



# Mathematical modeling of platinum and chlorine distributions within Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst prepared by impregnation

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Received 13 August 2014; received in revised form 4 November 2014; accepted 11 May 2015

## KEYWORDS

Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst;  
 Impregnation;  
 Modeling;  
 Competitive adsorption;  
 Radial distribution.

**Abstract.** A mathematical model for the impregnation step in the preparation of supported catalysts is developed. The kinetic parameters required for the model solution were obtained by considering the reversible competitive adsorption of ions on the same surface sites. The effects of pH of the impregnation solution and impregnation time, as two critical operating parameters, were investigated and their influence on radial distribution was evaluated. The model was applied to a Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst in the presence of HCl. The experimental data required for the model solution were obtained from impregnation tests performed in a tubular fixed-bed reactor with an external circulation for the impregnation solution; similar to configurations used in industrial cases. Kinetic parameter values obtained in the present modeling were compared with those reported in literature for similar cases. The order of magnitude for the present results is in an acceptable range. As the distribution of active metal in the supported catalyst plays an important role in its performance, this model is an invaluable tool by which such distributions can be predicted.

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## 1. Introduction

Supported platinum-based catalysts are widely used in hydrocarbon conversion processes, such as dehydrogenation of light and heavy alkanes and naphtha reforming [1,2]. In these catalysts, platinum is commonly dispersed over a high surface area support. Other metals are also incorporated in formulations to form bi-metallic or tri-metallic catalysts [3-6]. Bimetallic platinum-tin catalysts are broadly used in dehydro-

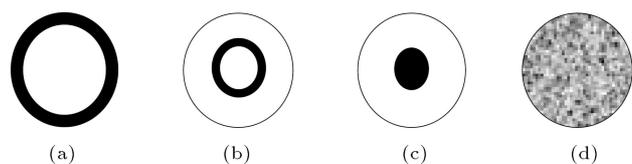
genation processes as they show relatively high activity and selectivity [7-11].

“Impregnation” is one of the most commonly used methods for preparing supported catalysts, wherein a porous support is contacted with a solution that contains the species on which it is to be adsorbed.

Two techniques can be applied for impregnation via the liquid phase [10]:

- At low adsorption strength, the impregnation technique chosen will be “dry” impregnation. In this case, the required amounts of metal compound are dissolved in a sufficient volume of water to fill about the total pore volume of the carrier batch (pore volume saturation);

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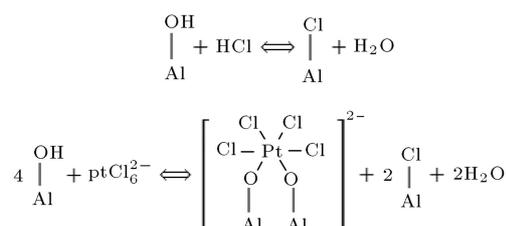


**Figure 1.** Type of active phase distribution: (a) Egg-shell; (b) egg-white; (c) egg-yolk; and (d) uniform.

- At strong adsorption, the carrier can be impregnated using an excess amount of solvent and by circulating the solution through a bed of carrier particles. The metal compound diffuses from the solution into the carrier particle and is then adsorbed (soaking procedure).

Distribution of an active catalytic constituent along the pellet radius may be very different. There are four types of distribution: egg-shell, egg-white, egg-yolk and uniform (Figure 1). In practical situations, it is important to control the impregnation profile of the active catalytic constituents on the supported catalysts. If the reaction is under mass transfer limiting conditions, it is desirable to have the catalytic constituent deposited on the external surface of the catalyst pellet (i.e. “egg-shell” distribution). When the reaction is kinetically limited, a uniformly distributed profile is desired. If the reaction may be poisoned by an impurity which is strongly adsorbed on the support, it may be best to produce an “egg-white” and “egg-yolk” distribution, as the exterior band of the pellet can immobilize the poison, keeping it spatially separated from the active catalytic constituent. An “egg-white” or “egg-yolk” distribution may also be beneficial in services which produce catalyst attrition and loss of catalyst fines from the reactor space, because only the support will be attrited and the active catalytic constituent can be retained.

The adsorption of  $\text{H}_2\text{PtCl}_6$  on alumina is an important step in the preparation of supported platinum catalysts with high dispersions. When alumina pellets are impregnated with  $\text{H}_2\text{PtCl}_6$ , by using amounts smaller than the adsorption capacity of the support, due to diffusion resistance, the metallic compound is deposited primarily in the outer shells of the particles. However, the radial profile of the deposited metal can be modified by co-impregnating the support with certain materials, such as HCl, being able to compete for the adsorption sites. The use of competitive adsorbates during the process of impregnation can lead to a notable increase in uniform metallic distribution [12-14]. It has been reported that the presence of competitive adsorbates, such as hydrochloric acid and carboxylic acids, can not only govern the active metal dispersion on the support [15], but also produce relatively strong interactions between the metal and the support [14]. The HCl competitive effect on



$\text{PtCl}_6^{2-}$  adsorption on  $\gamma\text{-Al}_2\text{O}_3$  can, schematically, be represented as [16,17].

The performance of supported catalysts usually depends on the radial distribution profiles of the species deposited on the internal surface of the support. The first research in this field dates back to 1957 [18]. Since that time, several mathematical models with different degrees of complexity and rigorousness have been reported. Vincent and Merrill [19] developed a model for one component adsorption in a single pore. In their model, unsteady-state condition and plug flow inside a pore were considered. Komiyama et al. [20] solved a model for two-component adsorption over spherical particles. Kulkarni et al. [21] developed a simple model with plug flow inside the pores. They assumed mass-transfer resistance and adsorption kinetics resistance at a solid-liquid interface. Hegedus et al. [22] and Melo et al. [23] presented more general models that take into account multi-component impregnation under different working conditions. Shyr and Ernst [24] showed that a variety of platinum profile distributions can be obtained using different acids as co-impregnants. Lee and Aris [25] described models for various phases of single- and multi-component impregnation. In other models [26-28], the chemistry of a solid-solution interface was investigated. Santacesaria et al. [29] investigated single component adsorption of platinum on  $\gamma$ -alumina under kinetic and equilibrium conditions. In their research, the effect of the presence of a competitor ion was not considered. Papageorgiou et al. [30] developed a model for multi-component impregnation in the presence of citric acid as the competitor. They used two parameters, namely, “solution effect” and “steric hindrance”, in their model. Castro et al. [16] developed a model for “egg-shell” type catalysts. They specifically studied a naphtha reforming catalyst. Scelza et al. [31] mathematically investigated platinum adsorption on cylindrical alumina pellets in the presence of hydrochloric acid.

The target catalyst of the present study is the bi-metallic Pt-Sn/ $\text{Al}_2\text{O}_3$  dehydrogenation catalyst in which Sn is impregnated prior to Pt, and the support is spherical  $\gamma$ -alumina. To the best of the authors knowledge, the kinetic data reported in literature for wet impregnation of Pt/ $\text{Al}_2\text{O}_3$  do not consider the presence of another pre-impregnated metal (i.e. Sn for this specific case). On the other hand, in the target

catalyst, in order to obtain a uniform distribution for platinum, a competitor ion was incorporated as well. Although investigation of the adsorption process during wet impregnation of Pt/Al<sub>2</sub>O<sub>3</sub> became the subject of interest in subsequent studies [32–34], to the best of our knowledge, no information is reported on co-adsorption of platinum and chlorine ions on Sn-impregnated  $\gamma$ -alumina.

The objective of the present study is to develop a mathematical model for multi-component impregnation of a porous support. Competitive adsorption with reversible kinetics is considered for adsorption sites. Radial distribution profiles for platinum and chlorine surface coverage on spherical alumina supports pre-impregnated with Sn were calculated.

## 2. Experimental

### 2.1. Material

Hexachloroplatinic acid (H<sub>2</sub>PtCl<sub>6</sub>.6H<sub>2</sub>O) and tin chloride (SnCl<sub>2</sub>.2H<sub>2</sub>O) from Merck Co. were used as precursors, and hydrochloric acid (HCl) from Merck Co. was used as the competitor. Commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (BET surface area: 205 m<sup>2</sup>/g, pore volume: 0.78 ml/g and particle diameter: 1.8 mm) provided by Sasol, was used as the catalyst support.

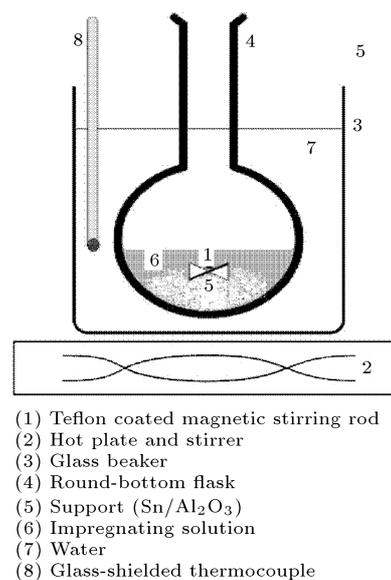
### 2.2. Apparatus

#### 2.2.1. Determination of adsorption capacity

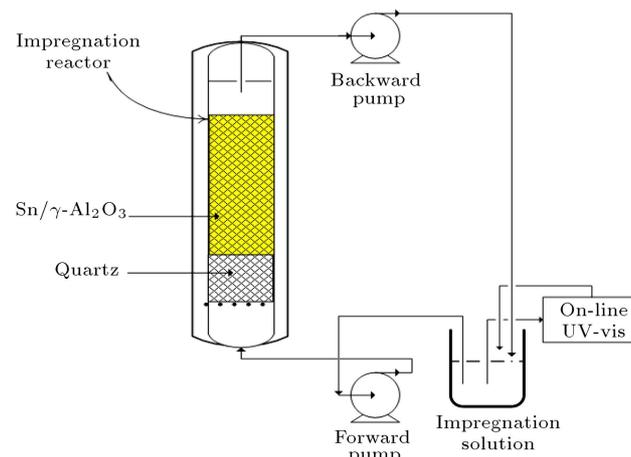
As the target catalyst was Pt-Sn/Al<sub>2</sub>O<sub>3</sub> containing 0.7 wt.% of tin, at first, Sn was impregnated by a wet technique, dried at 120°C for 12 h and calcined at 530°C for 2 h to “freeze” the adsorbed tin. In order to avoid mass transfer resistance and pore diffusion effects, Sn/Al<sub>2</sub>O<sub>3</sub> supports were ground with a ball-mill (RETSCH Co., PM100), sieved to 32–63  $\mu$ m with a vibrating sieve shaker and kept in a desiccator.

The impregnation solutions were prepared using DM water. The pH value for the platinum solution was adjusted by the addition of appropriate amounts of HCl (37%), and measured with a Metrohm 744 pH meter.

Four solutions, with concentrations of 4.21, 5.63, 7.03 and 8.43 mmol/L, corresponding to nominal platinum loadings of 0.3, 0.4, 0.5 and 0.6 wt.%, respectively, were prepared. 10 g of the powdered support were added to 40 ml of the impregnation solution of known concentration. All equilibrium adsorption tests were performed using the system shown in Figure 2. The Teflon-coated magnetic stirring rod, located inside the impregnation solution, minimized the concentration and temperature gradients within the vessel and maximized the contact with the liquid phase. 4 h was considered for each experiment to ensure that equilibrium was achieved. All the experiments were performed at constant temperature (25°C). The Langmuir isotherm



**Figure 2.** Experimental system used for the study of adsorption capacity of Sn-impregnated support.



**Figure 3.** Catalyst synthesis set-up.

was used to evaluate the platinum adsorption capacity of the Sn-impregnated support.

#### 2.2.2. Catalyst preparation

A fixed-bed experimental setup, a schematic diagram of which is depicted in Figure 3, was used for the kinetic study of platinum impregnation. A tubular fixed-bed quartz reactor with an inner diameter of 2 cm was used. The space below the support was packed with quartz powder (mesh 10) to ensure proper distribution of fluid flow.

The channeling and heat transfer effects in the reactor could be neglected, as the radial aspect ratio (bed diameter to catalyst particle diameter) was > 15. The axial aspect ratio, i.e. the ratio of catalyst bed length to catalyst particle diameter, was > 30. Hence, the dispersion effects could also be neglected [35].

The impregnation set-up consisted of a double-

wall quartz reactor, two peristaltic pumps for circulating the impregnation solution, and an on-line UV-Vis apparatus (T90, PG Instruments Limited Co.) for kinetic evaluation of platinum adsorption.

The target dehydrogenation catalyst (Pt-Sn/ $\text{Al}_2\text{O}_3$  catalyst) consists of 0.7 wt.% of tin and 0.5 wt.% of platinum. On the  $\gamma$ -alumina support, as the first step, Sn was impregnated using an acidic solution of  $\text{SnCl}_2$ , and a wet impregnation technique in rotary equipment at  $40^\circ\text{C}$  was dried at  $120^\circ\text{C}$  for 12 h and calcined at  $530^\circ\text{C}$  for 2 h in wet air with a programmed ramp of  $5^\circ\text{C}/\text{min}$ . In a subsequent step, Pt was impregnated, using a solution containing  $\text{H}_2\text{PtCl}_6$  and HCl, by wet impregnation, in the set-up depicted in Figure 3 at  $25^\circ\text{C}$ .

### 2.3. Metal content analysis

The UV-Visible (T90, PG Instruments Limited Co.) was used for platinum and chloride concentration measurements in all experiments.

For the adsorption capacity experiment, after each sorption equilibrium analysis, the suspension was centrifuged at 5000 rpm (ROTINA 46-Hettich, Zentrifugen Co.) and filtered with a syringe filter (cellulose acetate, CA20/25, CHROMAFIL). The supernatant was analyzed by UV-Visible for platinum at 450 nm and for chloride at 563 nm.

The concentration of platinum in the impregnating solution was determined spectrophotometrically. The analyte concentration was calculated from a calibration curve constructed by taking different concentrations of platinum. Two calibration curves were used for the measurement of platinum concentration in two different ranges, as below:

0.02 – 0.89 ( $\text{mmolPt}/\text{L}_{\text{solution}}$ ) :

$$y = 0.05221x - 0.00048 (R^2 = 0.999),$$

1.12 – 7.84 ( $\text{mmolPt}/\text{L}_{\text{solution}}$ ) :

$$y = 0.04884x - 0.00833 (R^2 = 0.9993),$$

where:

$y$  Absorbance  
 $x$  Concentration

For kinetic experiments, platinum concentration in the impregnation solution was determined by recycling the solution to the quartz cell and measuring the absorbance at 450 nm against the reagent blank (appropriate amount of HCl in  $\text{H}_2\text{O}$ ). The UV/Vis spectrophotometer was set to record an absorbance spectrum every 120 s for the duration of the particular experiment. The above-mentioned calibration curves were used for platinum concentration measurements.

The process for measuring chloride concentration was the same as the one used for platinum. The concentration of chloride in the impregnating solution was determined by recycling the solution to the quartz cell and measuring the absorbance at 563 nm against the reagent blank. The reagents used to make a colorful solution were Ammonium Iron (II) Sulfate Dodecahydrate and Mercury (II) thiocyanate. Appropriate amounts of Ammonium Iron (II) Sulfate Dodecahydrate and Mercury (II) thiocyanate in water were used as the reagent blank. The calibration curve used for measurement of chloride concentration was as below:

$$y = 0.00432x + 0.00021 (R^2 = 0.9963),$$

where:

$y$  Absorbance  
 $x$  Concentration

### 3. Mathematical modeling

The adsorption of solute(s) on the internal surface of a porous support, pre-wetted with pure water, involves a diffusion-adsorption process. Mass balances for species  $i$  in the solution diffusing into the pores and in the adsorbed state are, respectively, given by:

$$\varepsilon \frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i - v_i, \quad i = 1, 2, \dots, N \quad (1)$$

$$\frac{\partial \theta_i}{\partial t} = \frac{\lambda_i}{\rho_p C_s} v_i, \quad i = 1, 2, \dots, N \quad (2)$$

where  $C_i$  is the concentration of species  $i$  in the solution filling the pores,  $D_i$  is the effective diffusivity of species  $i$ ,  $\theta_i$  is the fractional surface coverage of species  $i$ ,  $\nu_i$  is the adsorption rate,  $\varepsilon$  is the porosity of the particle,  $\lambda_i$  is the stoichiometric coefficient of species  $i$ ,  $\rho_p$  is the apparent density of the particle, and  $C_s$  is the adsorption capacity of the support.

Considering the competitive adsorption of  $N$  species on the same kinds of surface site:



with Langmuir-type rate expressions, one can write:

$$v_i = k_i^+ C_i \left( 1 - \sum_{i=1}^N \theta_i \right) - k_i^- \theta_i, \quad (4)$$

where  $k^+$  and  $k^-$  are adsorption and desorption rate constants, respectively.

Applying Eqs. (1) and (2) to a spherical catalyst with negligible mass transfer in other directions except  $r$ , i.e., one dimensional diffusion, the following correlations are obtained:

$$\varepsilon \frac{\partial C_i}{\partial t} = D_i \left[ \frac{\partial^2 C_i}{\partial r^2} + \frac{2}{r} \frac{\partial C_i}{\partial r} \right] - \left[ k_i^+ C_i \left( 1 - \sum_{i=1}^N \theta_i \right) - k_i^- \theta_i \right], \quad (5)$$

$$\frac{\partial \theta_i}{\partial t} = \frac{\lambda_i}{\rho_P C_s} \left[ k_i^+ C_i \left( 1 - \sum_{i=1}^N \theta_i \right) - k_i^- \theta_i \right]. \quad (6)$$

The initial and boundary conditions are as below:

$$C_i(R, 0) = C_i^0, \quad (7)$$

$$C_i(r, 0) = 0, \quad 0 \leq r < R, \quad (8)$$

$$\theta_i(r, 0) = 0, \quad 0 \leq r \leq R, \quad (9)$$

$$\left. \frac{\partial C_i}{\partial t} \right|_{R,t} = -\frac{3}{\rho_P V_e R} D_i \left. \frac{\partial C_i}{\partial r} \right|_{R,t}, \quad (10)$$

$$\left. \frac{\partial C_i}{\partial r} \right|_{0,t} = 0, \quad (11)$$

where  $V_e$  is the volume of the external solution per gram of the support and  $R$  is the particle radius.

The sets of one dimensional, time-dependent differential equations with initial and boundary conditions were solved using the finite element method in a commercial CFD package, in order to have radial fractional surface coverage distribution and fractional surface coverage as a function of impregnation time.

In order to compute the radial profile for a particular case, a previous knowledge of parameter values is required. As the thermodynamic and kinetic parameters are not reported in literature for the specific system of the present study, it is necessary to estimate their values from experimental data. The parameters are estimated through the minimization of an objective function that computes the difference between the observed and predicted values. The concentrations of species remaining in solution at different impregnation

times are chosen as the variables in the objective function defined as:

$$e_i(t) = \frac{C_i^e(t) - C_i(R, t)}{C_i^0}, \quad (12)$$

where  $C_i^0$  is initial concentration of species  $i$  in solution,  $C_i^e(t)$  is the experimental value of the concentration of species  $i$  in the external solution, and  $C_i(R, t)$  is the predicted value of the concentration of species  $i$  in the external solution.

The objective function became:

$$S = \int_0^T \sum_{i=1}^N e_i^2(t) dt. \quad (13)$$

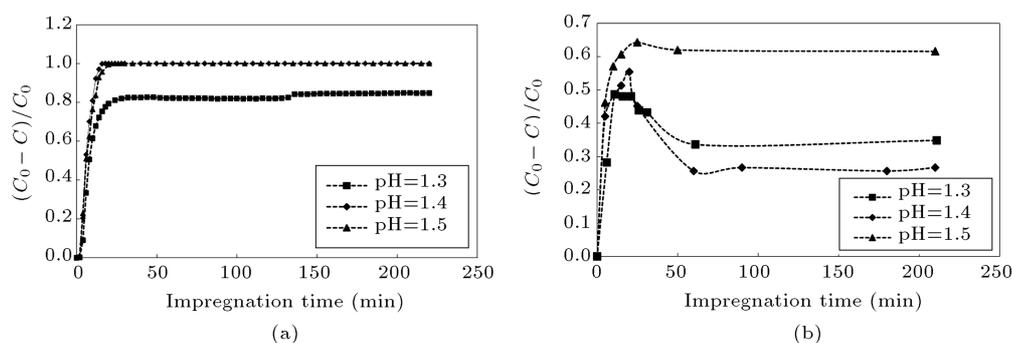
In this calculation, experimental data of catalyst synthesis (according to the procedure outlined in Section 2.2.2) are used for  $C_i^e(t)$ , and the data obtained from the solution of the above-mentioned equations are used for  $C_i(R, t)$ . The finite element method is used for this optimization.

## 4. Result and discussion

### 4.1. Experimental results

Figure 4 shows typical concentration-time data of the impregnation solution at different pH levels, being used for determination of kinetic parameters. Platinum adsorption at pH=1.4 and pH=1.5 was almost complete, and 100% adsorption occurred. At pH=1.3, only 80% adsorption was obtained.

The platinum adsorption increased rapidly with time and leveled out smoothly after a short time (Figure 4(a)). Chlorine concentration curves, on the other hand, showed a peak in the first hours of impregnation (Figure 4(b)). This implies that some chloride ion is released after longer time on stream, by hydrolysis of the adsorbed chloroplatinate ions. The extent of reaction would depend on the concentrations and impregnation time. It is reported that high pH and aging concentration shifts the coordination toward



**Figure 4.** Variations of impregnation solution concentration as a function of impregnation time at different pH values for Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst: (a) Platinum; and (b) chlorine.

the chlorine [36]. Chlorine can also be replaced by water to form chloroaquohydroxo palatinates of lower or no charge [33]. Using UV-Vis-diffuse reflectance spectroscopy, Maesen et al. [36] provided evidence for the partial substitution of halide ligands by oxygen-containing ligands when  $\text{H}_2\text{PtCl}_6$  interacted with  $\gamma\text{-Al}_2\text{O}_3$  surfaces. Therefore, the chlorine adsorption passes through a minimum. On the other hand, the Cl:O ligand ratio of the complex ions in the solution drops as they adsorb onto the support. The final pH value of the impregnation solution was found to be higher than that of the initial solution. The decreasing adsorption with increasing final pH can be explained by the decreasing positive charge density at the alumina surface as the pH of the solution approaches the value of the iso-electric point.

#### 4.2. Modeling results

##### 4.2.1. Parameter evaluation

Adsorption capacity,  $C_s$ , which was determined according to the procedure outlined in Section 2.2.1, along with other parameters required to solve the model, were listed in Table 1.

Adsorption and desorption rate constants, calculated using the minimization method described in Section 3, were reported in Table 2. The diffusion coefficients in solution containing  $\text{H}_2\text{PtCl}_6$  and HCl at various pH values were tabulated in Table 3.

As can be seen in Table 2, upon increasing pH (i.e. decreasing the amount of competing ion, chlorine), the adsorption rate constant of platinum increases, reaches its maximum value at pH=1.4, and then decreases. On the other hand, increasing pH causes desorption rate constant of platinum to be decreased. As chlorine is a competitor ion, the lower its amount in solution, the more the available vacant sites on support for platinum adsorption. This phenomenon confirmed the competing effect of chlorine. As can be seen in Table 2, adsorption rate constant values of platinum

Table 1. Data used for model solution.

| Parameter       | Value                 | Parameter             | Value |
|-----------------|-----------------------|-----------------------|-------|
| $C_s$ (mol/g)   | $1.02 \times 10^{-4}$ | $\lambda_{\text{Pt}}$ | 4     |
| $\rho_p$ (g/mL) | 0.55                  | $\lambda_{\text{Cl}}$ | 1     |
| $V_e$ (mL/g)    | 4                     | $\varepsilon$         | 0.43  |

Table 2. Adsorption and desorption rate constants.

| pH  | $\text{H}_2\text{PtCl}_6$    |                               | HCl                              |                               |
|-----|------------------------------|-------------------------------|----------------------------------|-------------------------------|
|     | $k^+$<br>( $\text{s}^{-1}$ ) | $k^-$<br>( $10^{-6}$ mol/L.s) | $k^+$<br>( $10^{-4}$ s $^{-1}$ ) | $k^-$<br>( $10^{-5}$ mol/L.s) |
| 1.3 | 0.05                         | 1.13                          | 1.88                             | 2.5                           |
| 1.4 | 0.15                         | 0.025                         | 7.5                              | 2.5                           |
| 1.5 | 0.12                         | 0.012                         | 3                                | 2.5                           |

Table 3. Platinum and chlorine diffusion coefficient [31].

| pH  | $\text{H}_2\text{PtCl}_6$ | HCl                     |
|-----|---------------------------|-------------------------|
|     | ( $10^{-6}$ cm $^2$ /s)   | ( $10^{-6}$ cm $^2$ /s) |
| 1.3 | 1.84                      | 8.39                    |
| 1.4 | 1.94                      | 8.95                    |
| 1.5 | 1.98                      | 8.98                    |

Table 4. A literature survey for platinum adsorption rate constant on alumina.

| BET surface area<br>(m $^2$ /g) | Adsorption rate constant<br>(L/mol.s) | Reference     |
|---------------------------------|---------------------------------------|---------------|
| 78 <sup>a</sup>                 | 2.46                                  | [30]          |
| 177 <sup>b</sup>                | 1.21                                  | [29]          |
| 195 <sup>c</sup>                | 0.18                                  | [37]          |
| 205 <sup>d</sup>                | 2 (pH=1.3)                            | Present study |
|                                 | 6 (pH=1.4)                            |               |
|                                 | 4.8 (pH=1.5)                          |               |

<sup>a</sup>: Pt adsorption (in the presence of citric acid) on  $\gamma\text{-Al}_2\text{O}_3$ ;

<sup>b</sup>: Pt adsorption on  $\gamma\text{-Al}_2\text{O}_3$ ;

<sup>c</sup>: Pt adsorption (in the presence of nitric acid-pH=0.54) on  $\text{TiO}_2\text{-Al}_2\text{O}_3$ ;

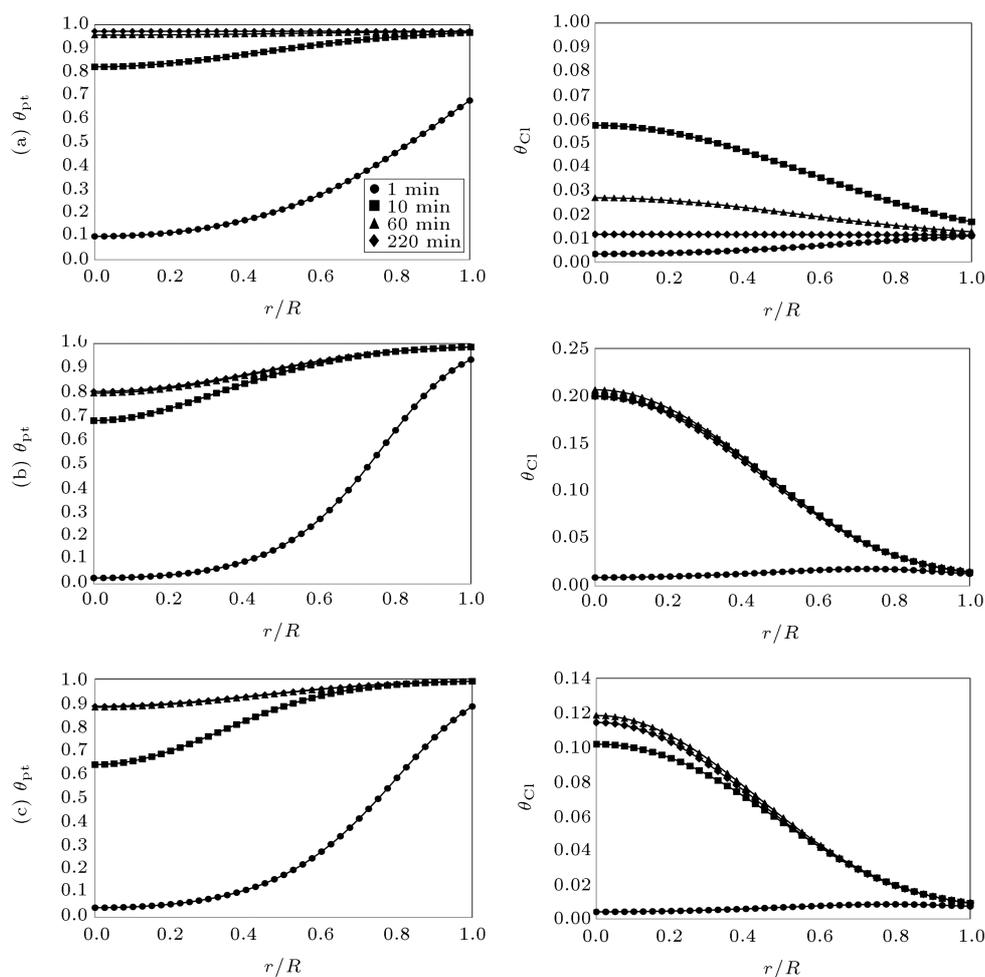
<sup>d</sup>: Pt adsorption (in the presence of hydrochloric acid) on  $\text{Sn}/\gamma\text{-Al}_2\text{O}_3$ .

and chlorine are much higher than their desorption rate constants, which can be explained by a positively charged alumina surface at pH levels lower than the iso-electric point. Hence, adsorption was the dominant phenomenon.

In Table 4, the values of the adsorption rate constant for platinum reported in literature were listed. Due to the difference between the structural characteristics of the supports reported in Table 4 and also the difference between the chemical characteristics of the impregnation solution, the exact values of adsorption rate constants reported in Table 4 should not be identical. The more the surface area of the support, the more the available adsorption sites; hence, a higher value of platinum adsorption rate constant was obtained for the results of the present research.

##### 4.2.2. Radial distribution of platinum and chlorine

The set of equations derived in Section 3, using parameters evaluated in Section 4.2.1, was solved and the



**Figure 5.** Radial distribution of fractional surface coverage as a function of impregnation time and pH of the impregnation solution for Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst: (a) pH=1.3; (b) pH=1.4; and (c) pH=1.5. (●): 1 min, (■): 10 min, (▲): 60 min, (◆): 220 min.

radial distribution of platinum and chlorine fractional surface coverage at various impregnation times was obtained (Figure 5). Most of the platinum penetration occurs within the first 10 min. For pH=1.3, the chlorine adsorption showed a peak around 10 min, after which it decreased due to desorption. For pH=1.4 and pH=1.5, this peak was also observed but at longer impregnation time.

In order to investigate and compare the internal profile of the final catalyst, the modeling results for 220 min impregnation time for radial distribution of platinum and chlorine are redrawn in Figure 6.

As can be seen in Figure 6, at pH=1.4 and pH=1.5, platinum distribution is nearly uniform (with a minor trend to extended “egg-shell” type distribution), and, at pH=1.3, its distribution is virtually uniform.

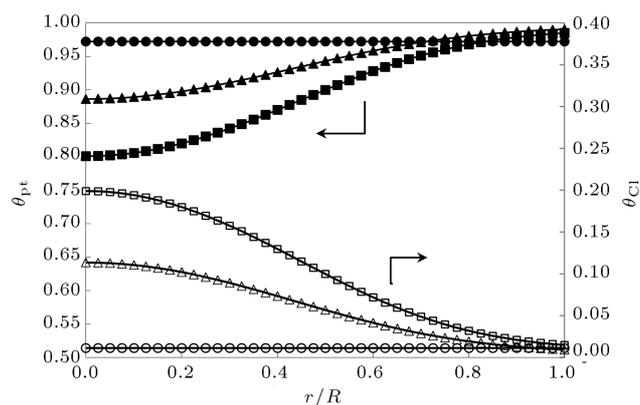
At pH=1.4 and pH=1.5, platinum surface coverage at the shell side of the final catalyst is somehow similar; but, from shell to center, increasing pH increased the amount of adsorbed platinum due to

the competing effect of chlorine. The higher the competitor ion concentration, the more uniform is radial Pt adsorption.

For chlorine surface coverage, at pH=1.3, chlorine distribution is completely uniform, and, at pH=1.4 and pH=1.5, its distribution is uniform with a mild trend towards a broadened “egg-yolk” type (Figure 6).

Comparing the results of Figure 6 for pH=1.4 and pH=1.5, the competing effect of chlorine is confirmed one more time. As can be seen, in different locations inside the support, the places where less chlorine is available, more platinum is adsorbed and vice-versa. Moreover, chlorine has the ability to penetrate inside the support, and platinum tends to adsorb more on the shell-side.

According to Table 2, the adsorption rate constant of platinum was two orders of magnitude larger than that of chlorine. Thus, platinum was adsorbed preferably on the surface of the support, and chlorine must penetrate deeply inside the support to be ad-



**Figure 6.** Radial distribution of fractional surface coverage in the final Pt-Sn/Al<sub>2</sub>O<sub>3</sub> catalyst for 220 min impregnation at various impregnation condition. (●): pH=1.3, (■): pH=1.4, (▲): pH=1.5; filled symbols are for Pt and empty symbols are for Cl.

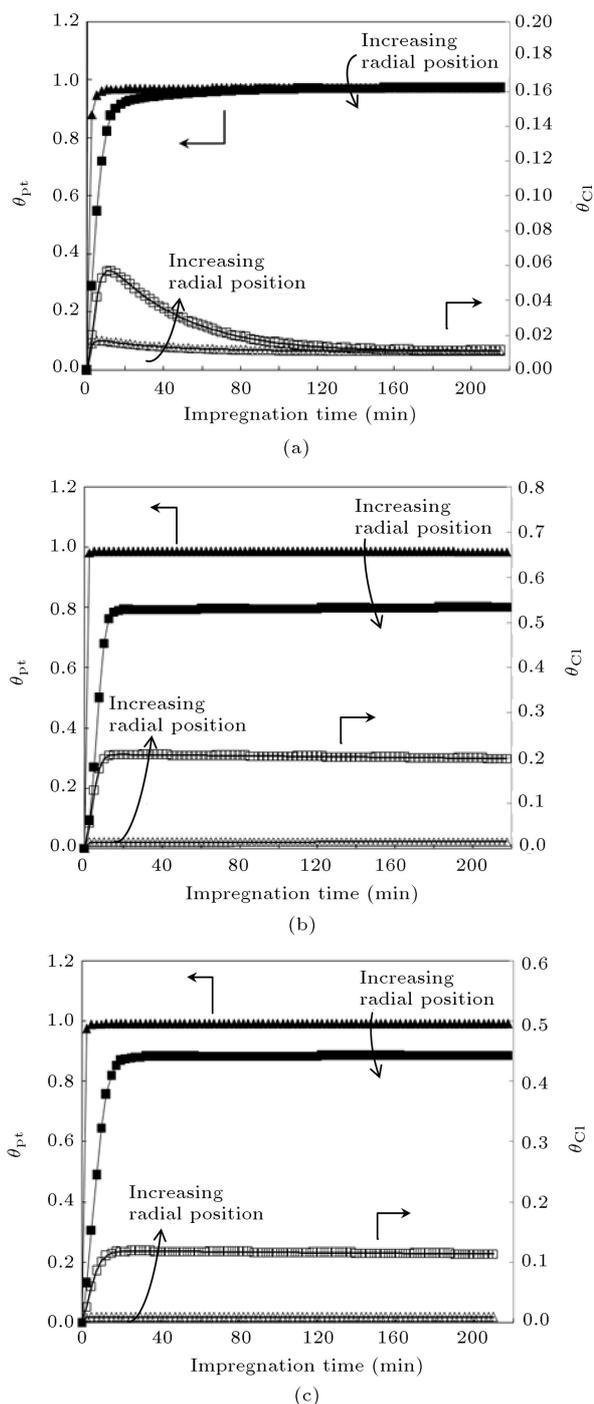
sorbed on vacant interior sites. This is in accordance with that observed in Figures 5 and 6.

According to Figure 6, at pH = 1.4, the highest amount of chlorine is adsorbed on the support. This result is in good agreement with data reported in Table 2, as chlorine adsorption rate constant at pH=1.4 has the highest value.

#### 4.2.3. The effect of impregnation time on surface coverage

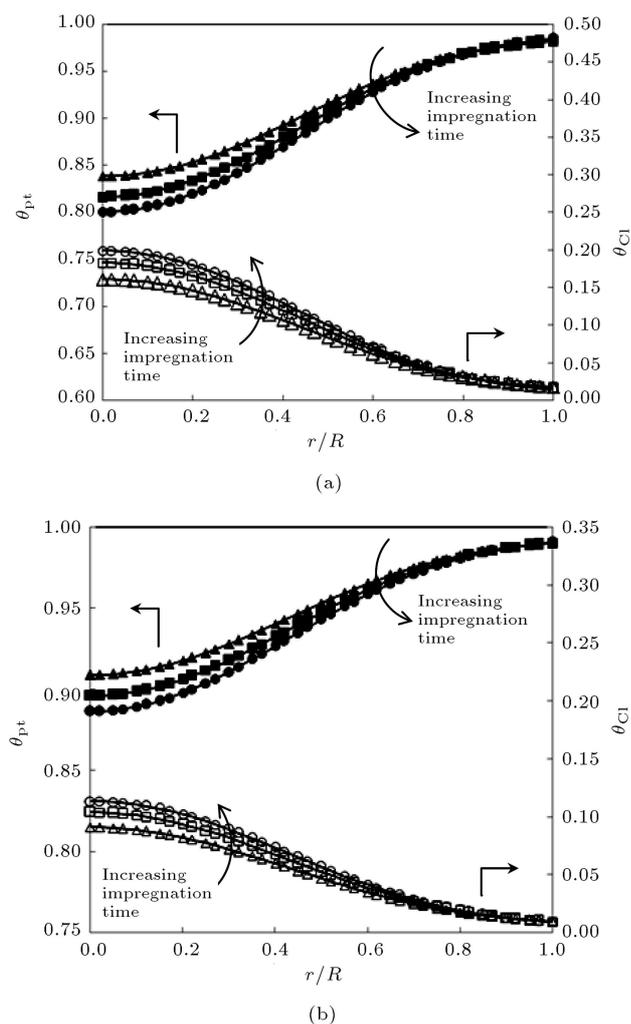
In order to investigate the platinum fractional coverage inside each catalyst particle precisely, in Figure 7, platinum and chlorine coverage at the shell and center, as a function of impregnation time, and the pH of the impregnation solution are illustrated. For pH=1.3, approximately, after an hour of impregnation, the amount of platinum and chlorine coverage on the shell and center are identical, and uniform distribution was obtained (Figure 7(a)). For pH=1.4, after 5 min of impregnation for the shell, and after 20 min of impregnation for the center, the amount of platinum and chlorine coverage reached its constant value. Obviously, there is a difference between final values of coverage on the shell and the center and that is why an extended “egg-shell” type distribution was obtained for platinum, and a broadened “egg-yolk” type distribution was obtained for chlorine. For pH=1.5, this steady-state time is 5 min and 25 min for the shell and the center, respectively.

The above modeling results show that with 220 min impregnation, platinum and chlorine uniform distributions are obtained only for pH=1.3. The question may arise as to whether it is possible to have a uniform profile with pH=1.4 and pH=1.5. The only promising variable is impregnation time. In order to investigate the influence of longer impregnation time on the radial distribution of platinum and chlorine, for these two pH values, radial distributions are calculated



**Figure 7.** Platinum and chlorine shell (▲) and center (■) fractional coverage as a function of impregnation time for various pH values: (a) pH=1.3; (b) pH=1.4; and (c) pH=1.5. Filled symbols are for Pt and empty symbols are for Cl.

for much longer impregnation times (10 hr and 20 hr) (Figure 8). As can be seen, by increasing impregnation time, radial distribution tends to approach uniform. But for its complete uniform configuration, it may take some days, which is not desirable from a practical point of view. This finding is theoretically logical. The longer



**Figure 8.** The effect of longer impregnation time on fractional platinum and chlorine radial distribution: (a) pH=1.4; and (b) pH= 1.5. (●): 220 min, (■): 10 hr, (▲): 20 hr; filled symbols are for Pt and empty symbols are for Cl.

the impregnation time, the further time platinum and chlorine have to adsorb and desorb on vacant sites, and, finally, a uniform distribution will be obtained, which is in accordance with thermodynamic equilibrium.

## 5. Conclusions

The process of impregnating a porous support to obtain a supported metallic catalyst is described by a diffusion-adsorption model. Reversible competitive adsorption of platinum and chlorine ion on the same surface sites was considered in the model. Adsorption and desorption rate constants, as kinetic impregnation parameters, were calculated. Adsorption rate constants of platinum and chlorine were higher than those for desorption, which proved that adsorption is the dominant phenomenon.

The pH of the impregnation solution (at three

values) and impregnation time were selected as two dominant operating parameters, and their influence on radial distribution of platinum and chlorine were investigated. For 220 min impregnation, a uniform distribution of platinum and chlorine was only obtained at pH=1.3. With pH=1.4 and pH=1.5, a non-uniform catalyst with egg-shell platinum distribution and egg-yolk chlorine distribution was obtained.

## Nomenclature

|             |  |
|-------------|--|
| $C_i$       | Concentration of species $i$ in the solution filling the pores (mol/mL)                  |
| $C_i^0$     | Initial concentration of species $i$ in solution (mol/mL)                                |
| $C_i^e(t)$  | Experimental value of the concentration of species $i$ in the external solution (mol/mL) |
| $C_i(R, t)$ | Predicted value of the concentration of species $i$ in the external solution (mol/mL)    |
| $C_s$       | Adsorption capacity of the support (mol/g)   |
| $D_i$       | Effective diffusivity of species $i$ ( $\text{cm}^2/\text{s}$ )                          |
| $k^+$       | Adsorption rate constant ( $\text{s}^{-1}$ )   |
| $k^-$       | Desorption rate constant (mol/(L.s))   |
| $r$         | Radial position (cm)   |
| $R$         | Particle radius (cm)   |
| $S$         | Objective function   |
| $t$         | Impregnation time (s)  |
| $T$         | Final impregnation time (s)  |
| $\nu_i$     | Adsorption rate (mol/(L.s))  |
| $V_e$       | Volume of the external solution per gram of support (mL/g)                               |

## Greek symbols

|               |  |
|---------------|--|
| $\varepsilon$ | Porosity of the particle                   |
| $\theta_i$    | Fractional surface coverage of species $i$ |
| $\lambda_i$   | Stoichiometric coefficient of species $i$  |
| $\rho_p$      | Apparent density of the particle (g/mL)    |

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