



Research/Technical Note

Study of the PPCA-Materials' Acid Sites and Basic Sites to Extract the MSB - 3-Methyl-3-Sulfanylbutan-1-Ol

Andry Tahina Rabeharitsara^{*}, Henri Rakotondrina^{*}, Nambinina Richard Randriana, Hanitraniaina Marie Ratsimba, Rakotomamonjy Pierre, Soloniaina Rakotoarijaona

Chemical Process Engineering Department (E. S. P. A), Antananarivo University, Antananarivo, Madagascar

Email address:

rabeharitsara_andrytahina@yahoo.fr (Andry Tahina Rabeharitsara), rakotondrinahenry@gmail.com (Henri Rakotondrina), richarrandriana@gmail.com (Nambinina Richard Randriana), ratsimbamarie@yahoo.fr (Hanitraniaina Marie Ratsimba), kotomamonjypr@yahoo.fr (Rakotomamonjy Pierre), soloniaina.rakotoarijaona@gmail.com (Soloniaina Rakotoarijaona)

^{*}Corresponding author

To cite this article:

Andry Tahina Rabeharitsara, Henri Rakotondrina, Nambinina Richard Randriana, Hanitraniaina Marie Ratsimba, Rakotomamonjy Pierre, Soloniaina Rakotoarijaona. Study of the PPCA-Materials' Acid Sites and Basic Sites to Extract the MSB - 3-Methyl-3-Sulfanylbutan-1-Ol. *American Journal of Applied and Industrial Chemistry*. Vol. 7, No. 2, 2023, pp. 38-46. doi: 10.11648/j.ajaic.20230702.12

Received: September 20, 2023; Accepted: October 12, 2023; Published: October 28, 2023

Abstract: The MSB - 3-Methyl-3-Sulfanylbutan-1-Ol is a thiol molecule which could be used as food additive flavor agent and encountered in the white wine, in the coffee perfume, in the passion fruit and in the cat urine where it's the responsible of its strong odor characteristics. Its extraction from the cat-litter and the synthesis of a new material based on black citric acid polymers (pn), pozzolana and citric acid named PPCA (pn-pozzolana-citric-acid) was studied in the previous manuscript. This manuscript consisted to valorize the PPCA as material to extract and to retain the MSB - 3-Methyl-3-Sulfanylbutan-1-Ol molecule. Thus, reaction tests were done between a MSB - 3-Methyl-3-Sulfanylbutan-1-Ol solution and the PPCA. The first part of this manuscript treated the description of these reaction tests procedure and the various experimental conditions which was at ambient temperature, in the open air and at atmospheric pressure inside a container without a cover. It was also described on this first part the quantifications of the molecules and PPCA's sites involved in this reaction such as citric acid residues, MSB, acid sites and basic sites which were especially considered as sites governing the reaction-extraction between the PPCA-material and the MSB - 3-Methyl-3-Sulfanylbutan-1-Ol molecules. The second part of this manuscript consisted on the analyzing of the previous reaction tests results which allowed to the evaluation of its kinetic parameters. In general, it was noted that the reacting basic sites increase as a primary product while the reacting acid sites evolved as a secondary product. Finally, a reaction mechanism governing the MSB extraction-reaction on the PPCA was proposed considering that the PPCA's reactive sites acid were grouped into either acid sites either basic sites by Boëhm titration which could regenerated during the reaction. This proposed reaction mechanism was validated by the determination of the extraction-reaction kinetic constant k equals to $8E-4$ superior to the kinetic constant determined by reaction results exploitation which is equals to $2.69E-08$.

Keywords: Pn-Black Citric Acid Polymer-PPCA, Acid Sites, Basic Sites, MSB (3-Methyl-3-Sulfanylbutan-1-Ol), Kinetics, Mechanism

1. Introduction

The first part of this publication treated the reaction-extraction between the MSB - 3-Methyl-3-Sulfanylbutan-1-Ol molecules and the PPCA-material characterized by its acid sites and basic sites. It was described in the previous manuscript that the

esterification between the citric acid and the MSB implicated not only the MSB's hydroxide $-OH$ organic function (Brönsted basic sites) but also the MSB's vacant cells (Lewis acid sites) with citric acid H^+ as catalyst [1]. In general, this reaction implicated acid sites and basic sites. Thus, the PPCA materials which contain acid sites and basic sites was synthesized in order to extract and to retain the MSB. In the

over words, this manuscript try to study the role of PPCA's basic sites and acid sites characterized by Boëhm titration during its addition reaction with the MSB. The experimental and titrations procedures were also described in this part. The second part is devoted to the experimental results analysis in order to evaluate the kinetic parameters of this reaction-extraction according to the PPCA's acid sites and basic sites. In addition, a reaction mechanism with the consideration of the acid sites and basic sites regeneration governing this MSB extraction-reaction on the PPCA was proposed, described and validated by the experimental results analysis. Materials and chemicals used during experimentations were KERN precision scale, chronometer, glass spatula, iron spatula, ceramic crucible, refractometer, magnetic stirrer, magnetic bar, flask-250ml, heating mantle-250ml, condenser, beaker-100ml, beaker-250ml, beaker-400ml, test tube, graduated burette, test tube, separating funnel, thick ash-free filter paper, glass funnel, pipette, mortar, oven, citric acid, pn-black citric acid polymer-PPCA, pozzolana, used cat-litter, distilled water, HNO₃, HCl-1N, HCl-0.1N, HF-0.0026N, NaOH-0.05N, BaCl₂-0.5N, helianthine, bromophenol blue, ethanol-90°.

2. pn-pozzolana-ac (PPCA) Tests as Materials to Extract the MSB Molecules

2.1. Description of the MSB Extraction Test Procedure

The tests of the pn-pozzolana-ac (ppca) materials to extract the MSB molecules was done at ambient temperature, in the open air and at atmospheric pressure inside a container either a beaker-100ml, either a test tube without a cover. Thus, first weigh the mass of ppca material required for the test reaction to be carried out and place it in the uncovered test vessel. Then secondly add 1ml of the MSB ethanolic solution which concentration is equal to 1.45E-2 [mol/l] and start timing the expected reaction time. The acidic and basic site mass concentrations of the ppca used in the various tests are the same, equal to 4.34E-3 [mol/g] and 3.77E-3 [mol/g] respectively, and the initial citric acid content of the ppca was 4.0078E-5 mol which synthesis and characterizations were done according to the procedure described on the bibliography [1]. When the reaction time corresponding to the test to be carried out has elapsed, immediately separate the aqueous phase from the ppca used by filtering through a glass funnel fitted with filter paper. Recover the residual ppca-used from the container using 90° ethanol, then filter through the same filtration assembly. Thirdly, recover the aqueous phase and leave the used ppca to dry in the filter paper for at least 17 hours. Then determine the concentrations of acidic and basic sites in the used ppca using the Boëhm-titration method. The various tests carried out during this study are presented in Table 1 below.

Table 1. Experimental conditions of the various tests carried out.

Reaction duration [secondes]	ppca weight [g]	MSB volume [ml]
180	0.5215	1

Reaction duration [secondes]	ppca weight [g]	MSB volume [ml]
300	0.5213	
420	0.5202	
2100	0.5202	

2.2. Description of the Quantification Method of the Molecules and Sites Involved in This Reaction

2.2.1. Determination of Citric Acid Residues Concentrations in the Recovered Solution

Once recovered after filtration, the volume of the solution is recorded. Next, place no more than a 2ml sample of this recovered solution in a 250ml separating funnel, then add 45ml ice-cold distilled water and 5ml dichloromethane. Leave to settle for at least 15 minutes, then recover and record the volume of dichloromethane (organic phase at bottom). Take 1ml sample of this organic phase and proceed with the determination of citric acid molecules according to the procedures described in the bibliography [2, 3]. Thus, add 30ml of distilled water to 1ml of sample, allow the resulting solution to settle for at least 15 minutes, then recover the aqueous phase in a 50ml test tube and record its volume. Transfer this recovered solution into a beaker-250ml and add three (3) drops of helianthine indicator solution. The solution turns to yellow. Then titrate this solution with NaOH-0.05N until the first clear change to orange-yellow occurs. Record this volume of NaOH-0.05N, which corresponds to the equivalent point of the determination of the free protons-H⁺ of the carboxylic acid functions of the citric acid molecules present in the solution at the pH of the helianthine color indicator. Then titrate this solution with NaOH-0.05N until the first clear change to orange-yellow occurs. Record this volume NaOH-0.05N which corresponds to the equivalent point of the titration of the citric acid molecules' carboxylic acid functions free H⁺ protons present in the solution at the helianthine color indicator turning point pH-4.5. Finally, deduce the citric acid molecules quantities present in the initial 2ml sample and the citric acid molecules conversion.

2.2.2. Acid Sites Weight Concentrations of the PPCA-Used Material Determination

The acid site rate of the ppca-used is determined by the Boëhm-titration method [4]. So, put a 0.0189g sample of the dried ppca-used in a 100ml beaker then add 6ml NaOH-0.05N. Place under magnetic stirring for one hour the beaker, then filter the resulting solution through a funnel fitted with filter paper, collect and record the volume of the filtrate. Then proceed with the titration of this filtrate by adding three (3) drops of helianthine color indicator (the solution turns yellow-orange) and then by titrating with HCl-0.1N solution to determine the excess NaOH-0.05N. Stop the titration and take the equivalent volume when the solution to be titrated turns clearly to red. Deduce the quantity of the ppca-used acid sites [5].

2.2.3. Basic Sites Weight Concentrations of the PPCA-Used Material Measuring-out

The basic site rate of the ppca-used is determined by the Boëhm-titration method [4]. So, put a 0.0178g sample of the

dried ppca-used in a 100ml beaker then add 6ml of HCl-0.1N. Place under magnetic stirring for one hour the beaker, then filter the resulting solution through a funnel fitted with filter paper, collect and record the volume of the filtrate. This filtrate is then assayed by adding three (3) drops of helianthine indicator solution, the solution turns red and it is titrated with NaOH-0.05N to determine the excess HCl-0.1N. Stop the titration and take the equivalent volume when the solution to be titrated turns clearly to orange-yellow. Deduce the quantity of the ppca-used basic sites [5].

2.2.4. Alkene Weight Concentration and MSB Weight Concentration of the PPCA-Used Measuring-out

The alkene content of the ppca-used is determined according to the procedure described in the bibliography [6, 7]. First, put a 0.0345g sample into a 250ml beaker, then add 30ml distilled water and three (3) drops of bromophenol blue indicator solution. Magnetic stirring is applied and the solution to be titrated turns to transparent blue. Then start

titration using HF-0.0026N; after a certain time, the solution to be titrated becomes clearly transparent; and when titration is continued, after a certain time the solution turns to transparent black chartreuse yellow-green, without changing color thereafter, even if titration continues. Take the volume corresponding to the first turning point V_1 [ml], which could correspond to the surface pn-content and eventually alkenes of the sample attacked by hydrofluoric acid-HF leading to a transparent-black greyish color of the assay solution and the difference between the final volume V_f [ml] corresponding to the transparent black chartreuse yellow-green color and the volume of the first change color to transparent could correspond to the attack of the sulfur compounds of the MSB extracted in the ppca-used sample and also to the attack of the alkenes of the ppca-used whose mass concentration is $[C=]$ and equal to $6.14E-5$ [mol/g]. Deduce the MSB concentration of the sample with weight m such as:

$$\text{MSB weight concentration} \left[\frac{\text{mol}}{\text{g}} \right] = \frac{(V_f - V_1) \times 0.001 \times 0.0026}{m} - [pn] \quad (1)$$

$$\text{MSB quantities [moles]} = \left(\frac{(V_f - V_1) \times 0.001 \times 0.0026}{m} - [pn] \right) \times M \quad (2)$$

M is the weight of ppca for the test.

3. Analyzing of the Test Results During MSB Extraction in pn-pozzolana-Citricacid PPCA

3.1. Kinetic Study and Determination of the Various Kinetic Parameters of the Extraction Reaction

Given that here an addition reaction takes place between the MSB molecules and the active sulfur sites to extract and retain the MSB molecules [1], the expression for the overall rate of this reaction could be written as follows:

$$v = k \times [\text{acid sites}]^\alpha \times [\text{basic sites}]^\beta \times [\text{MSB}]^\omega \quad (3)$$

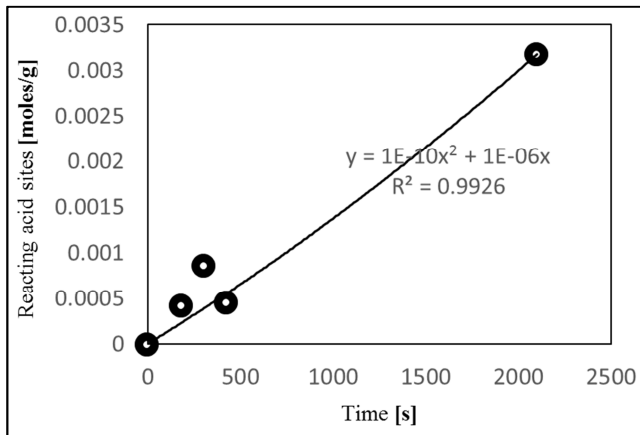


Figure 1. Evolution of the reacting acid sites concentrations with reaction time.

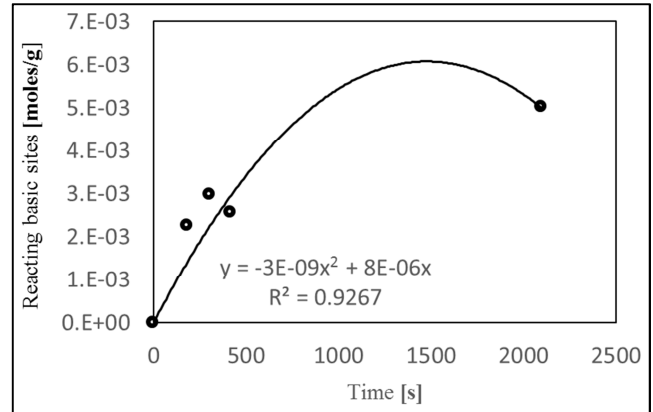


Figure 2. Evolution of the reacting basic sites concentrations with reaction time.

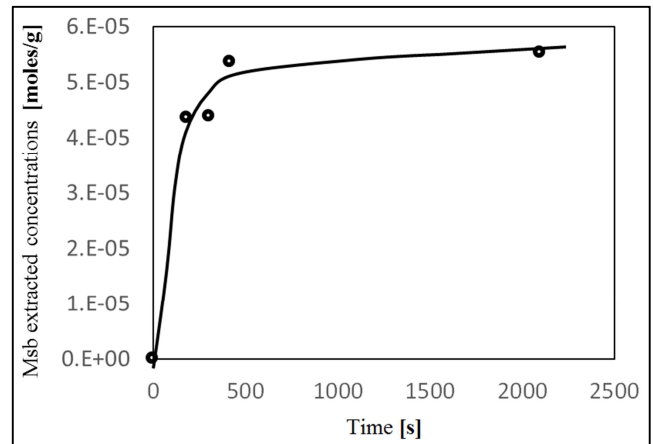


Figure 3. Evolution of the MSB extracted weight concentrations with reaction time.

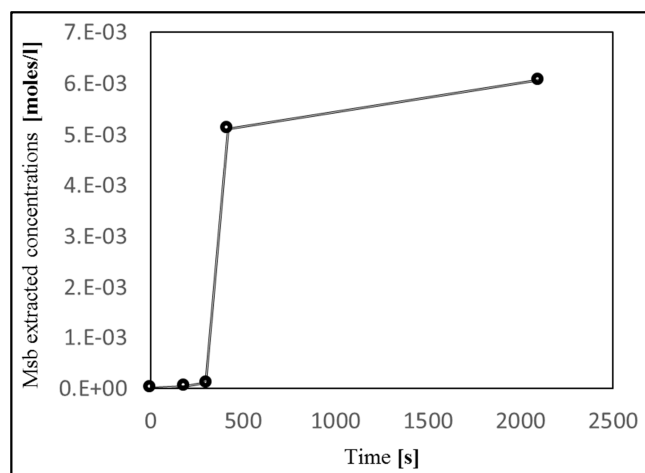


Figure 4. Evolution of the MSB extracted volume concentrations with reaction time.

To determine the values at the initial instants of these various kinetic parameters k , α , β and ω , an estimation of their initial quantities had been made by plotting curves of the evolutions of their concentrations as a function of time showed in the following figures [Figure 1 to the figure 5].

These figures show that the weight concentrations of acidic and basic sites on ppac increased with reaction time and could reach concentrations higher than the initial acidic and basic site concentrations, which are respectively equal to $4.34\text{E-}3$

[mol/g] and $3.77\text{E-}3$ [mol/g]. These results confirm that not only are MSB molecules progressively retained on ppca-used materials, but also citric acid molecules react during the reaction, depending on the reaction time, leading to these facts.

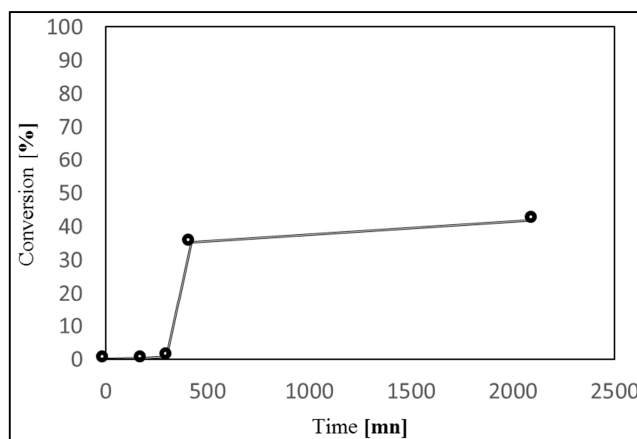


Figure 5. Evolution of the MSB extracted conversion with reaction time.

From these trend curves, the evaluation of the initial concentrations of acidic sites, basic sites and non-adsorbed MSB in the reaction medium at each instant t was done such that by applying the law of site conservation on acidic sites and basic sites the following equations are deduced:

$$S_{ATotal-reaction} = S_{Ainitial} = S_{Ainitialppca} + S_{AMSBinitial} = (S_{At} + S_{Areacting}) \text{ avec } S_{AMSB} = (9 \times n_{MSB})$$

$$S_{BTTotal-reaction} = S_{Binitial} = S_{Binitialppca} + S_{BMSBinitial} = (S_{Bt} + S_{Breacting}) \text{ avec } S_{BMSB} = (3 \times n_{MSB})$$

such as

$S_{ATotal-reaction}$ - The initial acid sites at the instant $t=0$ of the reaction

$S_{BTTotal-reaction}$ - The initial basic sites at the instant $t=0$ of the reaction

$S_{Ainitialppca}$ - The initial acid sites at the instant $t=0$ on the ppca

$S_{AMSBinitial}$ - The initial acid sites at the instant $t=0$ on the MSB

S_{At} - the non-reacting acid sites, at the instant t , still present in the reaction medium

S_{Bt} - the non-reacting basic sites, at the instant t , still present in the reaction medium

$S_{Areacting}$ - the reacting acid sites during the reaction present-dosed on ppca-used dried

$S_{Breacting}$ - the reacting basic sites during the reaction present-dosed on ppca-used dried

n_{MSB} - the initial MSB moles quantities

The following table 2 shows the estimated initial values at times 45s, 90s, 135s and 180s of the various entities cited above; based on the equation of their trend curves; and from which it was evaluated the various initial parameters of equation (1). Concerning the reaction rate, it had been described in the bibliography that the stability of sulfur taking on the stable configuration of the rare gas neon by reaction with basic sites such as citric acid citrate anions [1] is one of the factors favoring its retention on the ppca-used. Thus, the determination of the velocity with respect to the MSB is provided with the coefficient ($1/2=0.5$).

Table 2. Evaluated values at the initial times.

Instants [s]	45	90	135	180
reacting acid sites [mol/g]	4.52E-05	9.08E-05	1.37E-04	1.83E-04
reacting basic sites [mol/g]	3.54E-04	6.96E-04	1.03E-03	1.34E-03
reacting MSB [mol/g]	9.00E-06	1.80E-05	2.70E-05	3.60E-05
acid sites in solution [mol/l]	2.37E+00	2.34E+00	2.32E+00	2.29E+00
basic sites in solution [mol/l]	2.01E+00	1.82E+00	1.64E+00	1.47E+00
MSB in solution [mol/l]	1.4470E-02	1.4463E-02	1.4450E-02	1.4433E-02
réaction rate	3.33E-08	8.54E-08	1.37E-07	1.90E-07

By applying the natural logarithm function to equation (1) and using the values in the table above, a linear equation system with four unknowns is established, from which the evaluation of the various kinetic constants in equation (1) presented in the

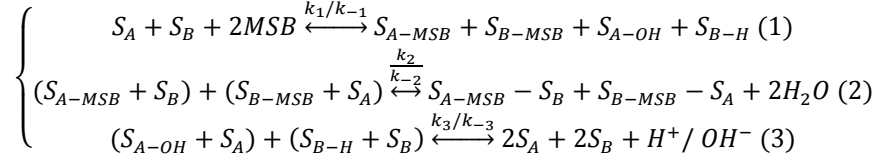
table 3 below is deduced.

Table 3. Evaluated kinetic constants of the MSB extraction-reaction on the ppca material.

α	β	ω	k
-0.15	+0.02	-0.3	2.69E-08

3.2. Proposed Reaction Mechanism Governing the MSB Extraction-Reaction on the PPCA Material

A proposed reaction mechanism governing these tests using the material pn-pozzolana-ac ppca characterized by its acidic and basic sites is presented below and will be compared with experimental data.



S_A – The ppca acid sites

S_B – The ppca basic sites

MSB - 3-Methyl-3-Sulfanylbutan-1-Ol

$S_{A-MSB} = S_{Areacting}$ - acid sites reacting with MSB during the reaction present-dosed on ppca-used

$S_{B-MSB} = S_{Breacting}$ - basic sites reacting with MSB during the reaction present-dosed on ppca-used

S_{A-OH} – acid sites deactivated during the formation of the $S_{A-MSB} = S_{Areacting}$

S_{B-H} – basic sites deactivated during the formation of the $S_{B-MSB} = S_{Breacting}$

$S_{A-MSB} - S_B$ – Products formed by the reaction of $S_{A-MSB} = S_{Areacting}$ with basic sites

$S_{B-MSB} - S_A$ – Products formed by the reaction of $S_{B-MSB} = S_{Breacting}$ with acid sites

Note that the third phase (3) of the reaction mechanism is the regeneration phase of the deactivated acidic and basic sites.

The speed of this reaction-extraction between the acidic and basic active sites of ppca with the MSB molecules is given by the first phase (1) of this mechanism and is equal to:

$$v = (k_1 \times [S_A] \times [S_B] \times [MSB]^2) - (k_{-1} \times [S_{A-MSB}] \times [S_{B-MSB}] \times [S_{A-OH}] \times [S_{B-H}])$$

$$\Leftrightarrow v = (k_1 [S_A] [S_B] [MSB]^2) - \{k_{-1} ([S_{ATotal-reaction}] - [S_A]) ([S_{BTotal-reaction}] - [S_B]) [S_{A-OH}] [S_{B-H}]\}$$

Applying the quasi-steady-state approximation to the intermediates S_{A-OH} and S_{B-H} thus

$$\begin{aligned} /S_{A-OH} \text{ et } /S_{B-H} &\Rightarrow \frac{d[S_{A-OH}]}{dt} = \frac{d[S_{B-H}]}{dt} = \\ \{ &(k_1 [S_A] [S_B] [MSB]^2) - (k_{-1} [S_{A-MSB}] [S_{B-MSB}] [S_{A-OH}] [S_{B-H}]) \} - (k_3 [S_A] [S_B] [S_{A-OH}] [S_{B-H}]) + \\ &k_{-3} [S_A]^2 [S_B]^2 [H^+] [OH^-] = 0 \\ \Leftrightarrow [S_{A-OH}] [S_{B-H}] &= \frac{(k_1 [S_A] [S_B] [MSB]^2 + k_{-3} [S_A]^2 [S_B]^2 [H^+] [OH^-])}{k_3 [S_A] [S_B] + k_{-1} [S_{A-MSB}] [S_{B-MSB}]} \end{aligned}$$

Thus, the speed expression is written as

$$v = (k_1 [S_A] [S_B] [MSB]^2) - (k_{-1} [S_{A-MSB}] [S_{B-MSB}]) \times \frac{(k_1 [S_A] [S_B] [MSB]^2 + k_{-3} [S_A]^2 [S_B]^2 [H^+] [OH^-])}{k_3 [S_A] [S_B] + k_{-1} [S_{A-MSB}] [S_{B-MSB}]}$$

Seeing that the reverse reaction of the third phase corresponding to the regeneration of acidic and basic sites could be negligible, the expression $k_{-3} [S_A]^2 [S_B]^2 [H^+] [OH^-]$ tend to zero

Thus, the speed expression became

$$v = (k_1 [S_A] [S_B] [MSB]^2) - (k_{-1} ([S_{ATotal-reaction}] - [S_A]) ([S_{BTotal-reaction}] - [S_B]) \times \frac{(k_1 [S_A] [S_B] [MSB]^2)}{k_3 [S_A] [S_B] + k_{-1} [S_{A-MSB}] [S_{B-MSB}]})$$

$$\Leftrightarrow v =$$

$$(k_1 [S_A] [S_B] [MSB]^2) - [(k_{-1} [S_{ATotal-reaction}] [S_{BTotal-reaction}]) - (k_{-1} [S_{ATotal-reaction}] [S_B]) -$$

$$(k_{-1} [S_{BTotal-reaction}] [S_A]) + (k_{-1} [S_A] [S_B])] \times \frac{(k_1 [S_A] [S_B] [MSB]^2)}{k_3 [S_A] [S_B] + k_{-1} [S_{A-MSB}] [S_{B-MSB}]}$$

Focusing on the denominator D, this expression is equivalent to

$$D = k_3 [S_A] [S_B] + k_{-1} [S_{A-MSB}] [S_{B-MSB}]$$

$$\Leftrightarrow D = k_3[S_A][S_B] + k_{-1}([S_{ATotal-reaction}] - [S_A])([S_{BTtotal-reaction}] - [S_B])$$

$$\Leftrightarrow D = k_3[S_A][S_B] + k_{-1}[S_{ATotal-reaction}][S_{BTtotal-reaction}] - k_{-1}[S_{ATotal-reaction}][S_B] - k_{-1}[S_{BTtotal-reaction}][S_A] + k_{-1}[S_A][S_B]$$

Given that this study was done at the initial time reactions and also the maximum conversion recorded after 2100s-35mn was 41.95% in the experimental values exploited, then the following expression could be considered $k_{-1}[S_A][S_B] \ll k_{-1}[S_{ATotal-reaction}][S_{BTtotal-reaction}]$ and therefore the expression for D can be simplified to

$$\Leftrightarrow D = [S_A][S_B](k_3 + k_{-1}) + k_{-1}([S_{ATotal-reaction}][S_{BTtotal-reaction}])$$

Let's assume the following constants

$$K_3 = (k_3 + k_{-1})$$

$$K_{-1} = k_{-1}[S_{ATotal-reaction}][S_{BTtotal-reaction}]$$

$$S_{ABT} = (k_1[S_A][S_B][MSB]^2)$$

$$\Leftrightarrow D = K_3[S_A][S_B] + K_{-1}$$

Thus, after development, the expression for speed can be written as follows

$$v = (k_1[S_A][S_B][MSB]^2) - \langle 1 \rangle + \langle 2 \rangle + \langle 3 \rangle - \langle 4 \rangle$$

Such as,

$$\text{The expression } \langle I \rangle = (k_1[S_A][S_B][MSB]^2) - \langle 1 \rangle = S_{ABT} - K_{-1} \frac{S_{ABT}}{K_3[S_A][S_B] + K_{-1}}$$

$$\Leftrightarrow \langle I \rangle = (k_1[S_A][S_B][MSB]^2) - \langle 1 \rangle = S_{ABT} \left(1 - \frac{1}{1 + \frac{(k_3 + k_{-1})[S_A][S_B]}{k_{-1}[S_{ATotal-reaction}][S_{BTtotal-reaction}]}} \right)$$

$$\Leftrightarrow \langle I \rangle = S_{ABT} \left(1 - \frac{1}{1 + \frac{(k_3 + k_{-1})[S_A][S_B]}{k_{-1}[S_{ATotal-reaction}][S_{BTtotal-reaction}]}} \right)$$

Given that this study was done at the initial time reactions and also the maximum conversion recorded after 2100s-35mn was 41.95% in the experimental values exploited, then the following expression could be considered $k_3 \ll k_{-1}$ and therefore the expression for $\langle I \rangle$ can be simplified to

$$\langle I \rangle = S_{ABT} \times \left(1 - \frac{1}{1 + \frac{[S_A][S_B]}{[S_{ATotal-reaction}][S_{BTtotal-reaction}]}} \right)$$

Seeing that $k_{-1}[S_A][S_B] \ll k_{-1}[S_{ATotal-reaction}][S_{BTtotal-reaction}]$ thus

$$\frac{[S_{ATotal-reaction}][S_{BTtotal-reaction}]}{[S_A][S_B]} \gg 1$$

Or

$$\frac{[S_A][S_B]}{[S_{ATotal-reaction}][S_{BTtotal-reaction}]} \ll 1$$

Thus,

$$\langle I \rangle = S_{ABT} \times \left(1 - \frac{1}{1} \right) = 0$$

Then, the expression

$$\langle 2 \rangle = S_{ABT} \frac{k_{-1}[S_{ATotal-reaction}][S_B]}{K_3[S_A][S_B] + K_{-1}} = S_{ABT} \frac{1}{\frac{K_3[S_A][S_B] + K_{-1}}{k_{-1}[S_{ATotal-reaction}][S_B]}}$$

$$\Leftrightarrow \langle 2 \rangle = S_{ABT} \times \frac{1}{\left(\frac{K_{-1}}{k_{-1}[S_{ATotal-reaction}][S_B]} + \frac{K_3[S_A]}{k_{-1}[S_{ATotal-reaction}]} \right)}$$

$$\begin{aligned}\Leftrightarrow \langle 2 \rangle &= S_{ABT} \times \frac{1}{\left(\frac{[S_{BT\text{Total-reaction}}]}{[S_B]} + \frac{K_3[S_A]}{k_{-1}[S_{AT\text{Total-reaction}}]} \right)} \\ \Leftrightarrow \langle 2 \rangle &= S_{ABT} \times \frac{1}{\frac{[S_{BT\text{Total-reaction}}]}{[S_B]}} \\ \Leftrightarrow \langle 2 \rangle &= S_{ABT} \times \frac{[S_B]}{[S_{BT\text{Total-reaction}}]}\end{aligned}$$

And the expression

$$\begin{aligned}\langle 3 \rangle &= S_{ABT} \frac{k_{-1}[S_{BT\text{Total-reaction}}][S_A]}{K_3[S_A][S_B] + K_{-1}} = S_{ABT} \frac{1}{\frac{K_3[S_A][S_B] + K_{-1}}{k_{-1}[S_{BT\text{Total-reaction}}][S_A]}} \\ \Leftrightarrow \langle 3 \rangle &= S_{ABT} \times \frac{1}{\left(\frac{K_{-1}}{k_{-1}[S_{BT\text{Total-reaction}}][S_A]} + \frac{K_3[S_B]}{k_{-1}[S_{BT\text{Total-reaction}}]} \right)} \\ \Leftrightarrow \langle 3 \rangle &= S_{ABT} \times \frac{[S_A]}{[S_{AT\text{Total-reaction}}]}\end{aligned}$$

Finally, the expression

$$\begin{aligned}\langle 4 \rangle &= S_{ABT} \frac{k_{-1}[S_B][S_A]}{K_3[S_A][S_B] + K_{-1}} = S_{ABT} \frac{1}{\frac{K_3[S_A][S_B] + K_{-1}}{k_{-1}[S_B][S_A]}} \\ \Leftrightarrow \langle 4 \rangle &= S_{ABT} \times \frac{1}{\left(\frac{K_{-1}}{k_{-1}[S_B][S_A]} + \frac{K_3[S_B][S_A]}{k_{-1}[S_B][S_A]} \right)} = S_{ABT} \times \frac{1}{\left(\frac{K_{-1}}{k_{-1}[S_B][S_A]} + \frac{K_3[S_B][S_A]}{k_{-1}[S_B][S_A]} \right)} \\ \Leftrightarrow \langle 4 \rangle &= S_{ABT} \times \frac{1}{\left(\frac{[S_{AT\text{Total-reaction}}][S_{BT\text{Total-reaction}}]}{[S_B][S_A]} \right)} \\ \Leftrightarrow \langle 4 \rangle &= S_{ABT} \times \frac{[S_A][S_B]}{[S_{AT\text{Total-reaction}}][S_{BT\text{Total-reaction}}]}\end{aligned}$$

Using these expressions $\langle 1 \rangle + \langle 2 \rangle + \langle 3 \rangle - \langle 4 \rangle$, the expression for speed can be written as follows

$$v = (k_1[S_A][S_B][MSB]^2) - \langle 1 \rangle + \langle 2 \rangle + \langle 3 \rangle - \langle 4 \rangle = \langle 1 \rangle + \langle 2 \rangle + \langle 3 \rangle - \langle 4 \rangle$$

$$\begin{aligned}\Leftrightarrow v &= 0 + S_{ABT} \times \frac{[S_B]}{[S_{BT\text{Total-reaction}}]} + S_{ABT} \times \frac{[S_A]}{[S_{AT\text{Total-reaction}}]} - S_{ABT} \times \frac{[S_A][S_B]}{[S_{AT\text{Total-reaction}}][S_{BT\text{Total-reaction}}]} \\ \Leftrightarrow v &= S_{ABT} \times \left(\frac{[S_B]}{[S_{BT\text{Total-reaction}}]} + \frac{[S_A]}{[S_{AT\text{Total-reaction}}]} - \frac{[S_A][S_B]}{[S_{AT\text{Total-reaction}}][S_{BT\text{Total-reaction}}]} \right) \\ \Leftrightarrow v &= S_{ABT} \times \left(\frac{[S_B][S_{AT\text{Total-reaction}}] + [S_A][S_{BT\text{Total-reaction}}] - [S_A][S_B]}{[S_{BT\text{Total-reaction}}][S_{AT\text{Total-reaction}}]} \right) \\ \Leftrightarrow v &= (k_1[S_A][S_B][MSB]^2) \times \left(\frac{[S_B][S_{AT\text{Total-reaction}}] + [S_A][S_{BT\text{Total-reaction}}] - [S_A][S_B]}{[S_{BT\text{Total-reaction}}][S_{AT\text{Total-reaction}}]} \right) \text{ EXPRESSION A}\end{aligned}$$

$$\Leftrightarrow v = \left((k_1[S_A][S_B][MSB]^2) \times \frac{[S_B][S_{AT\text{Total-reaction}}] + [S_A][S_{BT\text{Total-reaction}}]}{[S_{BT\text{Total-reaction}}][S_{AT\text{Total-reaction}}]} \right) - \left((k_1[S_A][S_B][MSB]^2) \times \frac{[S_B][S_A]}{[S_{BT\text{Total-reaction}}][S_{AT\text{Total-reaction}}]} \right)$$

EXPRESSION B

The value of the constant k_1 can be estimated by plotting speed v as a function of

$$[S_A][S_B][MSB]^2 \times \frac{[S_B][S_A]}{[S_{BT\text{Total-reaction}}][S_{AT\text{Total-reaction}}]}$$

These figures below shows these expressions A and B, which can be used to estimate the value of $k_1 = 8E^{-4}$

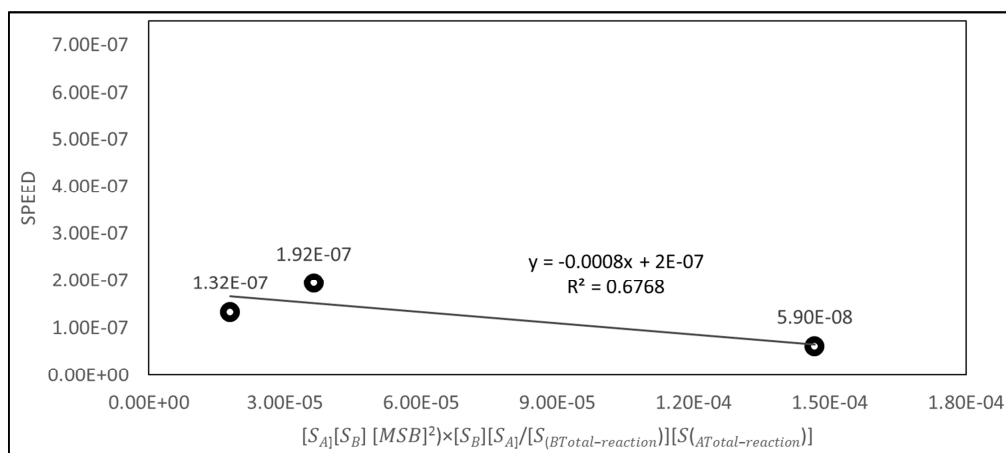


Figure 6. Evaluation of the constant k_1 validating the proposed reaction mechanism governing the MSB extraction-reaction on the ppca material by the expression B.

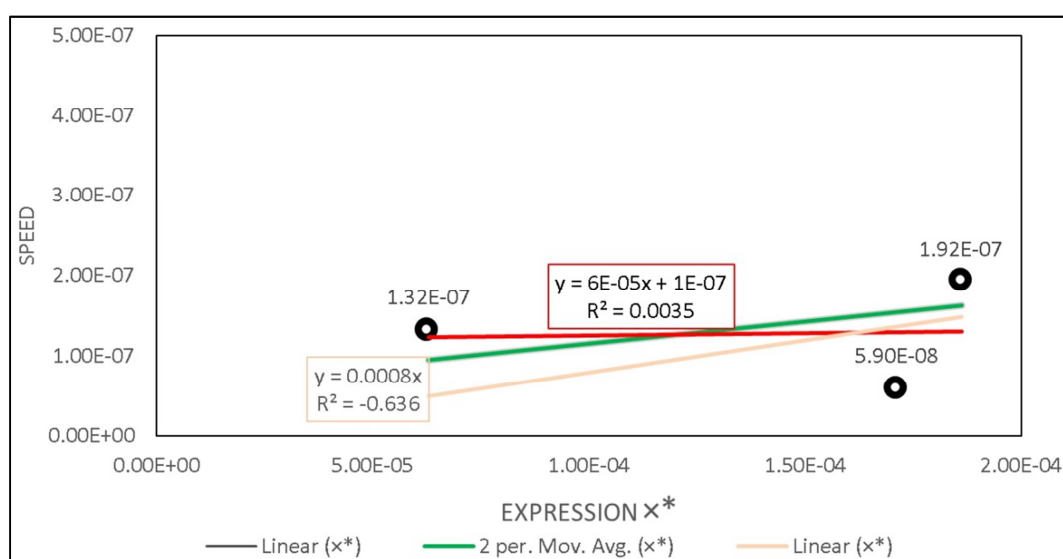


Figure 7. Evaluation of the constant k_1 validating the proposed reaction mechanism governing the MSB extraction-reaction on the ppca material by the expression B.

4. Conclusion

It was showed that the pn-black citric acid polymer-PPCA is efficiency to extract the MSB - 3-Methyl-3-Sulfanylbutan-1-Ol molecule because of its acid sites and particularly its basic sites which have a positive influence to the speed reaction. The characterization of the PPCA-material by its basic sites and acid sites according to the procedure described on the bibliography was important and efficiency to explain its activity. Indeed, the kinetic parameters evaluated after the experimental results analysis indicated that the basic sites play an important role to its activity on the reaction-extraction of the MSB - 3-Methyl-3-Sulfanylbutan-1-Ol molecule. In addition, the reaction mechanism governing this MSB extraction-reaction on the PPCA was validated and indicated the important role of the regeneration of the deactivated acid and basic sites phase explaining the non-negligible retention of the MSB even if this reaction-extraction was performed at ambient temperature,

in the open air and at atmospheric pressure with a recorded conversion 41.95% only after 2100s-35mn. Indeed, bibliographies confirmed that acidic and basic sites, their strength and their quantities in the material solid-catalyst like zeolite, zirconia, and alumina oxide Al_2O_3 played important role in many catalytic reactions [8-21]. In brief, the results on this manuscript confirmed not only the potentiality of the basic and acid sites to explain, to evaluate and to expect the activity of a material like PPCA but also the potentiality of this PPCA-material to react-extract in this case with the MSB - 3-Methyl-3-Sulfanylbutan-1-Ol molecules.

Acknowledgments

Sincere thanks to the President of the Ecole Supérieure Polytechnique Antananarivo Polytechnics. And, sincere respect to the Chemical Process Engineering Chief Department (E. S. P. A) as well as the Chemical Engineering Laboratory staff and those who directly or indirectly contributed to the realization of this manuscript.

References

- [1] Rabeharitsara Andry Tahina, Rakotondrina Henri, Randriana Nambinina Richard, Rakotoarijaona Soloniaina, Ratsimba Hanitriniaina Marie, Rakotomamonjy Pierre – Chemical Process Engineering Department (E. S. P. A), Antananarivo University – Madagascar – «MSB - 3-Methyl-3-Sulfanylbutan-1-ol Extraction Its Esterification with Citric Acid and PPCA Materials Synthesis» - American Journal of Applied and Industrial Chemistry in Vol. 7, Issue Number 2, December 2023. doi: 10.11648/j.ajaic.20230702.11.
- [2] Rabeharitsara Andry Tahina, Raharilaza Paulin Merix, Randriana Richard Nambinina – Chemical Process Engineering Department (E. S. P. A), Antananarivo University – Madagascar – “Esterification Between Citric Acid and Pumpkin Pips’ Organic Molecules – Esters Hydrolysis and Esters Used as Hydrocarbons Additives” - American Journal of Applied Chemistry in Vol. 6, Issue Number 3, June 2018. doi: 10.11648/j.ajac.20180603.12.
- [3] Raharilaza Paulin Merix - "Estérification entre les molécules d'acide citrique et les molécules organiques des graines de courges - hydrolyse et valorisations des esters comme additifs des hydrocarbures" - [Esterification between citric acid molecules and organic molecules of pumpkin seeds - hydrolysis and valuation of esters as hydrocarbon additives] - Mémoire de fin d'étude en vue de l'obtention du diplôme de Licence en Génie Chimique. E. S. P. A. Université d'Antananarivo. Promotion 2017.
- [4] Jan Schönherr, Johannes R. Buchheim, Peter Scholz and Philipp Adelhelm, « Boehm Titration Revisited (Part I): Practical Aspects for Achieving a High Precision in Quantifying Oxygen-Containing Surface Groups on Carbon Materials. ». Journal of Carbon research, Received: 7 March 2018; Accepted: 30 March 2018; Published: 6 April 2018.
- [5] Rabeharitsara Andry Tahina, Andriamitantsoa Havosoa, Randriana Nambinina Richard, Robijaona Baholy, Ratsimba Marie Hanitriniaina – Chemical Process Engineering Department (E. S. P. A), Antananarivo University, Antananarivo, Madagascar – “Study of Esterification Between the Used Tire and Citric Acid Molecules” - American Journal of Applied Chemistry, Vol. 10, Issue Number 5, October 2022.
- [6] Rabeharitsara Andry Tahina, Rabearimihaja Phandry Nomena Ndjiva – Chemical Process Engineering Department (E. S. P. A), Antananarivo University, Antananarivo, Madagascar – “Betacarotenes Dosage by Hydrofluoric Acid Solution and Validation of This New Process by SPC”. American Journal of Applied Chemistry. Vol. 4, No. 3, 2016, pp. 91-96. doi: 10.11648/j.ajac.20160403.14.
- [7] Rabearimihaja Phandry Taryh Nomena Ndjiva - «Valorisation Du Betacarotene Extrait De L'huile De Palme Brute Par De L'acide Acétique Pour La Détermination Des Teneurs En Eau De Produits Pétroliers (Gazole /Fuel-Oil) Et Dosage Des Teneurs En Betacarotene Par De L'acide Fluorhydrique» - [Valorization of Betacarotene Extracted from Crude Palm Oil by Acetic Acid for the Determination of Water Content of Petroleum Products (Diesel/Fuel Oil) and Determination of Betacarotene Content by Hydrofluoric Acid].- Mémoire de fin d'Etudes en vue de l'obtention du Diplôme de Master Titre Ingénieur en Génie des Procédés chimiques et Industriels – E. S. P. A. Université d'Antananarivo – Promotion 2015.
- [8] S. S. Barton, M. J. B. Evans, E. Halliop, J. A. F. MacDonald – “Acidic and basic sites on the surface of porous carbon” – Department of chemistry and chemical engineering, royal military college of Canada, Kingston, Ont., Canada – Carbon Volume 35, Issue 9, 1997, pages 1361-1366.
- [9] Chao Li, Lijun Zhang, Mortaza Gholizadeh, Roel Westerhoff, Zhenhua Cui, Bingqiang Liu, Yonggui Tang Xinghui Jin, Zhixiang Xu and Xun Hu – “Impact of acidic/basic of the catalyst on properties of the coke formed in Pyrolysis of Guaiacol: A model compound of the phenolics in bio-oil” – Energy fuels 2020, 34, 9, 11026-11040.
- [10] Minming Huang, Serge Kaliaguine, Aline Auroux - “Lewis basic and acidic sites in zeolites” – Studies in surface sciences and catalysis – volume 97, 1995, pages 311-318.
- [11] Valentina Verdoliva, Michelle Saviano, Stefania De Luca – “Investigation of the Acid/Basic sites of zeolite through some catalysed nucleophilic reactions” – Journal Foundations 2023, 3 (1), 72-81.
- [12] Farahnaz Maleki & Gianfranco Pacchioni – “Characterization of acid and basic sites on zirconia surfaces and nanoparticles: A theoretical study” – Topics in catalysis 63, 1717-1730 (2020)
- [13] Xue-Rui Tian, Xiao-Lei Jiang, Sheng-Li Hou, Zhuo-Hao Jiao, Jie Han, Bin Zhao – “Selectivity regulating acid-base sites in metal-organic frameworks for achieving turn-on/off the catalytic activity in different CO₂ reactions” – Angewandte chemie international edition, volume 61, issue 18.
- [14] Mohammad Reza Shabani, Mohammad Ali Moosavian, Yahya Zamani, Sayed Javid Royaei – “Effect of acid-base properties on design of catalyst for methanol thiolation” – Comptes rendus chimie 2020, 23, n°6-7, p. 433-444.
- [15] Donatus Setyawan Purwo Handoko, Triyono – “The effect of acid strength of Brønsted acid site on the ability of catalyst to break the carbon chain bonds of 1-octadecenes into alkanes and short chain alkenes as a substitute for fossil fuel – Scientific contributions Oil & gas, vol. 46, N°1, April 1-8.
- [16] Ana Palcic, Valentin Valtchev – “Analysis and control of acid sites in zeolites”.
- [17] Michel R. Guisnet – “Model reactions for characterizing the acidity of solid catalysts” – American Chemical Society publications 1990, 23, 11, 392-398.
- [18] Christian J. Breckner, Hien N. Pham, Michaël G. Dempsey, Michelle A. Perez-Ahuati, Alyssa C. Kohl, Corryn N. Lytle, Pr. Abhaya K. Datye, Pr. Jeffrey T. Miller – “ The role of 12wis acid in γ -Al₂O₃ oligomerization” – ChemPhysChem, volume 24, issue 14.
- [19] V. Silva Kumar, B. M. Nagaraja, V. Shashikala, P. Seetharamalu, A. H. Padmasri, B. David Raju, K. S. Rama Rao – “Role of acidic and basic sites of Al₂O₃ in predicting the reaction pathway of isophorone transformation” – Journal of molecular Catalysis A. Chemical – Volume 223, Issue 1-2, 1 december 2004, pages 283-288.
- [20] Gerardo Enrique Cordova Perez, José Gilberto Torres Torres, Filiberto Ortiz-Chi, Srinivas Godavarti – «Effect of Acid-Basic ratio on the catalytic activity to obtain 5-HMF from glucose using Al₂O₃-TiO₂-W catalysts” – Chemistry select 3 (45) 12854-12864.
- [21] Dusan Stosic – “Acidic-basic properties of catalysts for conversion of biomass” – Thèse de l'université de Lyon – 18 Décembre 2012.