \iff -\frac{(1+K_1 x)dx}{k_2 K_1 x} = [Fe]_o dt$$

$$\iff \int -\frac{(1+K_1 x)dx}{k_2 K_1 x} = \int [Fe]_0 dt \iff \frac{1}{k_2 K_1}\ln x + \frac{1}{k_2}x = -[Fe]_0 t + C$$

At the initial instant t = 0, $x = x_0 = [H_2O_2]_0 \Rightarrow the\ constant\ C = \frac{1}{k_2 K_1 x_0}\ln x_0 - \frac{1}{k_2}x_0$

As a result, the following expression for mechanism 2 at the initial instants was deduced,

$$\frac{1}{k_2 K_1}\ln \frac{x}{x_0} + \frac{1}{k_2}(x - x_0) = -[Fe]_0 t \tag{36}$$

$$\iff \ln \frac{x}{x_0} = -k_2 K_1 [Fe]_0 t + K_1(x_0 - x) \tag{37}$$

By plotting, $\ln \frac{x}{x_0} = f(t)$ from the experimental results in table 5 § 4.2, the same curve on the previous figure 12 was deduced. This figure 12 clearly shows that there were straight lines from which it is possible to derive the values of the kinetic constants k_2 *(slope of straight lines)* and the constant K_1 *(from the y − intercept)* for the tested catalysts FePNP-15% - ethanol and FePNP-15% - water.

To evaluate K_1, the value of $(x_0 - x)$ at the initial instant was determined by plotting the following figure 14 of its evolution as a function of time. Thus,
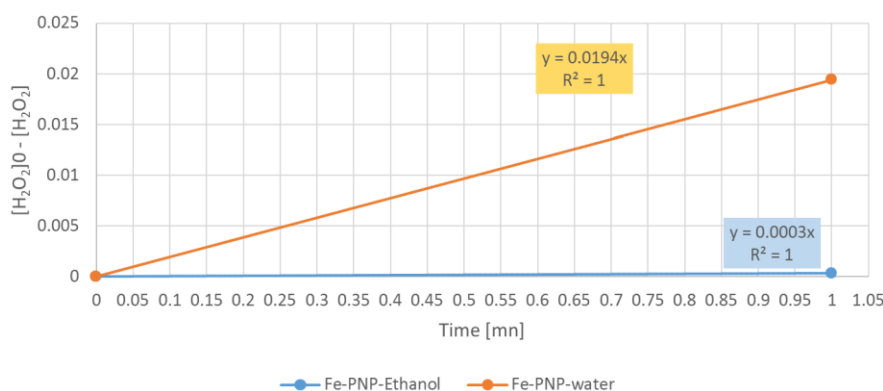

Figure 14. Evolution of $([H_2O_2]_0$ *- [H_2O_2])_{instants\ initiaux}$ *with time reaction.*

Taking an initial time value t=0,006min, the initial values of $(x_0 - x)$ for the catalyst Fe-PNP-15%-Ethanol and for the catalyst Fe-PNP-15%-water were respectively 1, 8E-06 and 1, 164E-04.

The various data and analyses of the above results allow to determine the values of the kinetics constants presented in the following table 7:

Table 7. The values of cinetic constants at the initial instants of the tested catalysts for mechanism1.

	K_1	k_2
Fe-PNP-15%-ethanol	6,666E+03	2,4789E-3
Fe-PNP-15%-water	6,0395E+02	7,5879E-1

These results in Table 6 show that not only the proposed mechanism number 2 agree and is confirmed by the experimental results, but also and more importantly the hydrogen peroxide catalytic test would allow a pragmatic comparison of catalysts and confirm that the Fe-PNP-15%-water catalyst is more active than the Fe-PNP-15%-ethanol catalyst for reduction reactions.

5. Conclusion

The results of the studies and experiments in this manuscript show that hydrogen peroxide could serve as a model molecule for the determination and evaluation of reducing catalysts such as NOx catalysts based on PNP-Fe (black iron-polymer of citric acid and pozzolana). In this case, two different catalysts were tested in relation to the solvent used in their synthesis. The results of the catalytic tests une-

quivocally confirm that the choice of solvent is very important and has a major influence on the dispersion of the PN-black polymer molecules on the pozzolana support, which in turn influences the quantity of Fe to be applied. Thus, it was pragmatically concluded that it is the PNP-water-15% catalyst synthesized with the solvent water that is more active during hydrogen peroxide reduction and exhibiting higher kinetic constants on the reaction mechanisms proposed in this manuscript than the PNP-water-15% catalyst synthesized with the solvent ethanol. Consequently, these reaction mechanisms for ethanol reduction decomposition detailed in this manuscript are also validated in these catalytic tests with the formation of hydrogen and oxygen molecules. However, if we refer only to the NO_2 catalytic reduction mechanism described in the literature [2], which involves only a reaction intermediate formed by NO_2 and the double bonds of the PNP-Fe catalyst; given the much higher double bond content of the 15% PNP-Fe-ethanol compared with the 15% PNP-Fe-water catalyst, it could be that the first is more active, which doesn't rule out the need for real-life testing of catalysts synthesized in catalytic converters.

Abbreviations

PN	Black Citric Acid Polymer
PNP	Black citric Acid Polymer Supported on Pozzolana
Fe-PNP	Iron Distributed on PNP

Acknowledgments

Conflicts of Interest

The authors declare no conflicts of interest.

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